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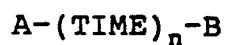
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W-8000 München 81(DE)**(54) **Silver halide color photographic material containing yellow colored cyan coupler.**

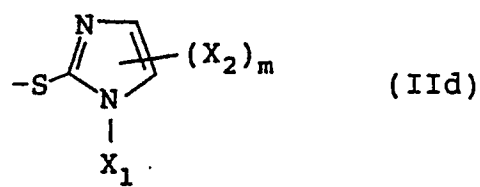
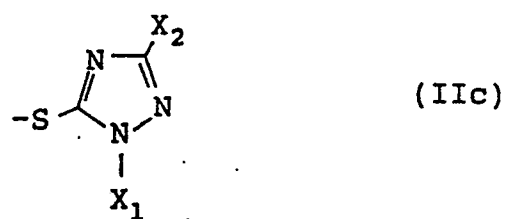
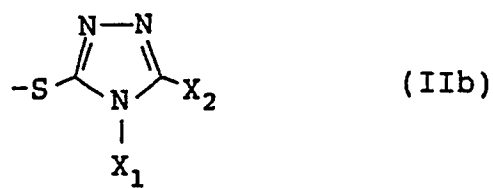
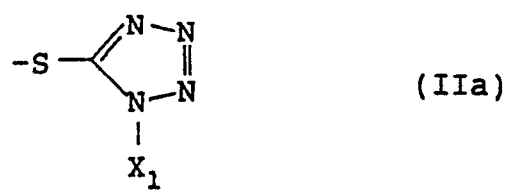
(57) A silver halide color photographic material comprising a support having thereon at least one red-sensitive silver halide emulsion layer containing a cyan coupler, at least one green-sensitive silver halide emulsion layer containing a magenta coupler and at least one blue-sensitive silver halide emulsion layer containing a yellow coupler, characterized in that the photographic material contains at least one compound represented by the following general formula (I) and at least one yellow colored cyan coupler:

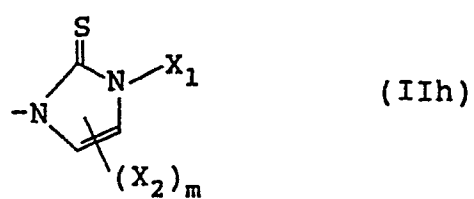
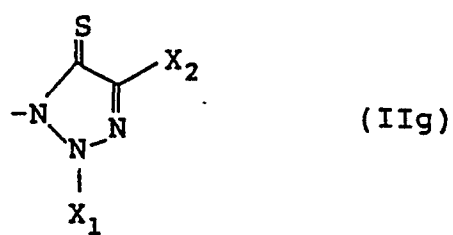
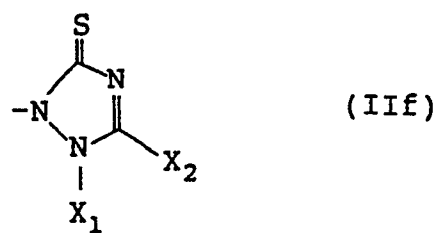
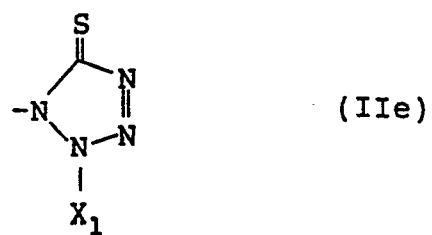


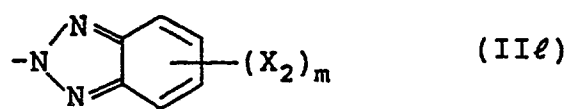
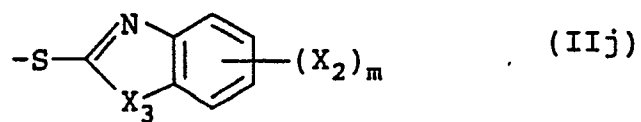
(I)

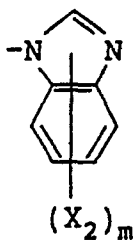
wherein A represents a coupler moiety which is released from (TIME)_n-B by a coupling reaction with an oxidation product of an aromatic primary amine developing agent; TIME represents a timing group which is bonded to the active coupling site of A and which releases B after release from A by the coupling reaction; B represents a group represented by the following general formulas (IIa), (IIb), (IIc), (IId), (IIe), (IIf), (IIg), (IIh), (IIi), (IIj), (IIk), (IIl), (IIm), (IIn), (IIo) or (IIp); and n represents 0 or 1 and when n is 0, B is directly bonded to A:

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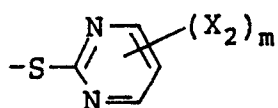




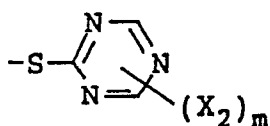




(IIIn)



(IIIo)



(IIIp)

wherein X_1 represents a substituted or unsubstituted aliphatic group having 1 to 4 carbon atoms or a substituted phenyl group; X_2 represents a hydrogen atom, an aliphatic group, a halogen atom, a hydroxyl group, an alkoxy group, an alkylthio group, an alkoxy carbonyl group, an acylamino group, a carbamoyl group, a sulfonyl group, a sulfonamido group, a sulfamoyl group, an acyloxy group, a ureido group, a cyano group, a nitro group, an amino group, an alkoxy carbonylamino group, an aryloxy carbonyl group, or an acyl group; X_3 represents an oxygen atom, a sulfur atom or an imino group having not more than 4 carbon atoms; m represents an integer of 1 or 2; the total of carbon atoms in X_2 or $(X_2)_m$ groups is not more than 8; and when m is 2, the two X_2 groups may be the same or different groups.

SILVER HALIDE COLOR PHOTOGRAPHIC MATERIAL CONTAINING YELLOW COLORED CYAN COUPLERBACKGROUND OF THE INVENTION

1. Field of the Invention

5 This invention relates to a silver halide color photographic material. More particularly, it relates to a photographic material which has excellent color reproducibility and sharpness as well as printability due to the incorporation of a novel yellow colored cyan coupler and a diffusing development inhibitor-releasing coupler therein.

10 2. Description of Related Art

It has been demanded in recent years to provide silver halide photographic materials which have excellent color reproducibility, sharpness, high sensitivity, as typified by ISO 400 photographic materials (e.g., Super HG-400 sold by Fuji Photo Film Co.) having high image quality comparable to ISO 100 materials, particularly in the field of photographic materials for photographing.

15 As means for improving color reproducibility and sharpness, it is known to use the DIR compounds described in JP-A-54-145135 (the term "JP-A" as used herein means an "unexamined published Japanese patent application"), JP-A-56-114946 and JP-A-57-151944 (corresponding to U.S. Patents 4,248,962, 4,409,323 and 4,477,563, respectively). Interlaminar and edge effects are improved, and color reproducibility and sharpness are also improved to some degree by these compounds. However, there are problems in that when the amount of restrainer released from these compounds is insufficient to restrain development, sufficient interlaminar and edge effects cannot be obtained; and when the sensitive layers to be restrained are not properly developed, the desired interlaminar effect cannot be obtained. Further, these compounds do not provide a sufficient effect over the whole exposure range, and their use lowers the sensitivity of the color-sensitive layers to which they have been added as well as the adjoining color-sensitive layers.

20 On the other hand, JP-A-61-221748 and West German Patent Laid-Open No. 3815469A disclose that effects similar (with respect to photographic performance) to interlaminar effect of from a red-sensitive emulsion layer to a blue-sensitive emulsion layer can be obtained by using a yellow colored cyan coupler in the red-sensitive emulsion layer. However, it is difficult to obtain sufficient effects over the whole exposure range by the methods described in the above patent specifications, that is, by the use of these compounds alone. Conventional yellow colored cyan couplers have problems in that the molecular extinction coefficients of their yellow dyes are low and their coupling activity is also low.

30 Further, there are problems in that since the molecular extinction coefficients of the yellow couplers used together therewith are low, the layers of photographic materials become comparatively thick and the interlaminar effects and sharpness become low. Further, since the developed dyes of the yellow couplers are not adapted to the spectral absorption of the yellow colored couplers, the printability in auto-printers used in local laboratories is insufficient.

40 SUMMARY OF THE INVENTION

A first object of the present invention is to provide a photographic material which has excellent color reproducibility.

45 A second object of the present invention is to provide a photographic material which has excellent sharpness.

A third object of the present invention is to provide a photographic material which has excellent printability in auto-printers.

A fourth object of the present invention is to provide a photographic material which is highly sensitive.

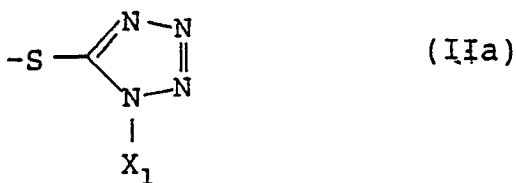
50 These objects of the present invention have been achieved by providing a silver halide color photographic material comprising a support having thereon at least one red-sensitive silver halide emulsion layer containing a cyan coupler, at least one green-sensitive silver halide emulsion layer containing a magenta coupler and at least one blue-sensitive silver halide emulsion layer containing a yellow coupler, wherein the photographic material contains at least one compound represented by the following general formula (I) and at least one yellow colored cyan coupler:



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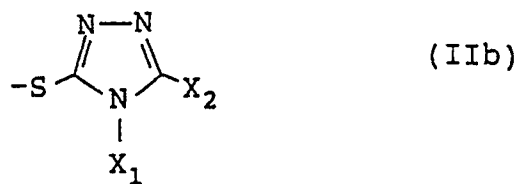
wherein A represents a coupler moiety which is released from $(\text{TIME})_n-B$ by a coupling reaction with an oxidation product of an aromatic primary amine developing agent; TIME represents a timing group which is bonded to the active coupling site of A and which is released B after release from A by the coupling reaction; B represents a group represented by the following general formulas (IIa), (IIb), (IIc), (IId), (IIe), (IIg), (IIh), (Iii), (Iij), (IIk), (Iil), (IIm), (IIn), (IIo) or (IIp); n represents an integer of 0 or 1 and when n is 0, B is directly bonded to A.

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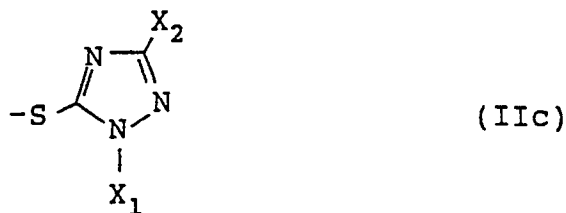
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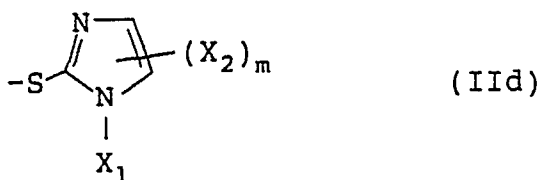
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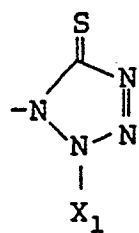
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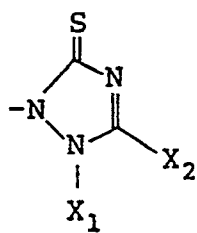
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(IIe)

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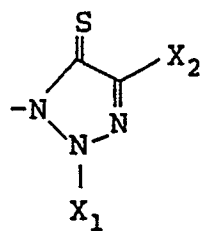
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(IIIf)

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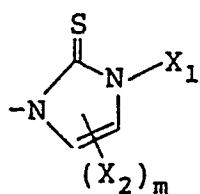
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(IIIg)

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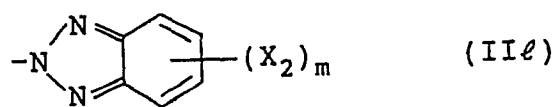
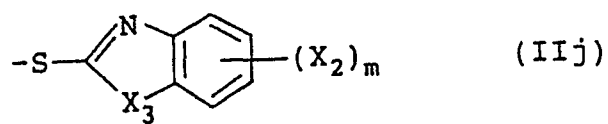
(IIH)

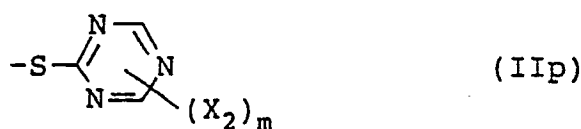
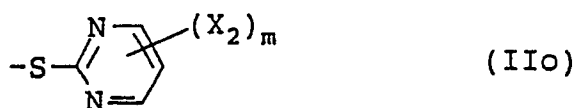
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In the above formulas, X_1 represents a substituted or unsubstituted aliphatic group having 1 to 4 carbon atoms (including no carbon atoms in the substituent: the same hereinafter unless otherwise defined) or a substituted phenyl group; X_2 represents a hydrogen atom, an aliphatic group, a halogen atom, a hydroxyl group, an alkoxy group, an alkylthio group, an alkoxycarbonyl group, an acylamino group, a carbamoyl group, a sulfonyl group, a sulfonamido group, a sulfamoyl group, an acyloxy group, a ureido group, a cyano group, a nitro group, an amino group, an alkoxycarbonylamino group, an aryloxy carbonyl group or an acyl group; X_3 represents an oxygen atom, a sulfur atom or an imino group having 0 to 4 carbon atoms; m represents an integer of 1 or 2; the total of carbon atoms in X_2 or $(X_2)_m$ groups is not more than 8; and when m is 2, the two X_2 groups may be the same or different groups. X_2 may be bonded at any position on the nucleus.

More specifically, X_1 is a substituted or unsubstituted aliphatic group having 1 to 4 carbon atoms (examples of substituent groups being an alkoxy group, an alkoxycarbonyl group, a hydroxyl group, an arylamino group, a carbamoyl group, a sulfonyl group, a sulfonamido group, a sulfamoyl group, an amino group, an acyloxy group, a cyano group, a ureido group, an acyl group, a halogen atom and an alkylthio group, the number of carbon atoms in these substituent groups being not more than 3; the aliphatic group may have one or more substituent groups; and these groups may be further substituted with these groups, an aliphatic group or an aromatic group) or a substituted phenyl group (examples of substituent groups being a hydroxyl group, an alkoxycarbonyl group, an acylamino group, a carbamoyl group, a sulfonyl group,

a sulfonamido group, a sulfamoyl group, an acyloxy group, a ureido group, a carboxyl group, a cyano group, a nitro group, an amino group, an alkoxy carbonyl amino group and an acyl group, the number of carbon atoms in these substituent groups being not more than 3, the phenyl group may have one or more substituent); X_2 is an aliphatic group, a halogen atom, a hydroxyl group, an alkoxy group, an alkylthio group, an alkoxy carbonyl group, an acylamino group, a carbamoyl group, a sulfonyl group, a sulfonamido group, a sulfamoyl group, an acyloxy group, a ureido group, a cyano group, a nitro group, an amino group, an alkoxy carbonyl amino group, an aryloxy carbonyl group or an acyl group (these groups may be further substituted with, e.g., a hydroxy group, an alkoxy carbonyl group, a carboxyl group, or an acyloxy group); X_3 is an oxygen atom, a sulfur atom or an imino group having 0 to 4 carbon atoms (the imino group may be substituted with an alkyl group); m is an integer of 1 or 2; the total of carbon atoms in X_2 or $(X_2)_m$ groups is not more than 8; and when m is 2, the two X_2 groups may be the same or different groups.

Terms for representing groups in the present invention are defined as follows unless otherwise defined.

The term "aliphatic group" means an aliphatic hydrocarbon group which may be a saturated or unsaturated hydrocarbon group or a straight-chain, branched or cyclic hydrocarbon group such as an alkyl group, a cycloalkyl group, an alkenyl group, a cycloalkenyl group, an alkynyl group, etc. The term "aryl group" means at least a substituted or unsubstituted phenyl and naphthyl groups. An acyl moiety (in acyl group, acylamino group, etc.) means an aliphatic and aromatic acyl moiety. A sulfonyl moiety (in sulfonyl group, sulfonamido group) means an aliphatic and aromatic sulfonyl moieties. A carbamoyl group, sulfamoyl group, amino group and ureido group include unsubstituted and substituted groups thereof. A heterocyclic group is a 3- to 8-membered having at least one of N, O and S atoms as hetero atom.

In the present invention, it is preferred to use a timing type DIR coupler where both residues A and B are bonded to each other through a TIME group where $n=1$.

The compounds represented by formula (I) will be discussed in more detail below.

The coupler moiety represented by A in formula (I) includes a coupler moiety which is coupled with an oxidation product of an aromatic primary amine developing agent to form a dye (e.g., yellow, magenta, cyan, etc.) and a coupler moiety which forms a coupling reaction product having substantially no absorption in the region of visible light.

Examples of yellow dye image-forming coupler moiety represented by A include pivaloylacetanilide, benzoylacetanilide, malondiester, malondiamide, dibenzoylmethane, benzothiazolylacetamide, malonester-monoamide, benzothiazolyl acetate, benzoxazolylacetamide, benzoxazolylacetate, malondiester, benzimidazolylacetamide and benzimidazolylacetate coupler moieties; coupler moieties derived from heterocyclic ring-substituted acetamides or heterocyclic ring-substituted acetates described in U.S. Patent 3,841,880; coupler moieties derived from acylacetamides described in U.S. Patent 3,770,446, U.K. Patent 1,459,171, West German Patent (OLS) 2,503,099, JP-A-50-139738 and Research Disclosure 15737; and heterocyclic coupler moieties described in U.S. Patent 4,046,574.

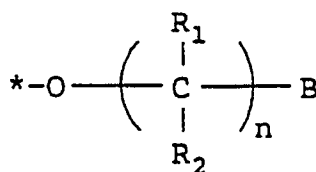
Preferred examples of magenta dye image-forming coupler moieties represented by A include coupler moieties having a 5-oxo-2-pyrazoline nucleus, a pyrazolo[1,5-a]benzimidazole nucleus, a pyrazoloimidazole nucleus, a pyrazolotriazole nucleus or a pyrazolotetrazole nucleus, and cyanacetophenone coupler moieties.

Preferred examples of cyan dye image-forming coupler moieties represented by A include coupler moieties having a phenol nucleus or an α -naphthol nucleus.

Further, there are couplers having the same effect as that of DIR couplers even when said couplers do not form substantially any dye after the release of a restrainer by a coupling with an oxidation product of a developing agent. Examples of this type of coupler moieties represented by A include the coupler moieties described in U.S. Patents 4,052,213, 4,088,491, 3,632,345, 3,958,993 and 3,961,959.

Preferred examples of TIME in formula (I) include the following groups.

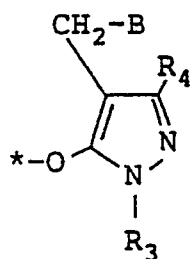
(1) Groups which utilize the cleavage reaction of hemi-acetal as described in U.S. Patent 4,146,396 and JP-A-60-249148, JP-A-60-249149 and JP-A-60-218645. An example thereof is a group represented by the following general formula:



In the above formula, the mark * represents the position where the group is bonded to the coupling site of A; R₁ and R₂ each represents a hydrogen atom or a substituent group; n represents 1 or 2; when n is 2, the two R₁ groups or the two R₂ groups may be the same or different groups; R₁ and R₂ or any one of the two R₁ groups and any one of the two R₂ groups may be combined together to form a ring structure; and B is as defined above in formula (I).

(2) Groups which cause a cleavage reaction by an intramolecular nucleophilic substitution reaction, such as the timing group described in U.S. Patent 4,248,962.

(3) Groups which cause a cleavage reaction by an electron transfer reaction along a conjugated system, such as the group described in U.S. Patent 4,409,323 and the group represented by the following general formula (described in U.K. Patent 2,096,783A):



In the above formula, the mark * represents a position where the group is bonded to the coupling site of A; R₃ and R₄ each represents a hydrogen atom or a substituent group; and B is as defined above in formula (I). Examples of R₃ include an alkyl group having 1 to 24 carbon atoms (e.g., methyl, ethyl, benzyl, dodecyl) or an aryl group having 6 to 24 carbon atoms (e.g., phenyl, 4-tetradecyloxyphenyl, 4-methoxyphenyl, 2,4,6-trichlorophenyl, 4-nitrophenyl, 4-chlorophenyl, 2,5-dichlorophenyl, 4-carboxyphenyl, p-tolyl). Examples of R₄ include a hydrogen atom, an alkyl group having 1 to 24 carbon atoms (e.g., methyl, ethyl, undecyl, pentadecyl), an aryl group having 6 to 36 carbon atoms (e.g., phenyl, 4-methoxyphenyl), a cyano group, an alkoxy group having 1 to 24 carbon atoms (e.g., methoxy, ethoxy, dodecyloxy), an amino group having 0 to 36 carbon atoms (e.g., amino, dimethylamino, piperidino, dihexylamino, anilino), a carbonamido group having 1 to 24 carbon atoms (e.g., acetamido, benzamido, tetradecaneamido), a sulfonamido group having 1 to 24 carbon atoms (e.g., methylsulfonamido, phenylsulfonamido), a carboxyl group, an alkoxycarbonyl group having 2 to 24 carbon atoms (e.g., methoxycarbonyl, ethoxycarbonyl, dodecyloxycarbonyl) and a carbamoyl group having 1 to 24 carbon atoms (e.g., carbamoyl, dimethylcarbamoyl, pyrrolidinocarbonyl).

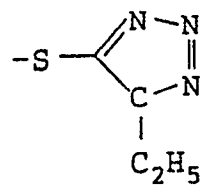
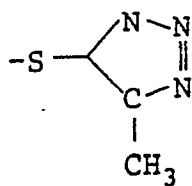
Substituent groups represented by X₁, X₂ and X₃ in general formulas (IIa) to (IIp) will be discussed in detail below.

Examples of X₁ include methyl, ethyl, propyl, butyl, methoxyethyl, ethoxyethyl, isobutyl, allyl, dimethylaminoethyl, propargyl, chloroethyl, methoxycarbonylmethyl, methylthioethyl, 4-hydroxyphenyl, 3-hydroxyphenyl, 4-sulfamoylphenyl, 3-sulfamoylphenyl, 4-carbamoylphenyl, 3-carbamoylphenyl, 4-dimethylaminophenyl, 3-acetamidophenyl, 4-propaneamidophenyl, 4-methoxyphenyl, 2-hydroxyphenyl, 2,5-dihydroxyphenyl, 3-methoxycarbonylaminophenyl, 3-(3-methylureido)phenyl, 3-(3-ethylureido)phenyl, 4-hydroxyethoxyphenyl and 3-acetamido-4-methoxyphenyl. Examples of X₂ include methyl, ethyl, benzyl, n-propyl, i-propyl, n-butyl, i-butyl, cyclohexyl, fluorine atom, chlorine atom, bromine atom, iodine atom, hydroxymethyl, hydroxyethyl, hydroxy, methoxy, ethoxy, butoxy, allyloxy, benzyloxy, methylthio, ethylthio, methoxycarbonyl, ethoxycarbonyl, acetamido, propaneamido, butaneamido, octaneamido, benzamido, dimethylcarbamoyl, methylsulfonyl, methylsulfonamido, phenylsulfonamido, dimethylsulfamoyl, acetoxyl, ureido, 3-methylureido, cyano, nitro, amino, dimethylamino, methoxycarbonylamino, ethoxycarbonylamino, phenoxy carbonyl, methoxyethyl and acetyl. Examples of X₃ include oxygen atom, sulfur atom, imino group, methylimino group, ethylimino group, propylimino group and allylimino group.

Among the groups represented by formulas (IIa) to (IIp), the groups represented by formulas (IIa), (IIb), (IIi), (IIj), (IIk) and (IIl) are preferred. Particularly preferred are the groups represented by formulas (IIa), (IIi), (IIj) and (IIk).

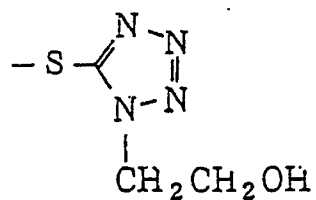
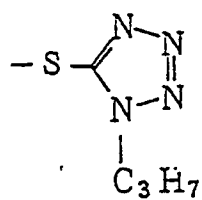
Examples of the groups represented by B in formula (I) include the following groups.

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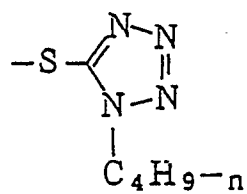
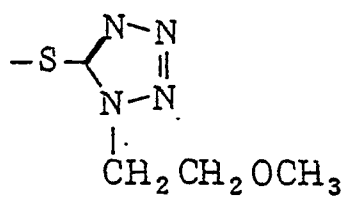
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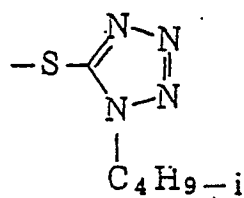
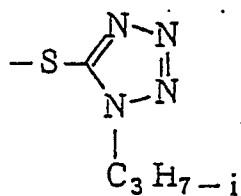
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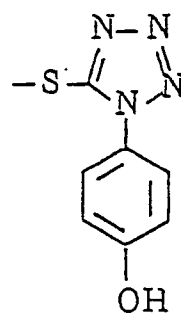
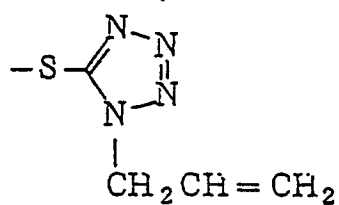
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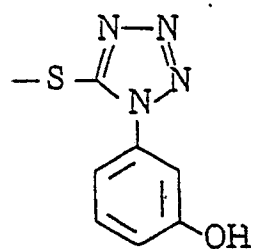
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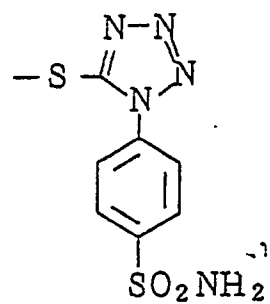
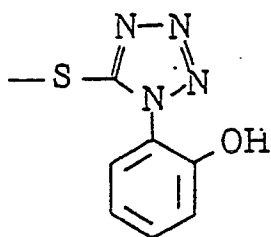
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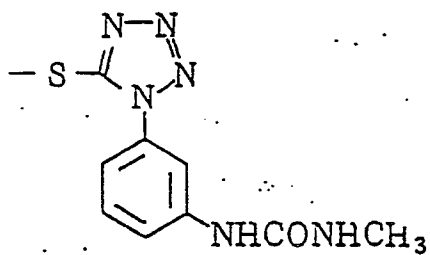
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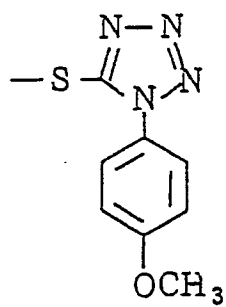
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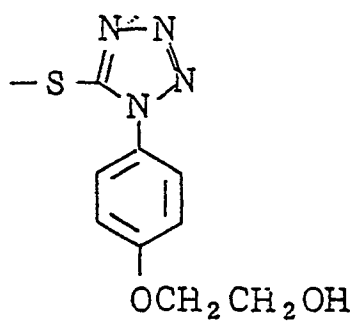
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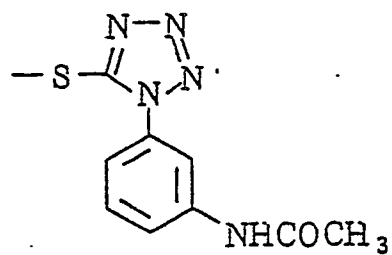
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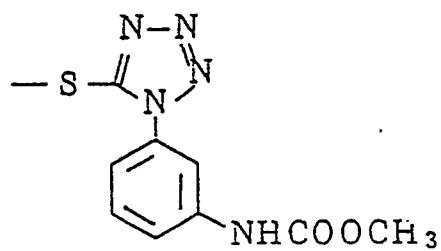


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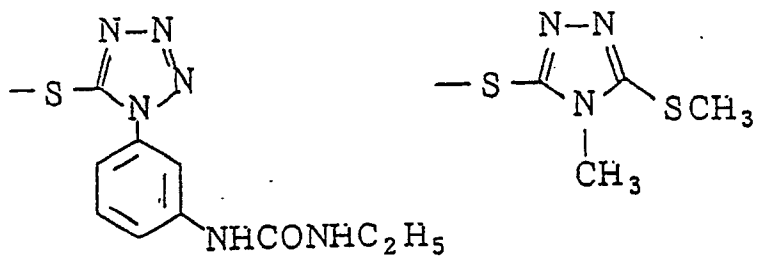


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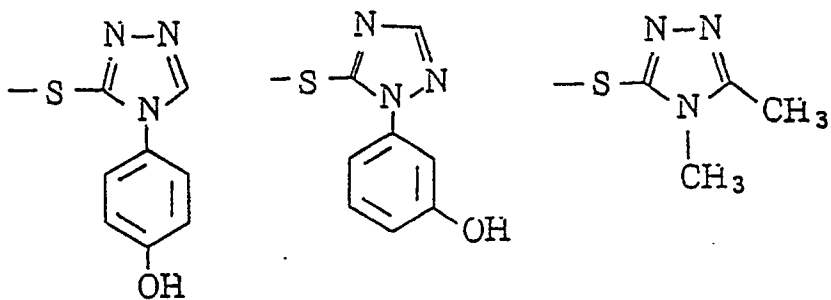
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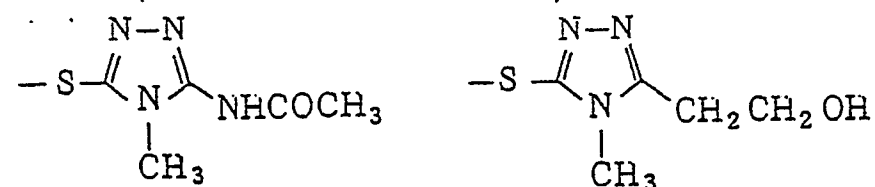
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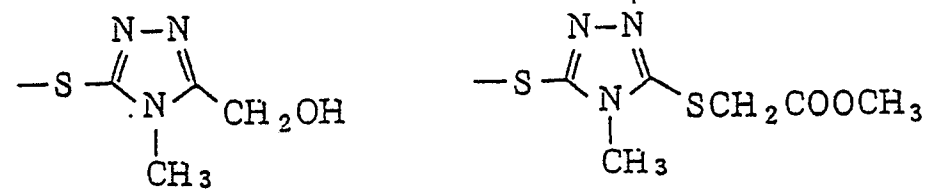


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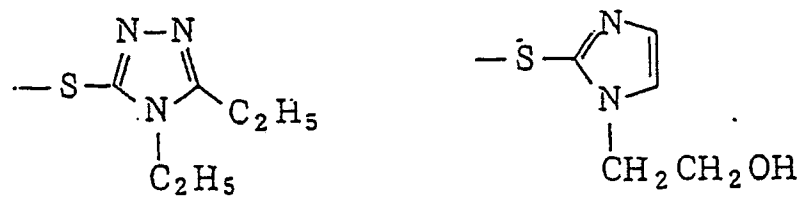


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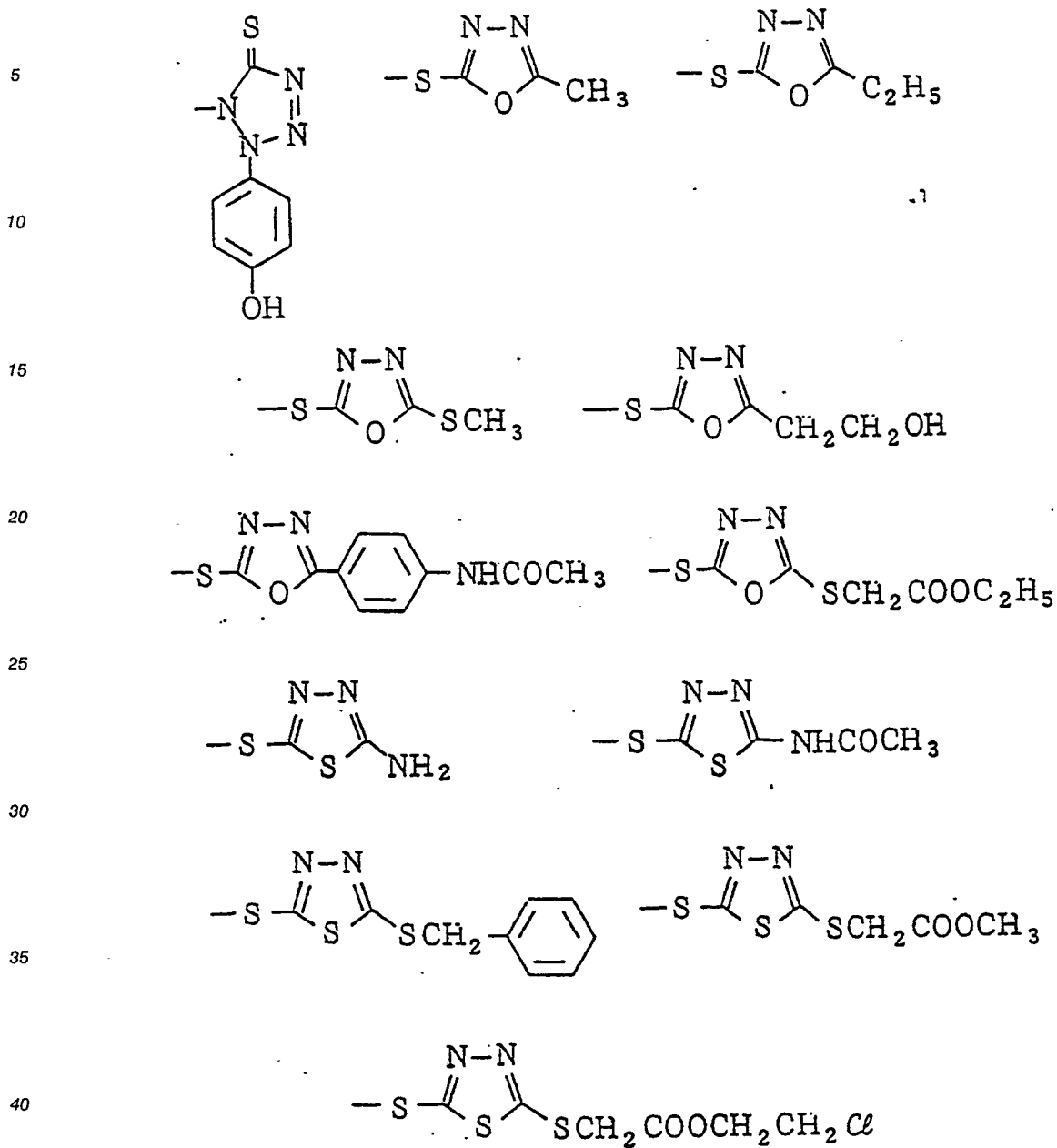
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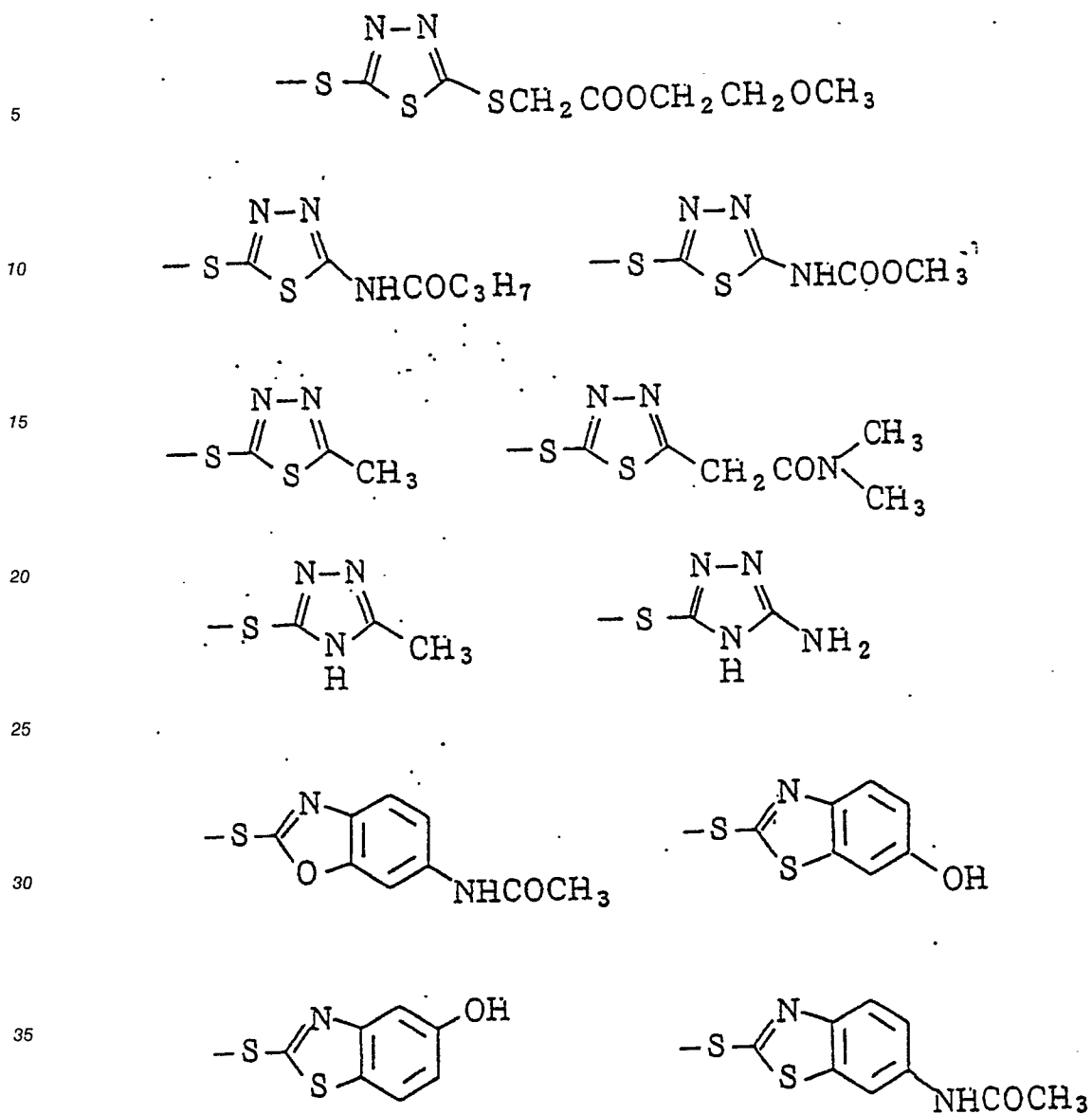


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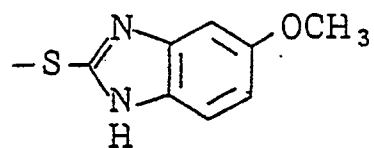
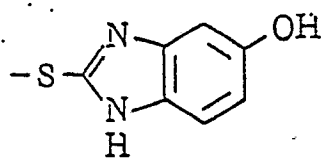
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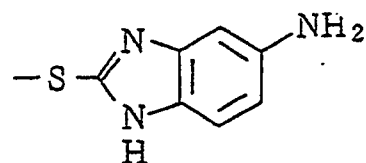
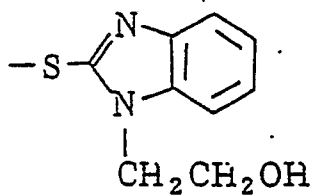




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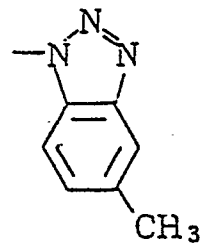
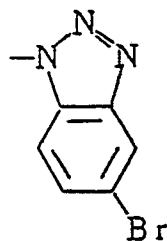
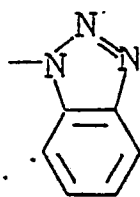


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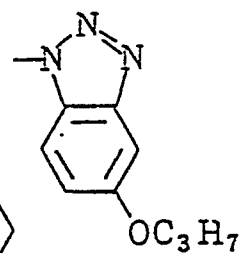
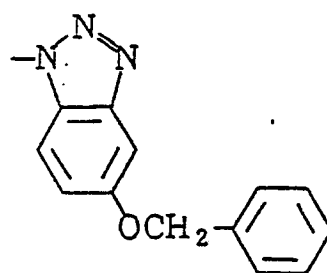
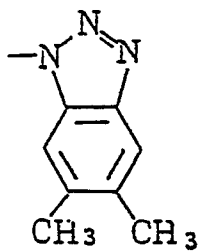


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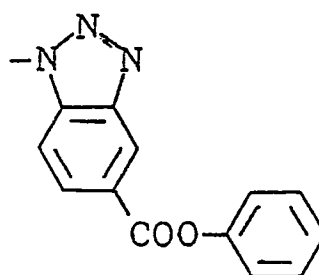
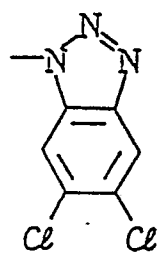
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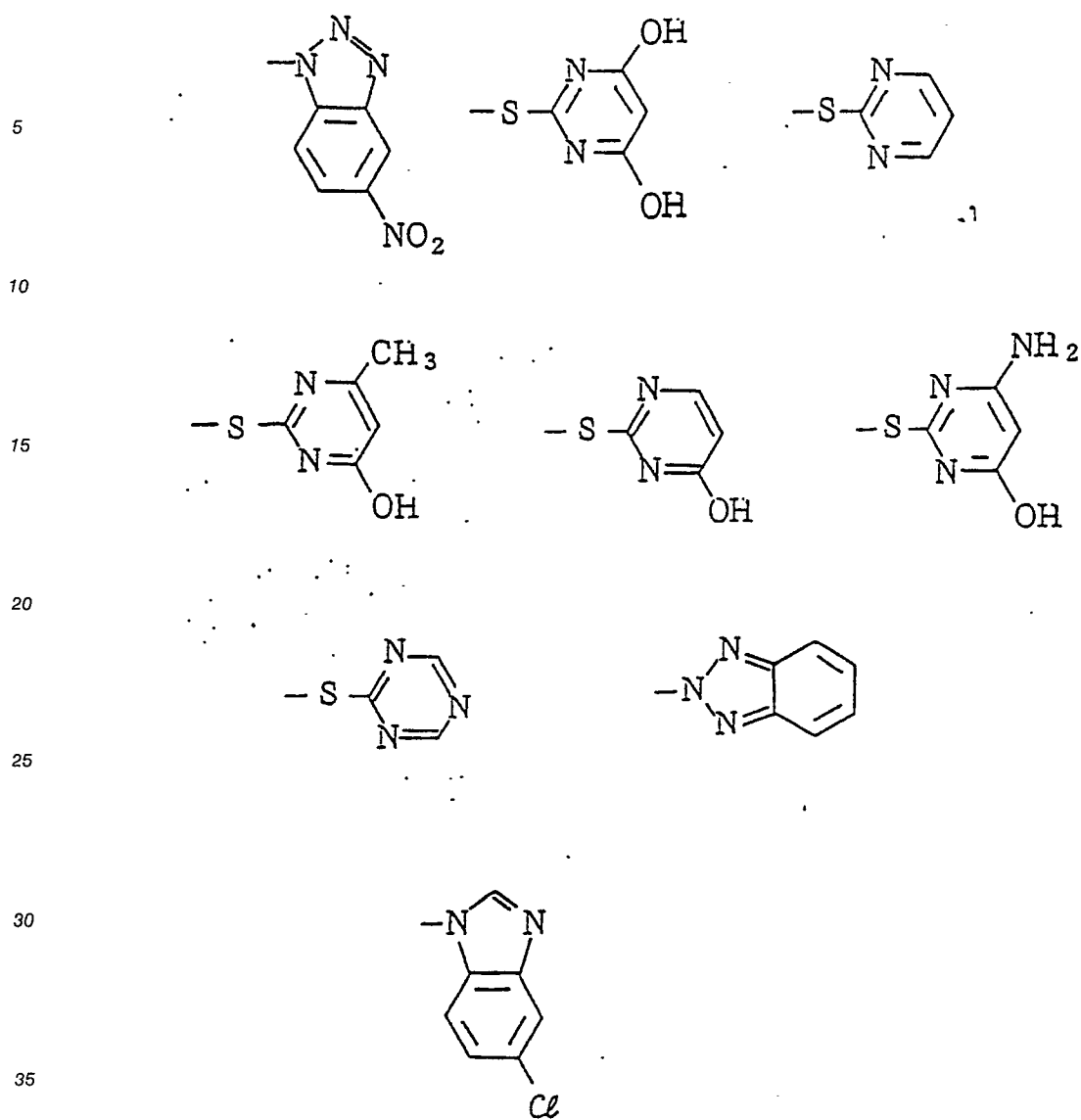
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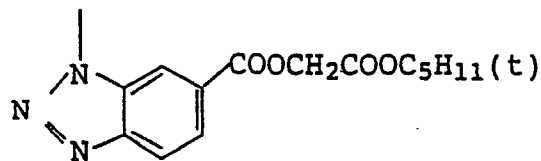
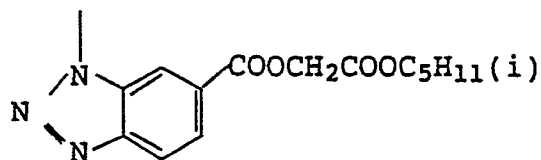
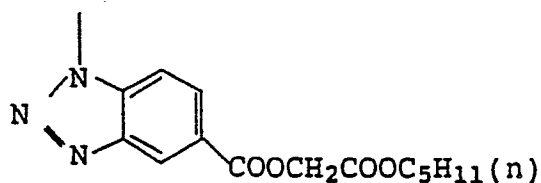
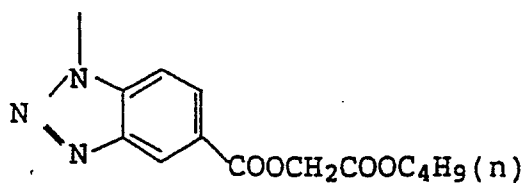
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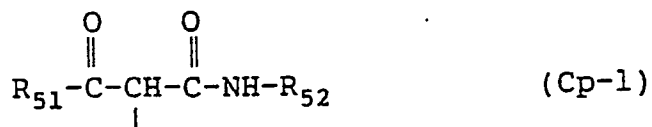




35 The compound represented by formula (I) is incorporated into at least one of blue-, green- and red-sensitive layer and a light-insensitive intermediate layer adjacent thereto, preferably into a red-sensitive layer.

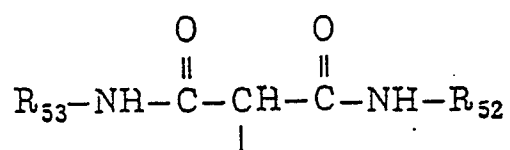
Generally, the couplers of the present invention are used together as a mixture with principal couplers. The ratio of the coupler of the present invention to the principal coupler is 0.1 to 100 mol%, preferably 1 to 50 mol%. The proportion of the coupler of the present invention to silver halide is 0.01 to 20 mol%, preferably 0.5 to 10 mol% per mol of silver halide in the same layer when the compound is incorporated into a silver halide emulsion layer, or silver halide in the adjacent silver halide emulsion layer containing a larger amount of silver halide contained in adjacent silver halide emulsion layers when the compound is incorporated into a light-insensitive intermediate layer.

40 The effects obtained by the present invention are particularly remarkable when A in formula I is a coupler moiety represented by the following general formulas (Cp-1), (Cp-2), (Cp-3), (Cp-4), (Cp-5), (Cp-6), (Cp-7), (Cp-8), (Cp-9), (Cp-10) or (Cp-11). These couplers are preferable, because the coupling rate thereof is high.



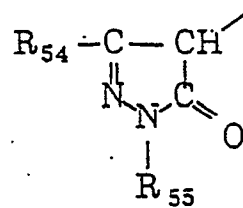
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(Cp-2)

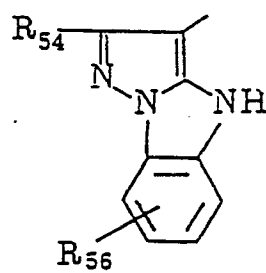
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(Cp-3)

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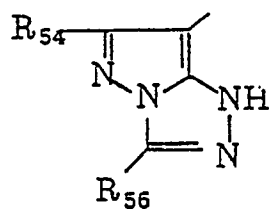
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(Cp-4)

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(Cp-5)

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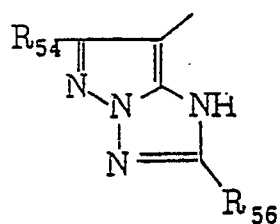
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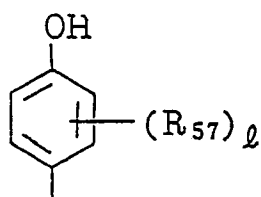
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(Cp-6)

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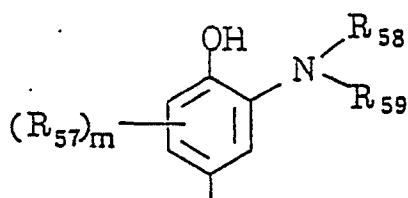
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(Cp-7)

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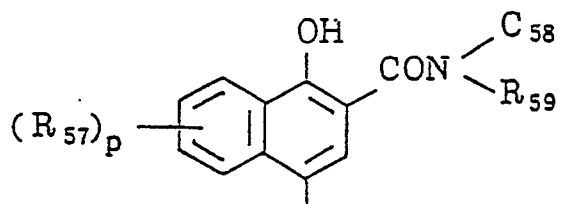
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(Cp-8)

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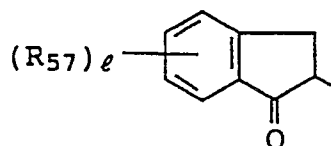
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(Cp-9)

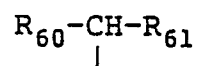
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(Cp-10)

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(Cp-11)

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In the above formulas, the free bond derived from the coupling site represents the position where the coupling moiety is bonded to the group which is eliminated by coupling. When R_{51} , R_{52} , R_{53} , R_{54} , R_{55} ,

R₅₆, R₅₇, R₅₈, R₅₉, R₆₀ or R₆₁ in the above formulas has a non-diffusing group, each substituent group is so chosen that the total of carbon atoms thereof is 8 to 32, preferably 10 to 22. In other case, the total of carbon atoms is preferably not more than 15.

R₅₁ to R₆₁, l, m and p in the above formulas (Cp-1) to (Cp-11) will be discussed below.

- 5 R₅₁ is an aliphatic group, an aromatic group, an alkoxy group or a heterocyclic group, and R₅₂ and R₅₃ are each an aromatic group or a heterocyclic group.

The aliphatic group represented by R₅₁ is an aliphatic hydrocarbon group having preferably 1 to 22 carbon atoms, which may be a substituted or unsubstituted straight-chain, branched or cyclic hydrocarbon group and may optionally have one or more substituent groups. Preferred examples of substituent groups
10 for the aliphatic group include an alkoxy group, an aryloxy group, an amino group, an acylamino group and a halogen atom. If desired, these substituent groups may be further substituted with at least one substituent such as a hydroxy group, a nitro group, a cyano group, a group having from 0 to 32 carbon atoms, such as an amino group, a sulfo group, a carbonamido group, a sulfonamido group, a carbamoyl group, a sulfamoyl group, a ureido group, an alkoxycarbonyl group, and an aryloxycarbonyl group.

- 15 Specific examples of useful aliphatic groups for R₅₁ include isopropyl, isobutyl, tert-butyl, isoamyl, tert-amyl, 1,1-dimethylbutyl, 1,1-dimethylhexyl, 1,1-diethylhexyl, dodecyl, hexadecyl, octadecyl, cyclohexyl, 2-methoxyisopropyl, 2-phenoxyisopropyl, 2-p-tert-butylphenoxyisopropyl, α -aminoisopropyl, α -(diethylamino)-isopropyl, α -(succinimido)isopropyl, α -(phthalimido)isopropyl and α -(benzenesulfonamido)isopropyl.

When R₅₁, R₅₂ or R₅₃ is an aromatic group (particularly a phenyl group), the aromatic group may be
20 substituted. The aromatic group (such as a phenyl group) may be substituted by an alkyl group, an alkenyl group, an alkoxy group, an alkoxycarbonyl group, an alkoxycarbonylamino group, an aliphatic amido group, an alkylsulfamoyl group, an alkylsulfonamido group, an alkylureido group or an alkyl-substituted succinimido group, each group having not more than 32 carbon atoms. The alkyl moiety in these groups may be substituted with an aromatic group such as an alkyl-substituted phenylene group. Further, the phenyl group
25 represented by R₅₁, R₅₂ or R₅₃ may be substituted by an aryloxy group, an aryloxycarbonyl group, an arylcarbamoyl group, an arylamido group, an arylsulfamoyl group, an arylsulfonamido group or an arylureido group. The aryl portion of these substituent groups may be further substituted with one or more alkyl groups (the total of carbon atoms being 1 to 22).

Furthermore, the phenyl group represented by R₅₁, R₅₂ or R₅₃ may be substituted by an unsubstituted
30 or C₁ to C₆ lower alkyl-substituted amino group, hydroxy group, carboxy group, sulfo group, nitro group, cyano group, thiocyno group or a halogen atom.

R₅₁, R₅₂ or R₅₃ may be a condensed group wherein a phenyl group is condensed with an other ring, such as a naphthyl group, a quinolyl group, an isoquinolyl group, a chromanyl group, a coumaranyl group and a tetrahydronaphthyl group. These groups themselves may be further substituted.

- 35 When R₅₁ is an alkoxy group, the alkyl moiety of the alkoxy group is a straight chain or branched alkyl or alkenyl group or a cyclic alkyl or alkenyl group, each group having 1 to 32 carbon atoms, preferably 1 to 22 carbon atoms. These groups may be substituted by a halogen atom, an aryl group or an alkoxy group.

When R₅₁, R₅₂ or R₅₃ is a heterocyclic group, the heterocyclic group is bonded through one carbon atom as a member of the ring to the carbon atom of the carbonyl group of the acyl group in α -
40 acylacetamido or to the nitrogen atom of an amido group. Examples of such heterocyclic rings include thiophene, furan, pyran, pyrrole, pyrazole, pyridine, pyrazine, pyrimidine, pyridazine, indolizine, imidazole, thiazole, oxazole, triazine, thiadiazine and oxazine. These rings may have substituent such as a hydroxy group, a nitro group, a cyano group, a group having from 1 to 32 carbon atoms, such as an amino group, a sulfo group, a carbonamido group, a sulfonamido group, a carbamoyl group, a sulfamoyl group, a ureido group, an alkoxycarbonyl group, and an aryloxycarbonyl group.
45

In formula (Cp-3), R₅₅ has 1 to 32 carbon atoms (including carbon atoms of the substituent if it has any), preferably 1 to 22 carbon atoms, R₅₅ is a straight-chain or branched alkyl group (e.g., methyl, isopropyl, tert-butyl, hexyl, dodecyl), a straight-chain or branched alkenyl group (e.g., allyl), a cyclic alkyl group (e.g., cyclopentyl, cyclohexyl, norbornyl), an aralkyl group (e.g., benzyl, β -phenethyl) or a cyclic
50 alkenyl group (e.g., cyclopentenyl, cyclohexenyl), each of which may have one or more substituent groups. Examples of the substituent groups include a halogen atom, a nitro group, a cyano group, an aryl group, an alkoxy group, an aryloxy group, a carboxy group, an alkylthiocarbonyl group, an arylthiocarbonyl group, an alkoxycarbonyl group, an aryloxycarbonyl group, a sulfo group, a sulfamoyl group, a carbamoyl group, an acylamino group, a diacylamino group, a ureido group, a urethane group, a thiourethane group, a sulfonamido group, a heterocyclic group, an arylsulfonyl group, an alkylsulfonyl group, an arylthio group, an alkylthio group, an alkylamino group, a dialkylamino group, an anilino group, an N-arylanilino group, an N-alkylanilino group, an N-acylanilino group, a hydroxyl group and a mercapto group.

Further, R₅₅ may be an aryl group (e.g., phenyl, α - or β -naphthyl) which may have one or more

substituent groups preferably having 1 to 18 carbon atoms. Examples of the substituent groups include an alkyl group, an alkenyl group, a cyclic alkyl group, an aralkyl group, a cyclic alkenyl group, a halogen atom, a nitro group, a cyano group, an aryl group, an alkoxy group, an aryloxy group, a carboxyl group, an alkoxy carbonyl group, an aryloxy carbonyl group, a sulfo group, a sulfamoyl group, a carbamoyl group, an acylamino group, a diacylamino group, a ureido group, an aminocarbonyloxy group, an alkoxy carbonylamino group, an aryloxy carbonylamino group, a sulfonamido group, a heterocyclic group, an arylsulfonyl group, an alkylsulfonyl group, an arylthio group, an alkylthio group, an alkylamino group, a dialkylamino group, an anilino group, an N-alkylanilino group, an N-arylanilino group, an N-acylanilino group and a hydroxyl group.

Further, R_{55} may be a heterocyclic group (e.g., a 5-membered or 6-membered heterocyclic ring containing at least one hetero-atom selected from nitrogen, oxygen and sulfur, and a condensed heterocyclic group such as pyridyl, quinolyl, furyl, benzothiazolyl, oxazolyl, imidazolyl, and naphthoxazolyl), a substituted heterocyclic group (examples of substituent groups being those described above in the description of the substituent groups for the aryl group), an aliphatic or aromatic acyl group, an alkylsulfonyl group, an arylsulfonyl group, an alkylcarbamoyl group, an arylcarbamoyl group, an alkylthiocarbamoyl group or an arylthiocarbamoyl group.

R_{54} is a hydrogen atom, or a group having 1 to 32 carbon atoms, preferably 1 to 22 carbon atoms and is a straight-chain or branched alkyl, alkenyl, cyclic alkyl, aralkyl or cyclic alkenyl group (these groups may have one or more substituent groups; examples of the substituent groups are those described above in the description of the substituent groups for R_{55}), an aryl group or a heterocyclic group (these groups may have one or more substituent groups; examples of the substituent groups are those described above in the description of the substituent groups for R_{55}), an alkoxy carbonyl group (e.g., methoxycarbonyl, ethoxycarbonyl, stearyloxycarbonyl), an aryloxy carbonyl group (e.g., phenoxycarbonyl, naphthoxycarbonyl), an aralkyloxycarbonyl group (e.g., benzyloxycarbonyl), an alkoxy group (e.g., methoxy, ethoxy, heptadecyloxy), an aryloxy group (e.g., phenoxy, tolyloxy), an alkylthio group (e.g., ethylthio, dodecylthio), an arylthio group (e.g., phenylthio, α -naphthylthio), a carboxyl group, an acylamino group (e.g., acetamino, 3-[(2,4-di-tert-amylphenoxy)acetamido]benzamido), a diacylamino group, an N-alkylacylamino group (e.g., N-methylpropionamido), an N-arylacylamino group (e.g., N-phenylacetamido), a ureido group (e.g., ureido, N-arylureido, N-alkylureido), an aminocarbonyloxy group, an alkoxy carbonylamino group, an aryloxy carbonylamino group, an aminocarbonylthio group, an alkylthiocarbonylamino group, an arylthiocarbonylamino group, an arylamino group (e.g., phenylamino, N-methylanilino, diphenylamino, N-acetylanilino, 2-chloro-5-tetradecaneamidoanilino), an alkylamino group (e.g., n-butylamino, methylamino, cyclohexylamino), a cycloamino group (e.g., piperidino, pyrrolidino), a heterocyclic amino group (e.g., 4-pyridylamino, 1,2-benzoxazolylamino), an alkylcarbonyl group (e.g., methylcarbonyl), an arylcarbonyl group (e.g., phenylcarbonyl), a sulfonamido group (e.g., alkylsulfonamido, arylsulfonamido), a carbamoyl group (e.g., ethylcarbamoyl, dimethylcarbamoyl, N-methylphenylcarbamoyl, N-phenylcarbamoyl), a sulfamoyl group (e.g., N-alkylsulfamoyl, N,N-dialkylsulfamoyl, N,N-arylsulfamoyl, N-alkyl-N-arylsulfamoyl, N-diarylsulfamoyl), a cyano group, a hydroxyl group or a sulfo group.

R_{56} is a hydrogen atom, a straight-chain or branched alkyl group, an alkenyl group, a cyclic alkyl group, an aralkyl group or a cyclic alkenyl group, each having 1 to 32 carbon atoms, preferably 1 to 22 carbon atoms. These groups may be substituted. Examples of substituent groups are those described above in the description of the substituent groups for R_{55} .

Further, R_{56} may represent an aryl group or a heterocyclic group, each of which may have one or more substituent groups. Examples of the substituent groups are those described above in the description of the substituent groups for R_{55} .

Furthermore, R_{56} may represent a cyano group, an alkoxy group, an aryloxy group, a halogen, a carboxy group, an alkoxy carbonyl group, an aryloxy carbonyl group, an acyloxy group, a sulfo group, a sulfamoyl group, a carbamoyl group, an acylamino group, a diacylamino group, a ureido group, an aminocarbonyloxy group, an alkoxy carbonylamino group, an aryloxy carbonylamino group, a sulfonamido group, an arylsulfonyl group, an alkylsulfonyl group, an arylthio group, an alkylthio group, an alkylamino group, a dialkylamino group, an anilino group, an N-arylanilino group, an N-alkylanilino group, an N-acylanilino group or a hydroxyl group. These groups may be further substituted with a substituent as described above for R_{55} .

R_{57} , R_{58} and R_{59} are each a group used in conventional four equivalent type phenol or α -naphthol couplers. Specifically, R_{57} represents a hydrogen atom, a halogen atom, an alkoxy carbonylamino group, an aliphatic hydrocarbon group, an N-arylureido group, an acylamino group or a group of $-O-R_{62}$ or $-S-R_{62}$ (wherein R_{62} is an aliphatic hydrocarbon groups). The carbon number of the groups represented by R_{57} is preferably from 1 to 32. When the two or more R_{57} groups per molecule exist, two or more R_{57} groups may

be different. The aliphatic hydrocarbon residue may have one or more substituent groups such as those described above in the description of the substituents for the alkyl group. The carbon numbers of these substituents is preferably from 1 to 28. R₅₇ may be substituted at any position on the nucleus.

When these substituent groups have an aryl group, the aryl group may have one or more substituent groups. Examples of the substituent groups are those described above in the description of the substituent for R₅₅.

R₅₈ and R₅₉ are each a group selected from the group consisting of an aliphatic hydrocarbon group, an aryl group and a heterocyclic group. The carbon number of these groups is preferably from 1 to 32. Alternatively, one of them may be hydrogen atom. These groups may have one or more substituent groups. If desired, R₅₈ and R₅₉ may be combined together to form a nitrogen-containing heterocyclic nucleus which may have further at least one of N, O, and S atoms.

The aliphatic hydrocarbon group may be a saturated or unsaturated hydrocarbon group or a straight-chain, branched or cyclic hydrocarbon group. Preferably, the hydrocarbon group is an alkyl group (e.g., methyl, ethyl, propyl, isopropyl, butyl, t-butyl, isobutyl, dodecyl, octadecyl, cyclopropyl, cyclohexyl) or an alkenyl group (e.g., allyl, octenyl). Examples of the aryl group include a phenyl group and a naphthyl group. Typical examples of a heterocyclic group include pyridinyl, quinolyl, thienyl, piperidyl and imidazolyl. Examples of substituent groups which may be introduced into the aliphatic hydrocarbon group, the aryl group and the heterocyclic group include a halogen atom, a nitro group, a hydroxy group, a carboxyl group, an amino group, a substituted amino group, a sulfo group, an alkyl group, an alkenyl group, an aryl group, a heterocyclic group, an alkoxy group, an aryloxy group, an arylthio group, an arylazo group, an acylamino group, a carbamoyl group, an ester group (including an alkoxycarbonyl group, and an aryloxycarbonyl group), acyl group, an acyloxy group, a sulfonamido group, a sulfamoyl group, a sulfonyl group and a morpholino group.

l is an integer of 1 to 4, m is an integer of 1 to 3 and p is an integer of 1 to 5.

R₆₀ represents an arylcarbonyl group, an alkanoyl group having 2 to 32 carbon atoms, preferably 2 to 22 carbon atoms, an arylcarbamoyl group, an alkanecarbamoyl group having 2 to 32 carbon atoms, preferably 2 to 22 carbon atoms, an alkoxycarbonyl group having 1 to 32 carbon atoms, preferably 1 to 22 carbon atoms, or an aryloxycarbonyl group, each of which may have one or more substituent groups. Examples of the substituent groups include an alkoxy group, an alkoxycarbonyl group, an acylamino group, an alkylsulfamoyl group, an alkylsulfonamido group, an alkylsuccinimido group, a halogen atom, a nitro group, a carboxyl group, a nitrile group, an alkyl group and an aryl group.

R₆₁ represents an arylcarbonyl group, an alkanoyl group having 2 to 32 carbon atoms, preferably 2 to 22 carbon atoms, an arylcarbamoyl group, an alkanecarbamoyl group having 2 to 32 carbon atoms, preferably 2 to 22 carbon atoms, an alkoxycarbonyl group having 1 to 32 carbon atoms, preferably 1 to 22 carbon atoms, an aryloxycarbonyl group, an alkylsulfonyl group having 1 to 32 carbon atoms, preferably 1 to 22 carbon atoms, an arylsulfonyl group, an aryl group or a 5-membered or 6-membered heterocyclic group (the hetero-atom being selected from nitrogen, oxygen and sulfur) such as a triazolyl group, an imidazolyl group, a phthalimido group, a succinimido group, a furyl group, a pyridyl group or a benzotriazolyl group, each of which may have one or more substituent groups. Examples of the substituent groups are those described above in the description of the substituent groups for R₆₀.

Among the above-described yellow coupler moieties, preferred moieties are those of formula (Cp-1) where R₅₁ is a t-butyl group or a substituted or unsubstituted aryl group and R₅₂ is a substituted or unsubstituted aryl group, and those of formula (Cp-2) where R₅₂ and R₅₃ are each a substituted or unsubstituted aryl group.

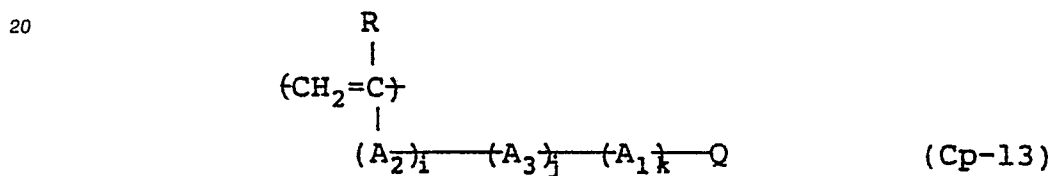
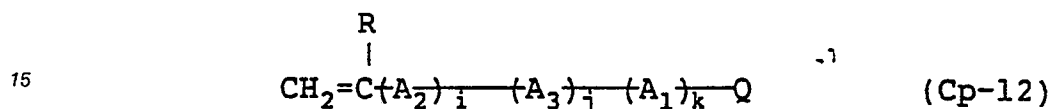
As magenta coupler moieties, preferred moieties are those of formula (Cp-3) where R₅₄ is an acylamino group, a ureido group or an arylamino group and R₅₅ is a substituted aryl group; those of formula (Cp-4) where R₅₄ is an acylamino group, a ureido group or an arylamino group and R₅₆ is a hydrogen atom; and those of formulas (Cp-5) and (Cp-6) where R₅₄ and R₅₅ are each a straight-chain or branched alkyl group, an alkenyl group, a cyclic alkyl group, an aralkyl group or a cyclic alkenyl group.

As cyan coupler moieties, preferred moieties are those the group of formula (Cp-7) where R₅₇ is an acylamino group or a ureido group at the 2 position, an acylamino group or an alkyl group at the 5 position and a hydrogen atom or a chlorine atom at the 6 position, and those of formula (Cp-9) where R₅₇ is a hydrogen atom, an acylamino group, a sulfonamido group or an alkoxycarbonyl group at the 5 position, R₅₈ is a hydrogen atom and R₅₉ is a phenyl group, an alkyl group, an alkenyl group, a cyclic alkyl group, an aralkyl group or a cyclic alkenyl group.

As non-color forming coupler moieties, preferred moieties are those of formula (Cp-10) where R₅₇ is an acylamino group, a sulfonamido group or a sulfamoyl group, and those of formula (Cp-11) where R₆₀ and R₆₁ are each an alkoxycarbonyl group.

A compound having at least two coupler moiety such as bis-, tris- or tetrakis compound, or polymer may be formed through any one of R₅₁ to R₆₁. The polymer may be a polymer of a monomer having an ethylenically unsaturated group at any one of these groups or a copolymer thereof with a non-color forming monomer.

5 When the coupler is a polymer, the polymer is either (1) a polymer derived from a monomer coupler represented by the following general formula (Cp-12) and composed of a repeating unit represented by the following general formula (Cp-13); or (2) a copolymer of said monomer coupler with at least one non-color forming monomer having at least one ethylene group and incapable of coupling with an oxidation product of an aromatic primary amine developing agents. Two or more monomer couplers may be polymerized
10 simultaneously.



In the above formulas, R is a hydrogen atom, a lower alkyl having 1 to 4 carbon atoms or a chlorine atom; A₁ is -CONR', -NR'CONR', -NR'COO-, -COO-, -SO₂-, -CO-, -NRCO-, -SO₂NR', -NR'SO₂-, -OCO-,
30 -OCONR', -NR'-or -O-; A₂ is -CONR' or -COO-; R' is a hydrogen atom, an aliphatic group or an aryl group; when two or more R groups per molecule exist, the two or more R' groups may be the same or different groups; A₃ is an unsubstituted or substituted alkylene group having 1 to 10 carbon atoms, an aralkylene group or an unsubstituted or substituted arylene group (the alkylene group may be a straight-chain or branched alkylene group such as methylene, methylenemethylene, dimethylenemethylene, dimethylene,
35 trimethylene, tetramethylene, pentamethylene, hexamethylene, decylenemethylene and an aralkylene group such as phenylene and naphthylene); Q is a group which allows the groups of formulas (Cp-1) to (Cp-11) through any one of R₅₁, to R₆₁ to be bonded to the compound of formula (Cp-12) or (Cp-13); i, j and k are each 0 or 1 and there is no case where all of i, j and k are 0 simultaneously.

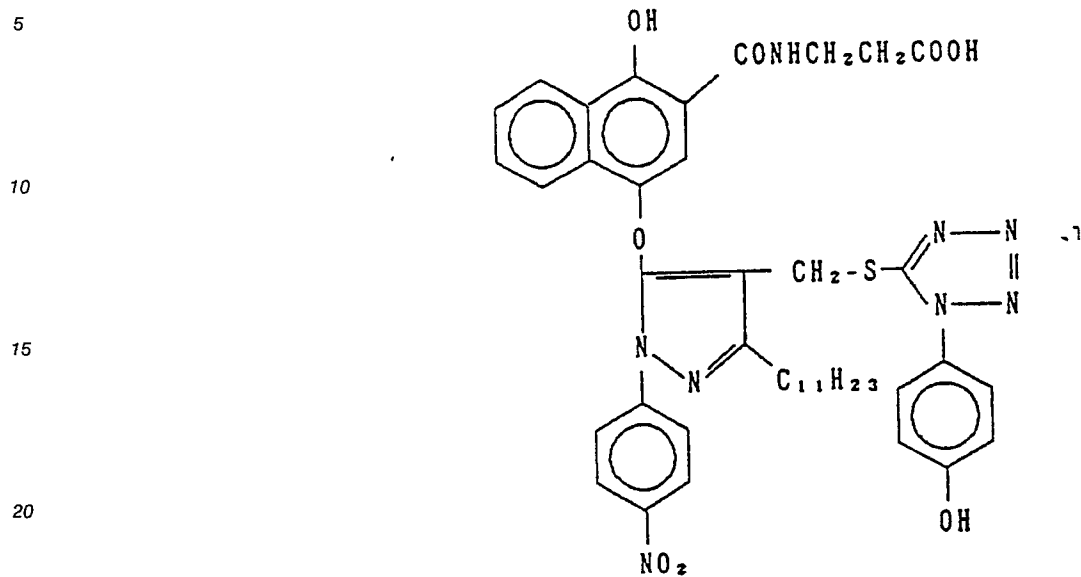
Examples of substituent groups for the alkylene group, the aralkylene group or the arylene group represented by A₃ include an aryl group (e.g., phenyl), a nitro group, a hydroxyl group, a cyano group, a sulfo group, an alkoxy group (e.g., methoxy), an aryloxy group (e.g., phenoxy), an acyloxy group (e.g.,
40 acetoxyl), an acylamino group (e.g., acetylaminyl), a sulfonamido group (e.g., methanesulfonamido), a sulfamoyl group (e.g., methylsulfamoyl), a halogen atom (e.g., fluorine, chlorine, bromine), carboxyl group, a carbamoyl group (e.g., methylcarbamoyl), an alkoxycarbonyl group (e.g., methoxycarbonyl) and a sulfonyl
45 group (e.g., methylsulfonyl). When two or more substituent groups exist, they may be the same or different groups.

Examples of compounds represented by formula (I) are shown below.

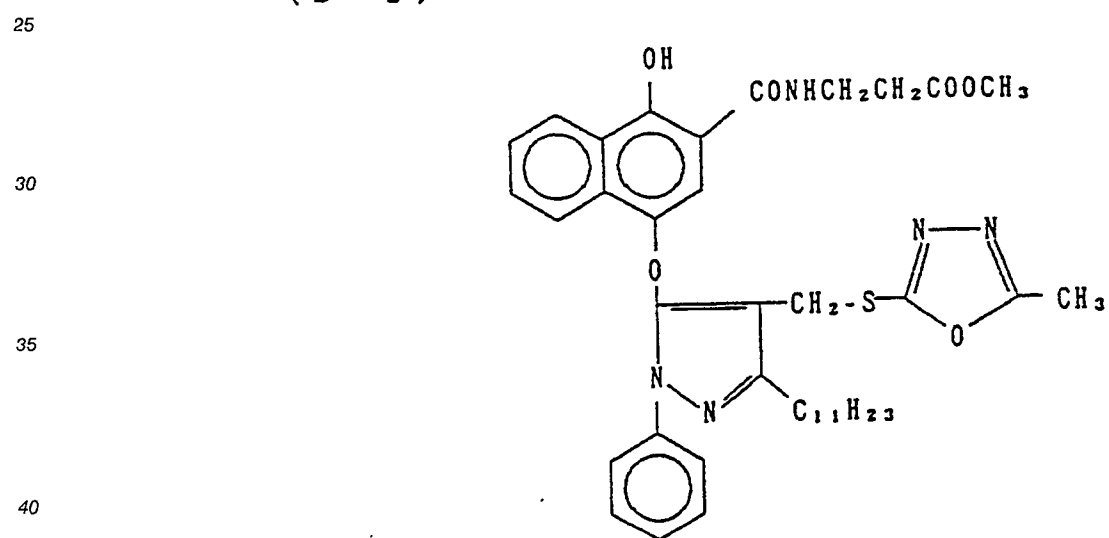
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(D - 1)



(D - 2)

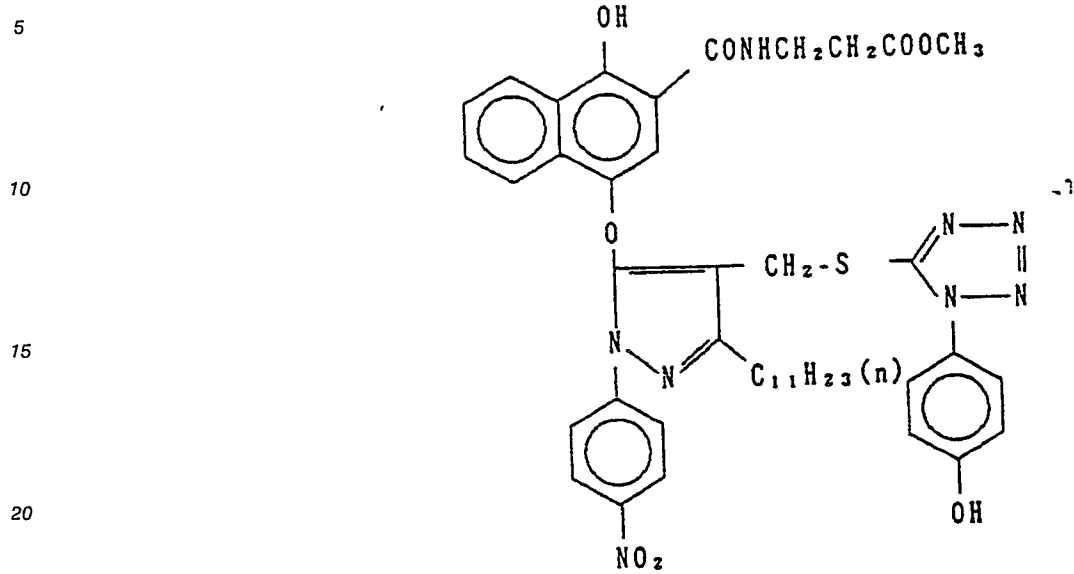


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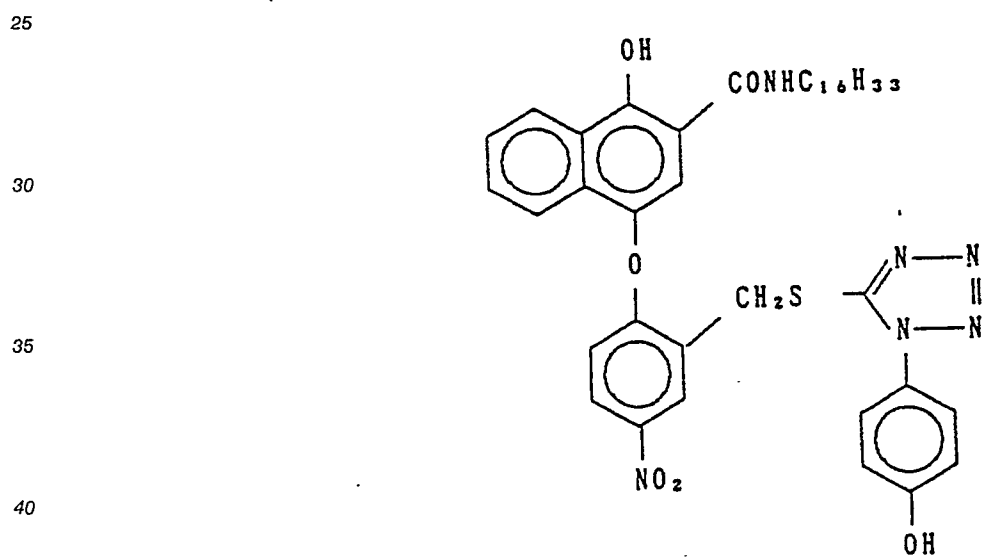
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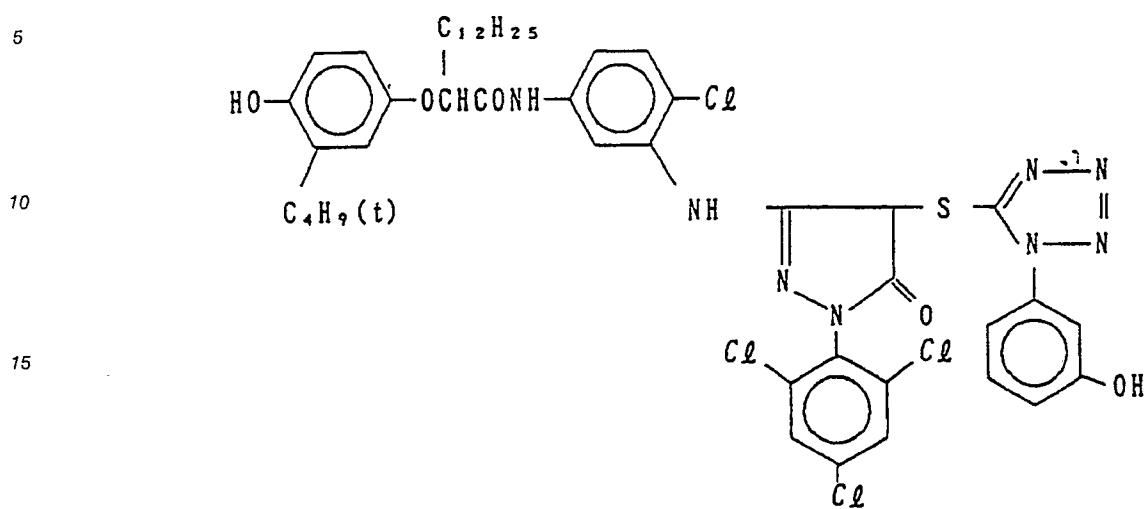
(D - 3)



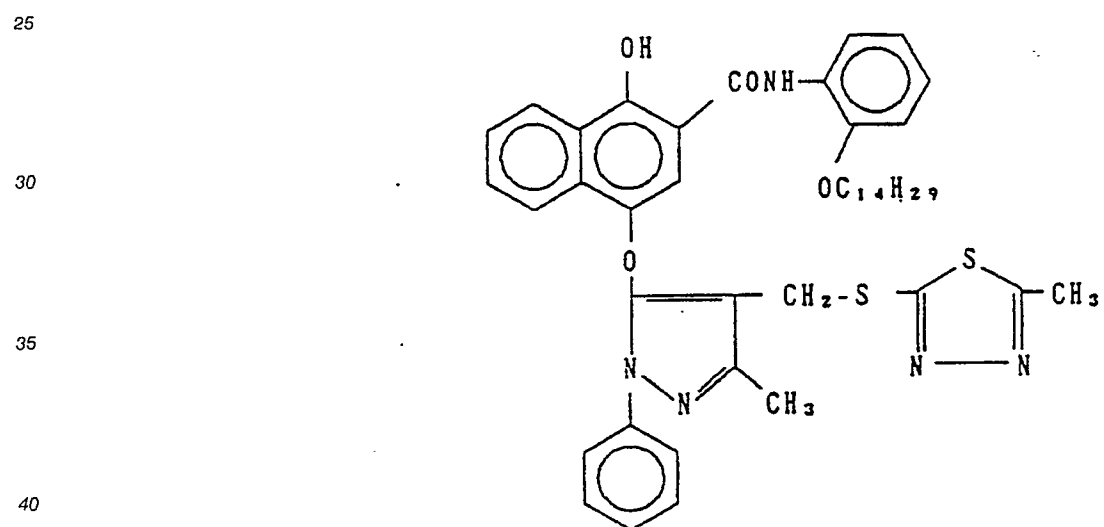
(D - 4)



(D - 5)



(D - 6)



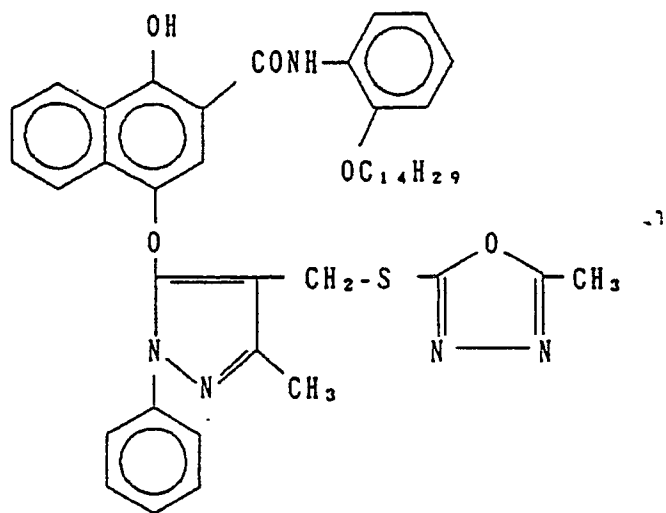
(D - 7)

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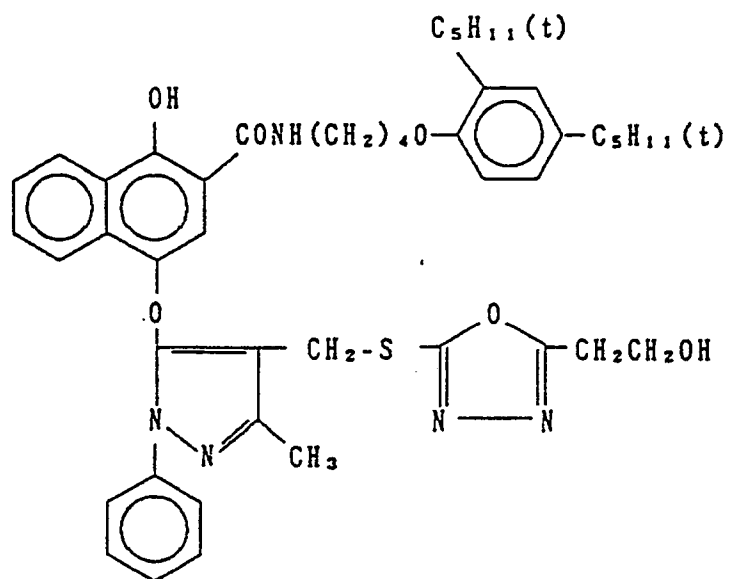
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(D - 8)

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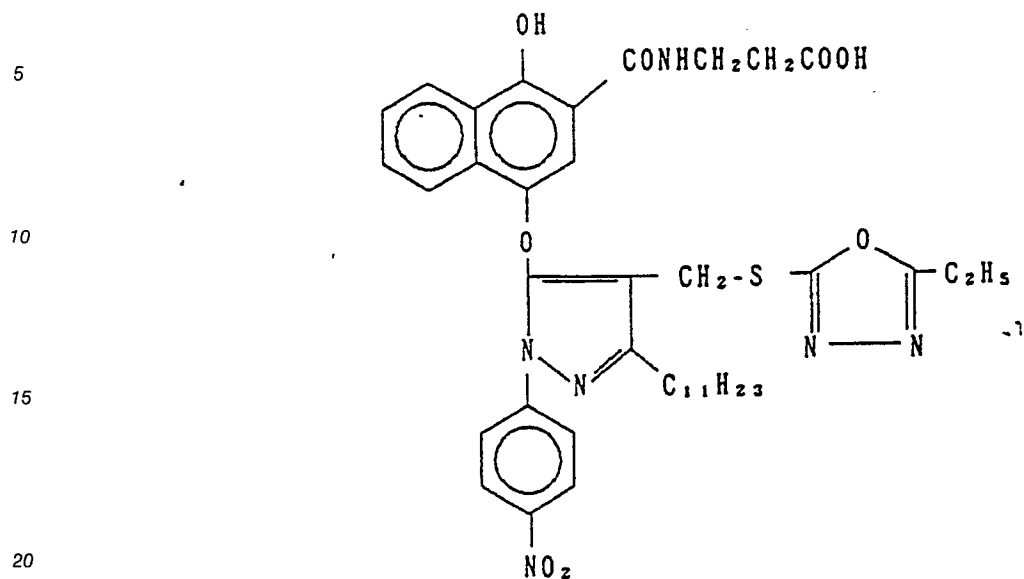


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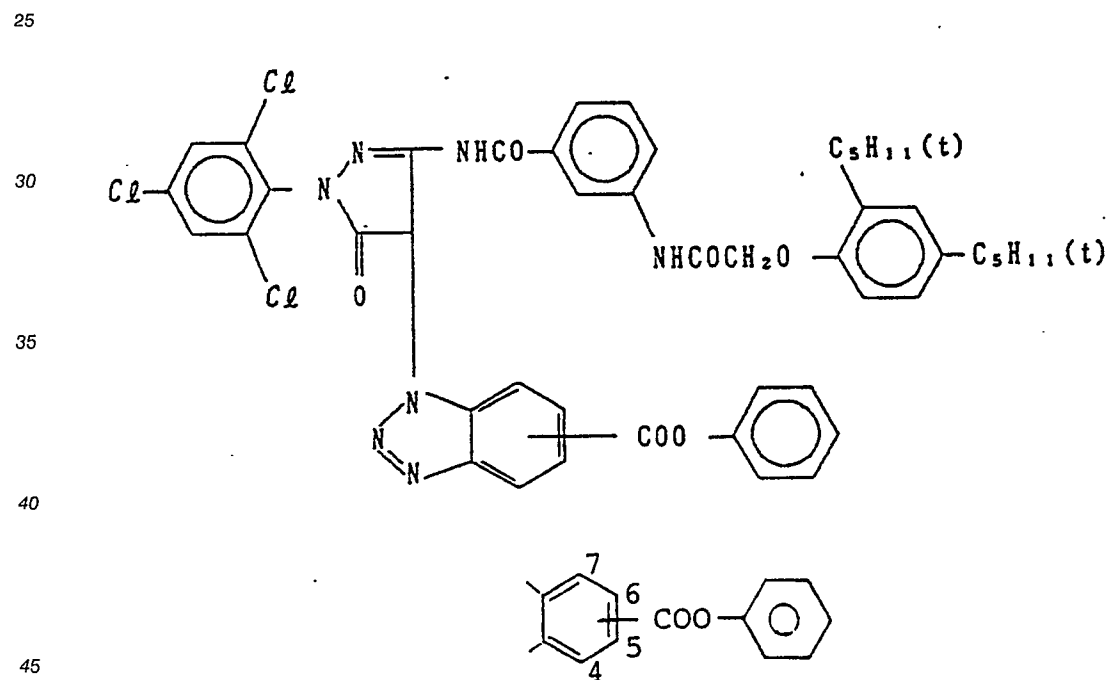
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(D - 9)



(D - 10)



(A mixture of compounds substituted at 5- and 6-positions: the same for (D-12), (D-14), (D-27), (D-29), (D-46), (D-47), (D-48), (D-49), (D-50), (D-52), (D-53) and (D-54)).

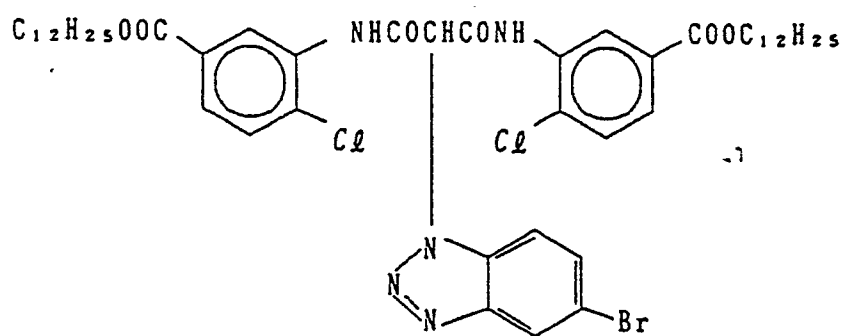
(D - 1 1)

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(D - 1 2)

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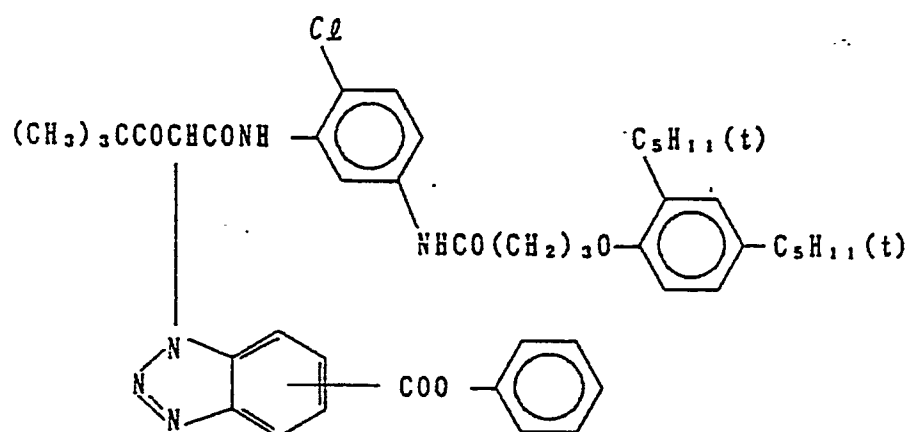
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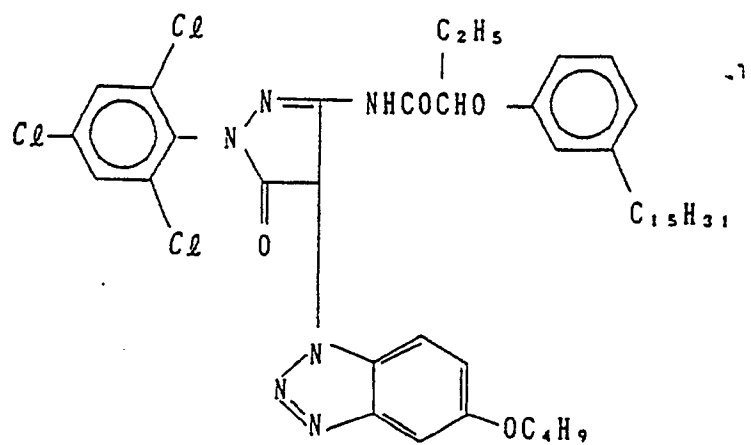
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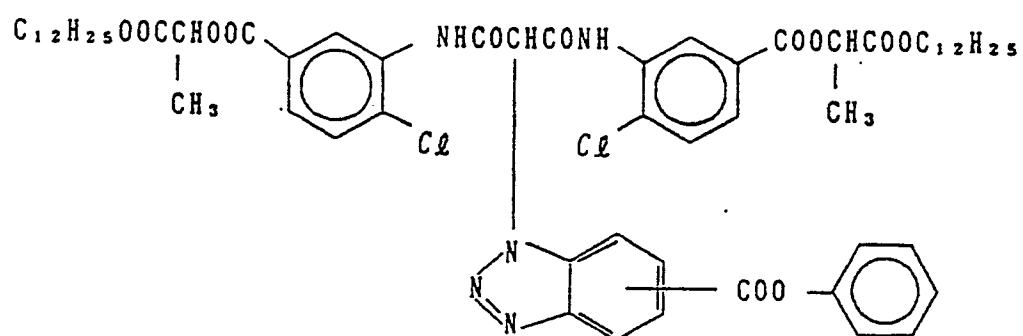
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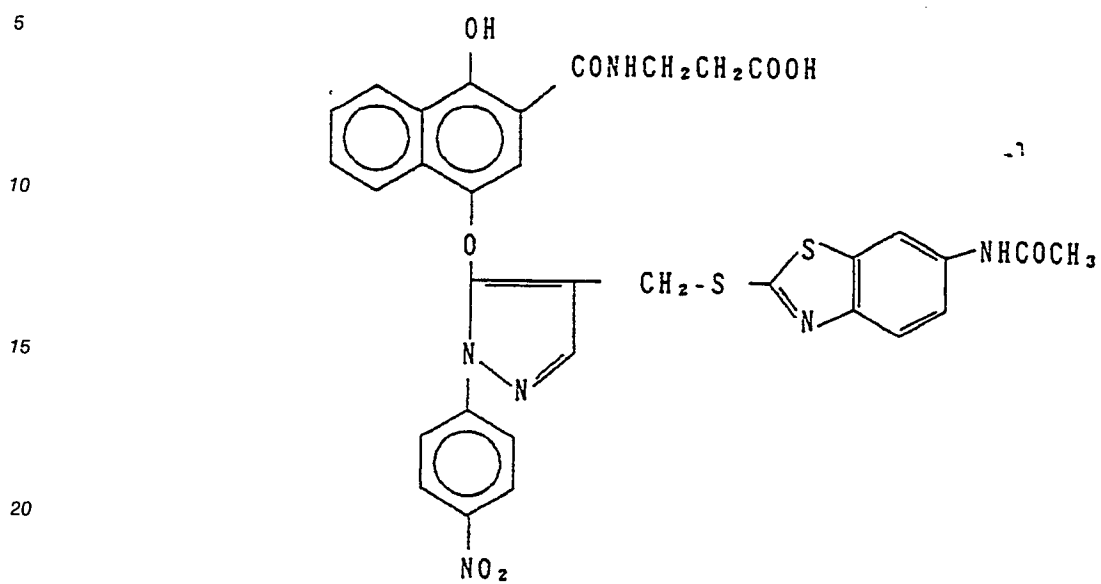
(D - 1 3)



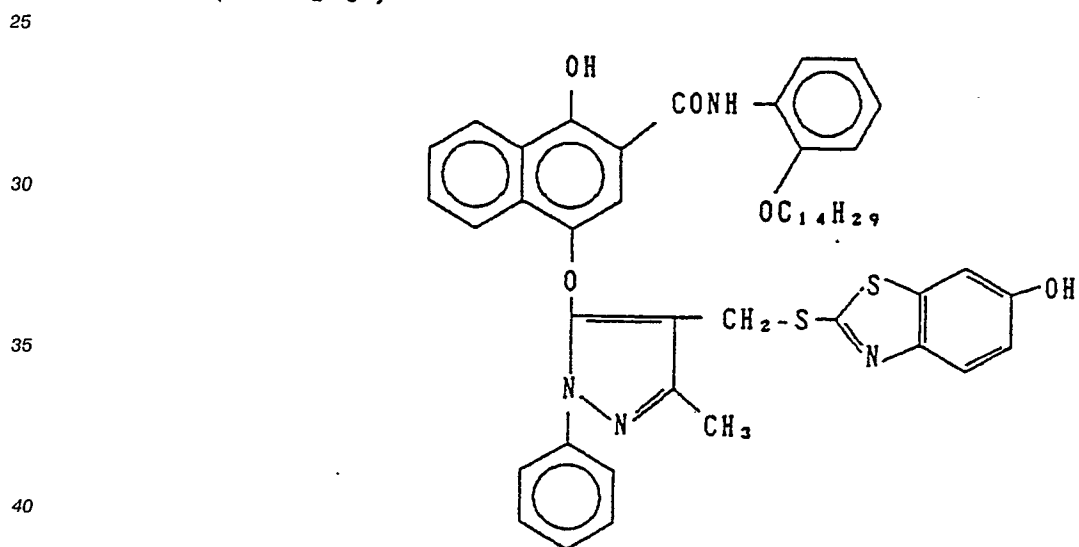
(D - 1 4)



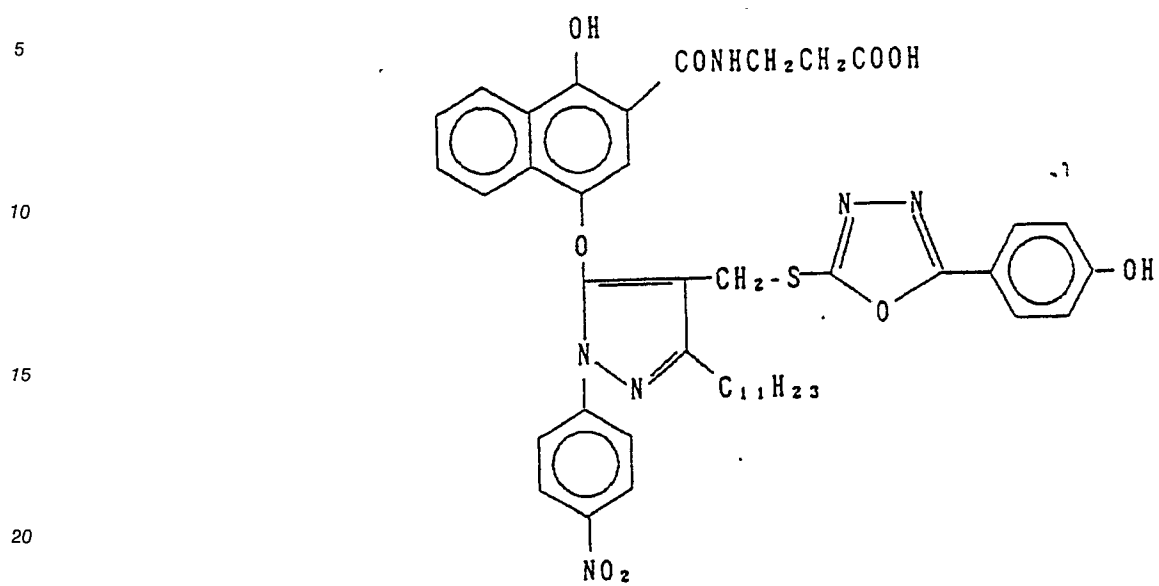
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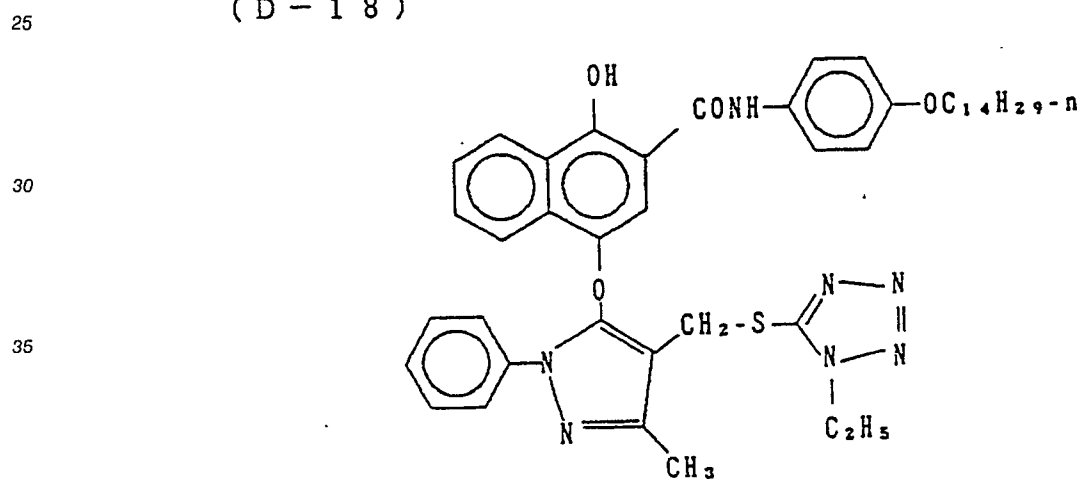
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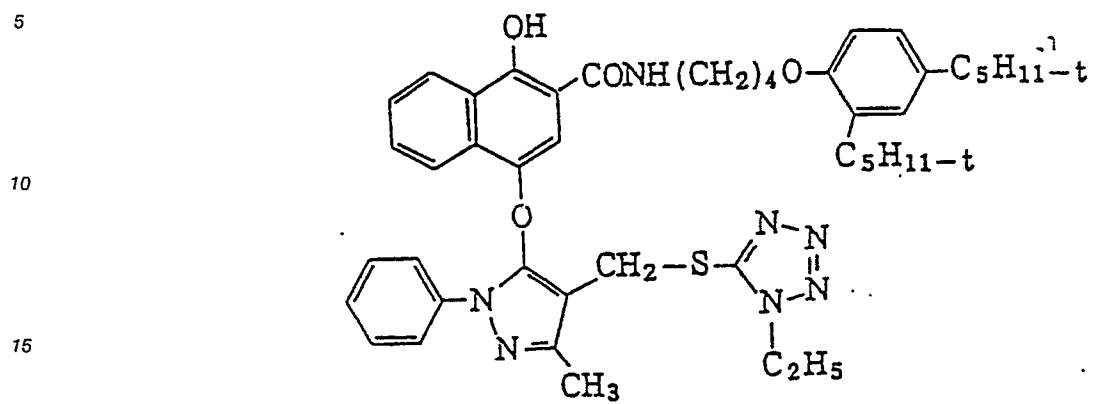
(D - 17)



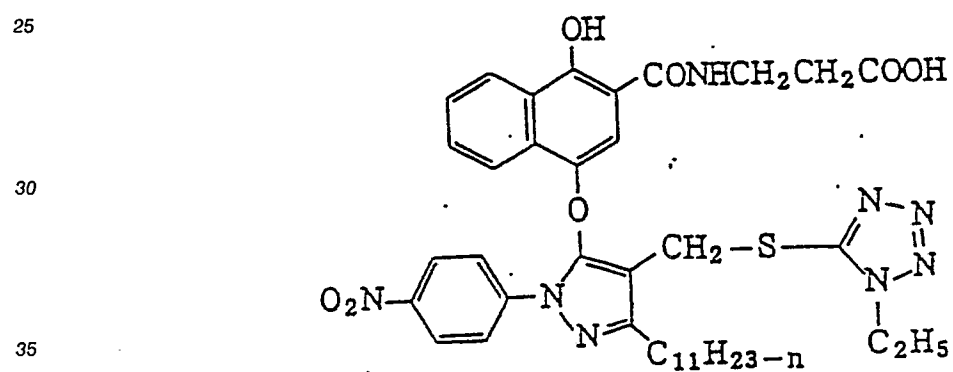
(D - 18)



(D - 1 9)



(D - 2 0)

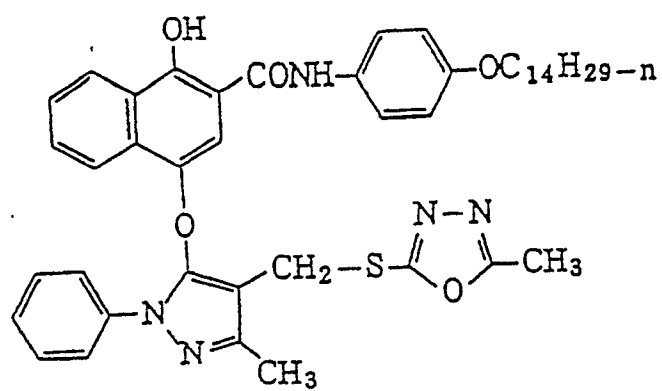


(D - 2 /)

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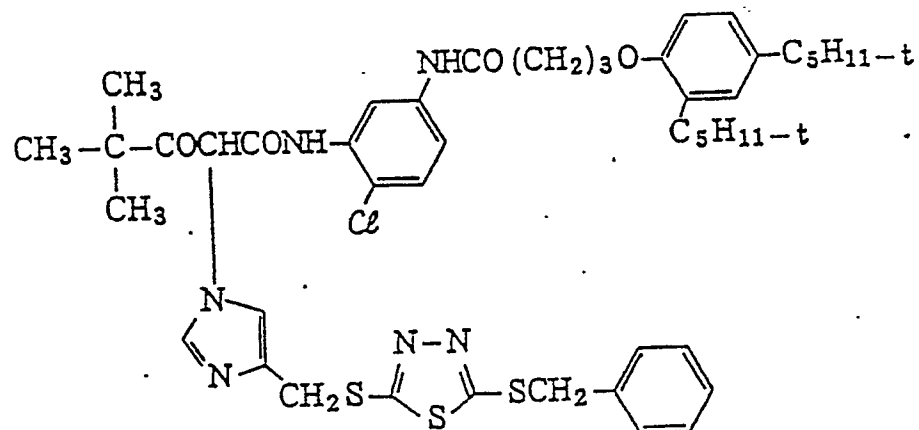
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(D - 2 /)

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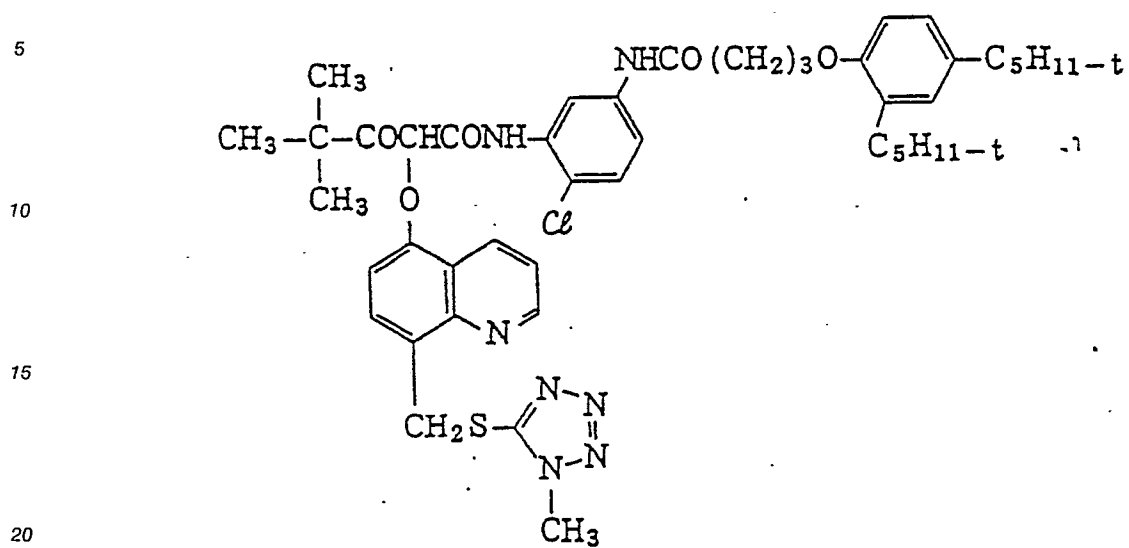
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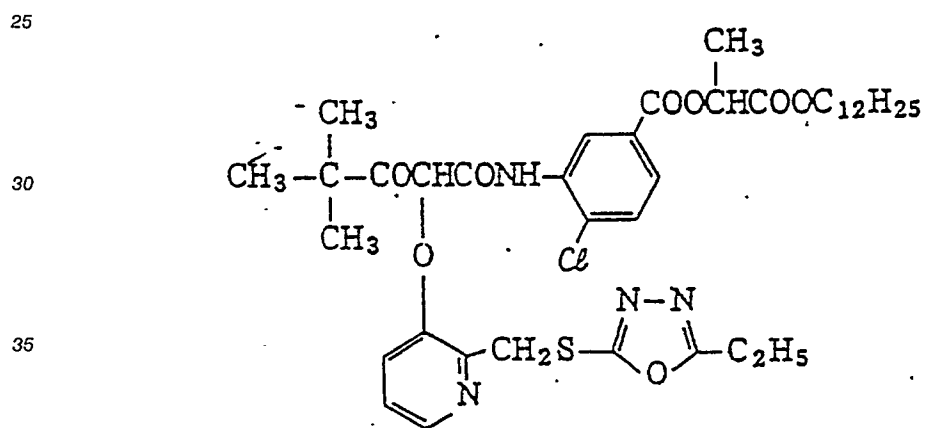
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(D - 2 2)



(D - 2 3)



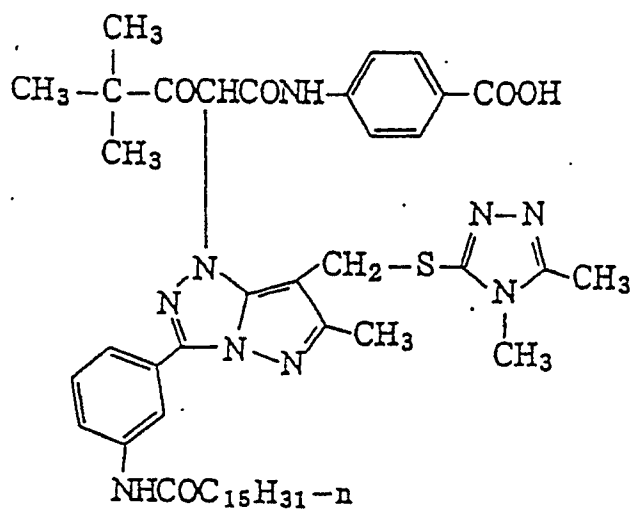
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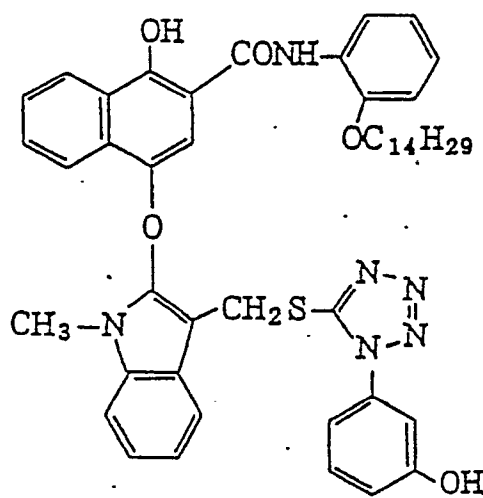
(D - 2 5)

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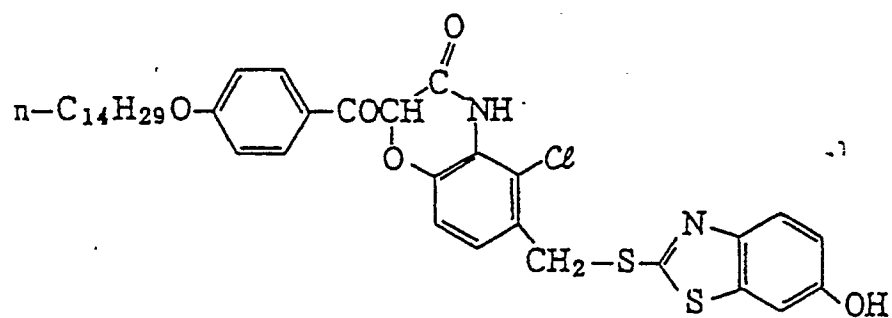


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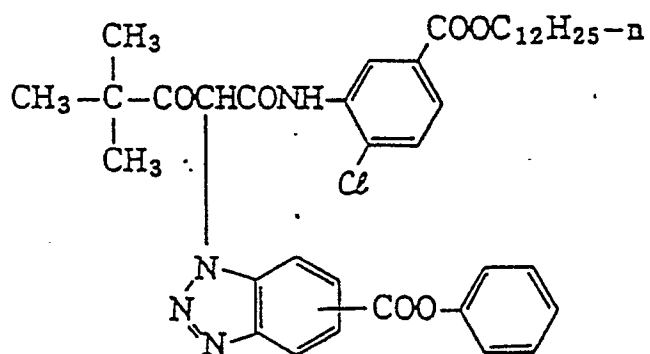
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(D - 2 6)



(D - 2 7)



(D - 3 0)

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(D - 3 1)

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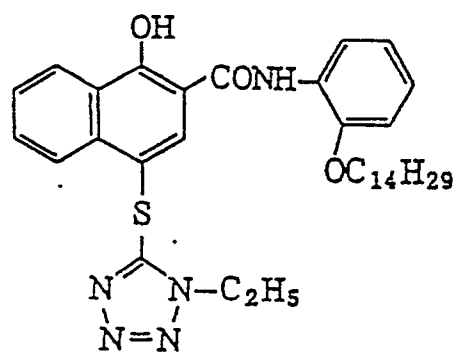
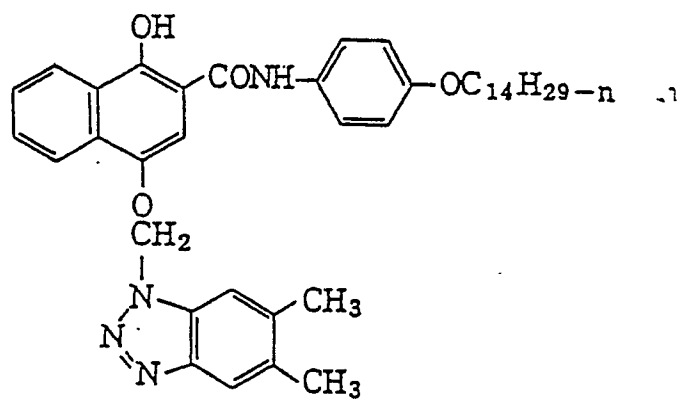
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(D - 3 2)

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(D - 3 3)

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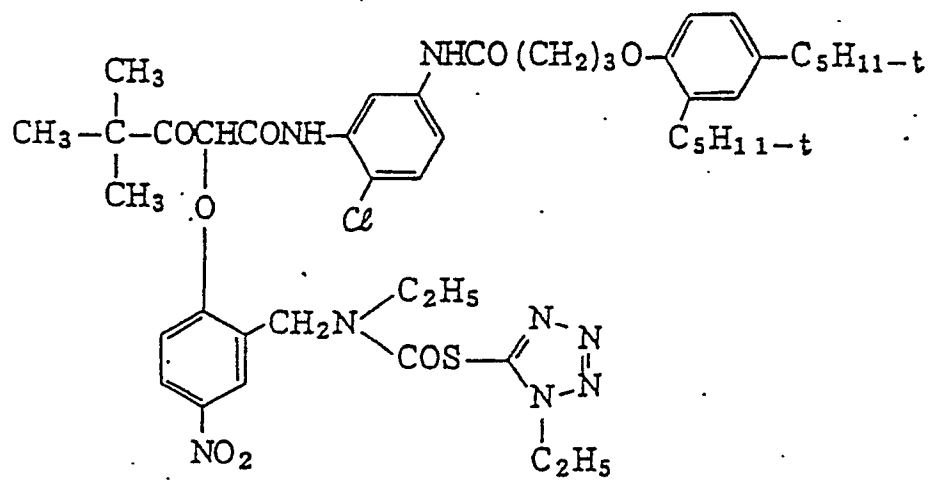
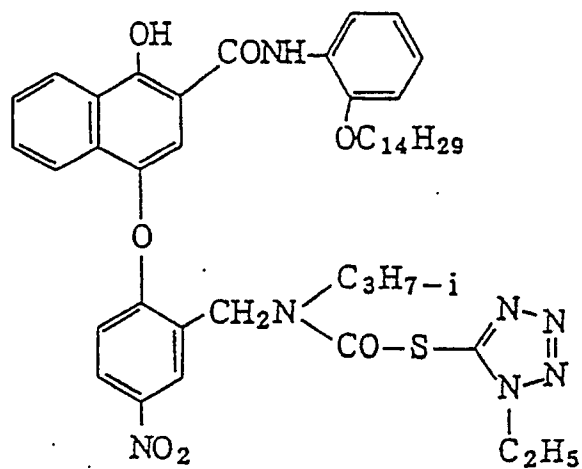
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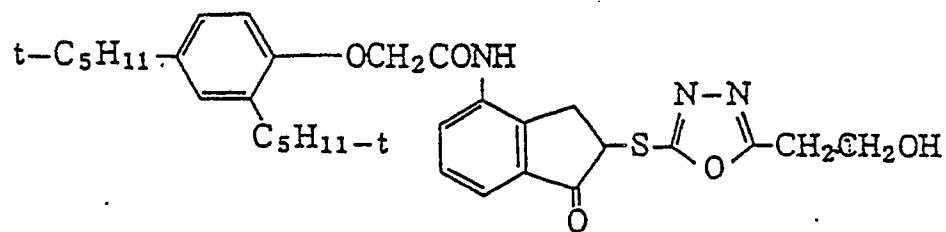
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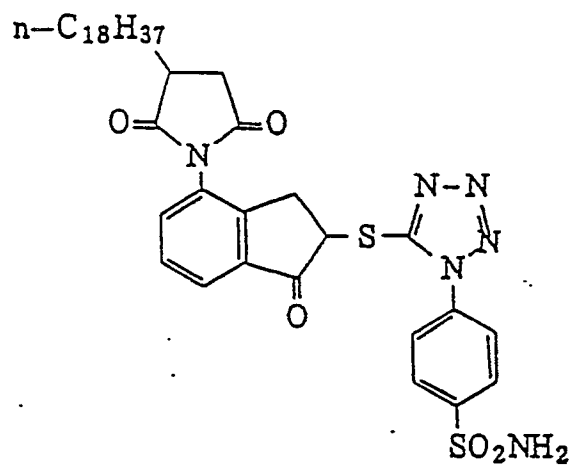
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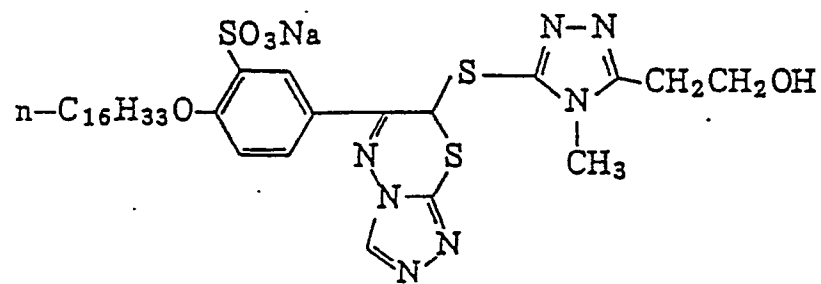
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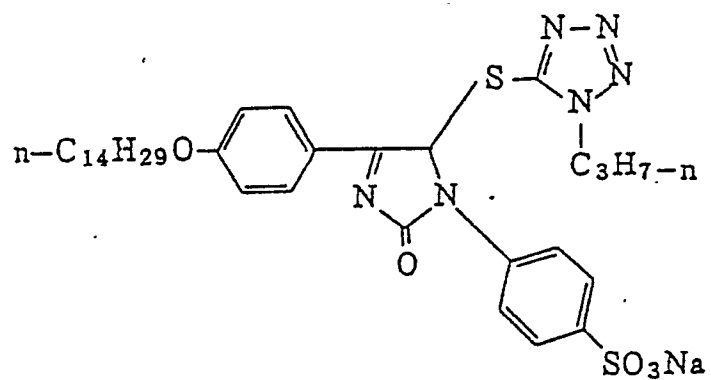
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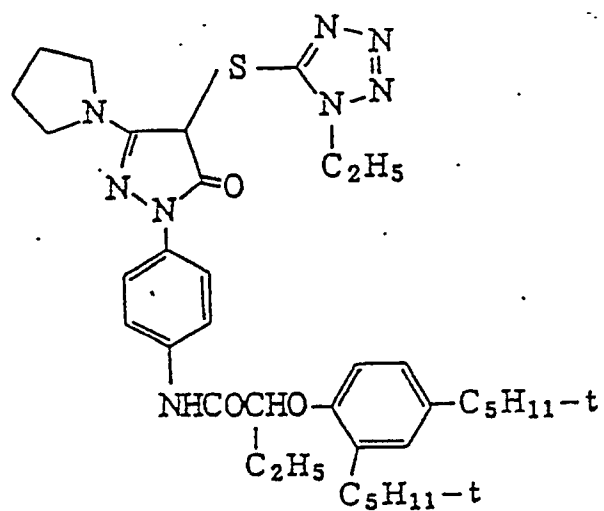
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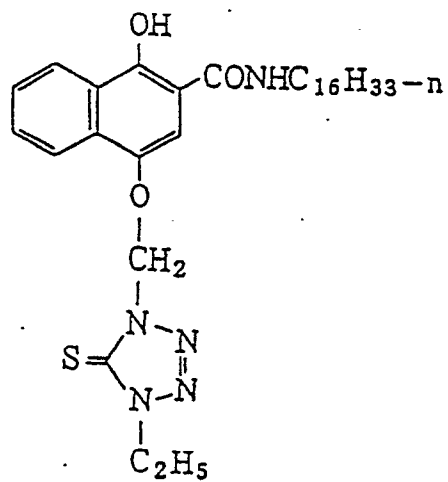
(D - 3 7)



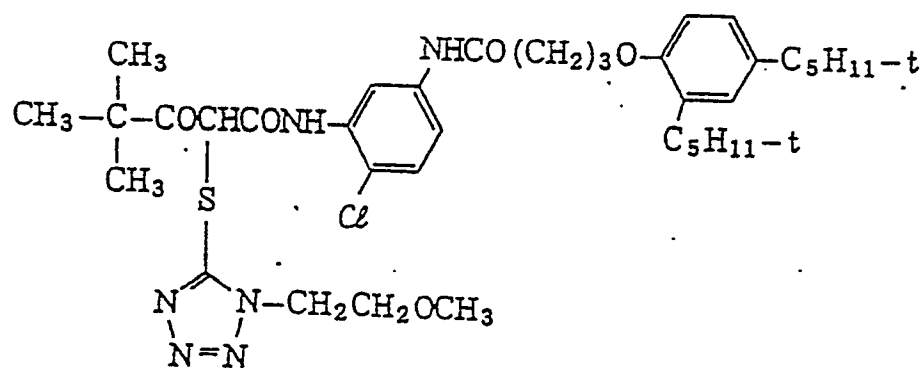
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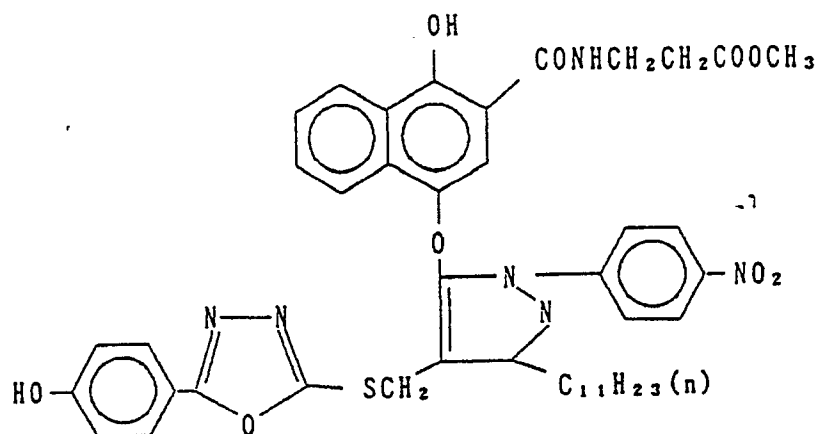
(D - 3 9)



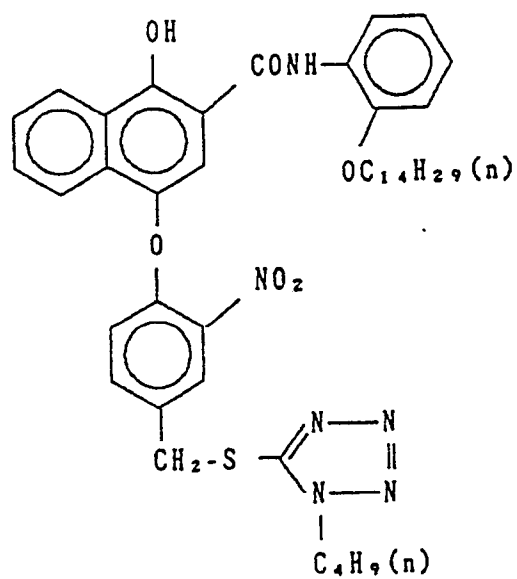
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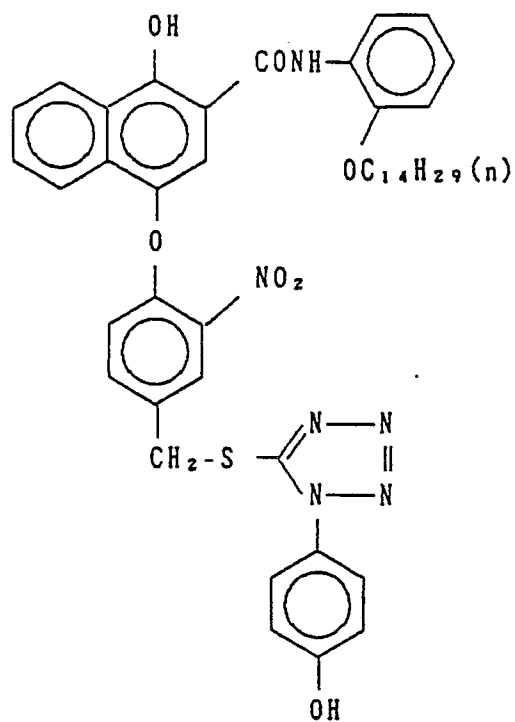
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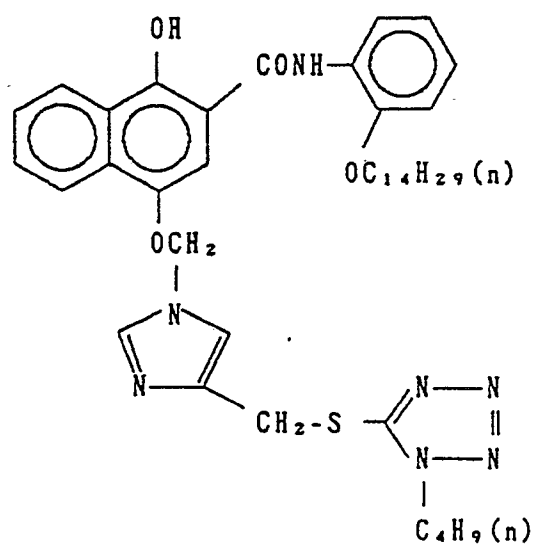
D - 4 2



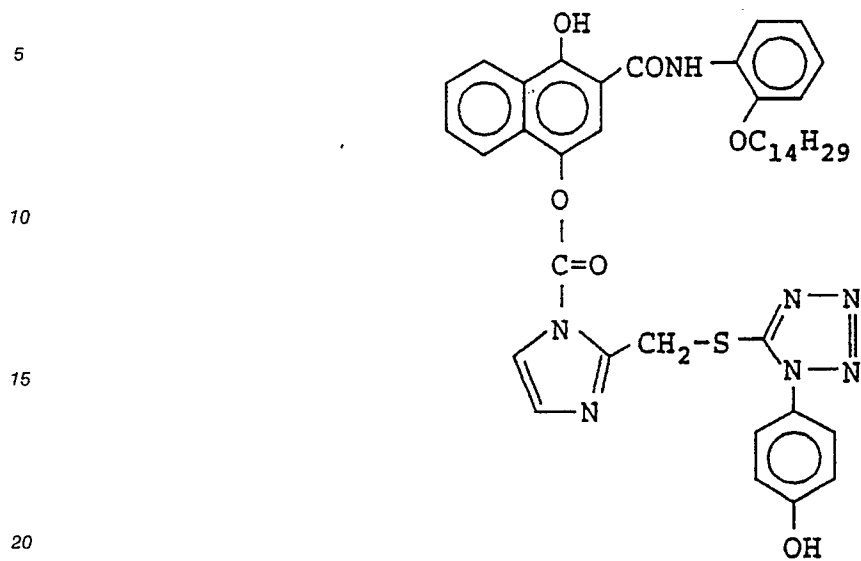
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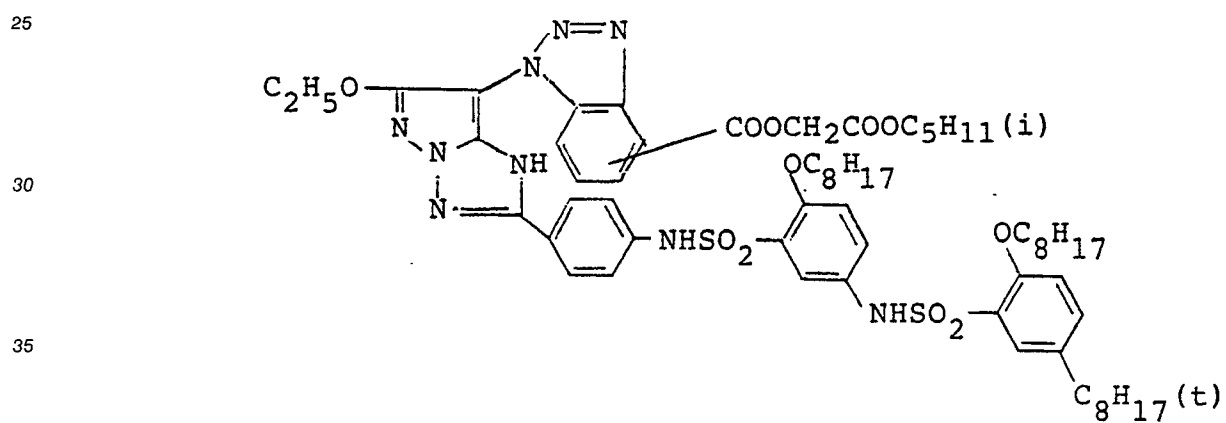
D - 4 4



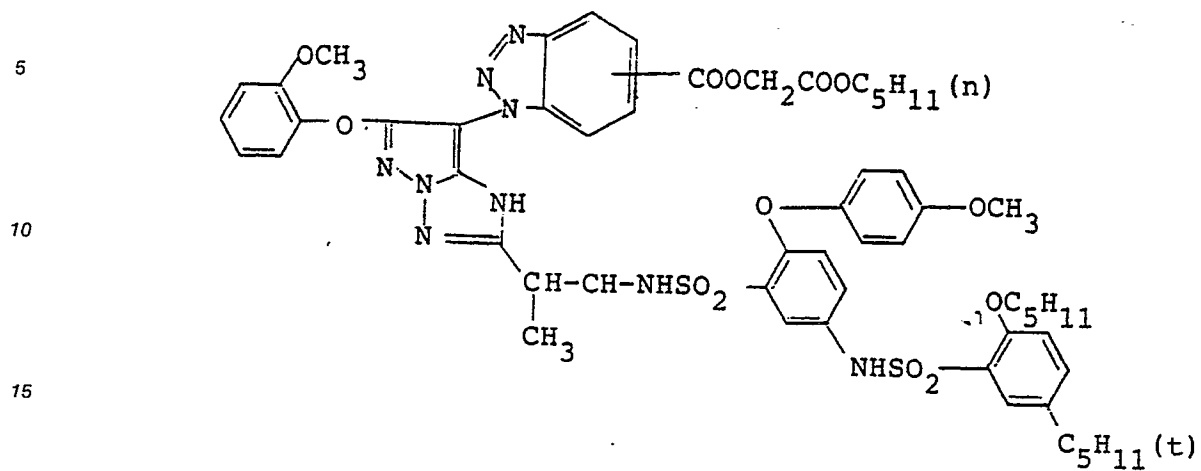
D-45



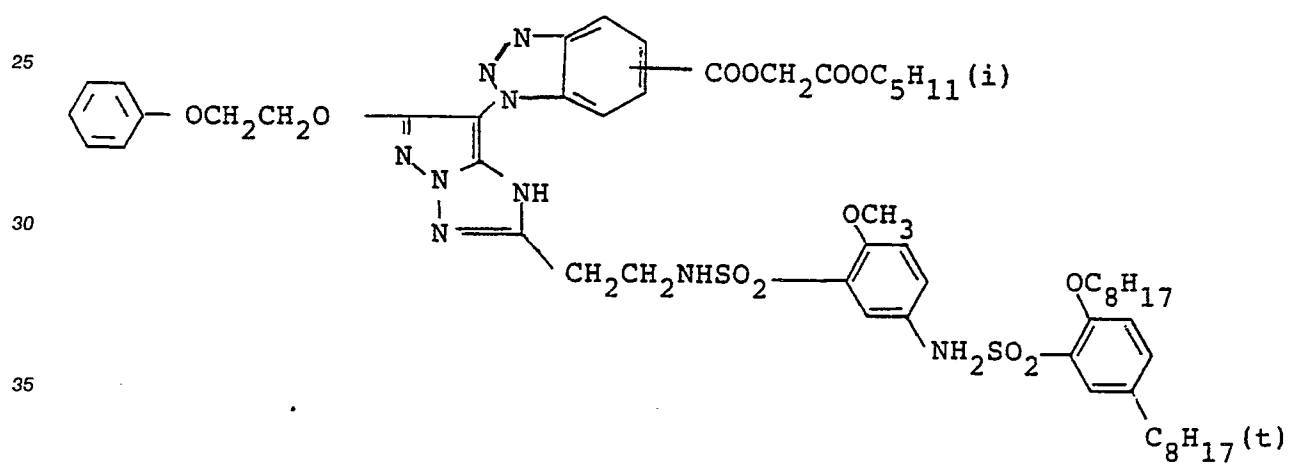
D-46



D-47



D-48

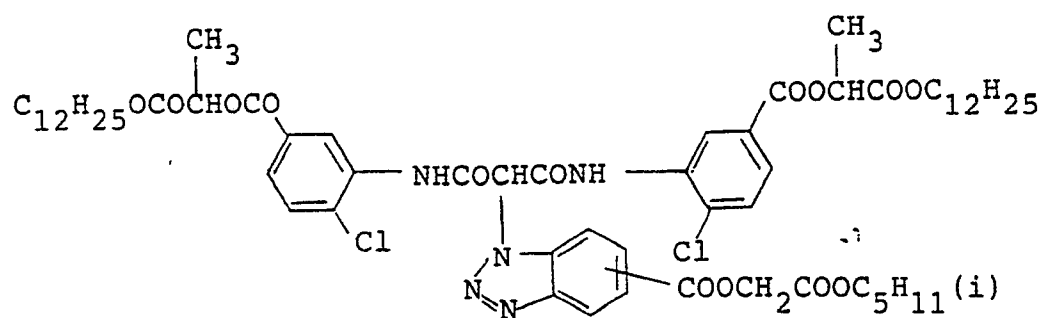


D-49

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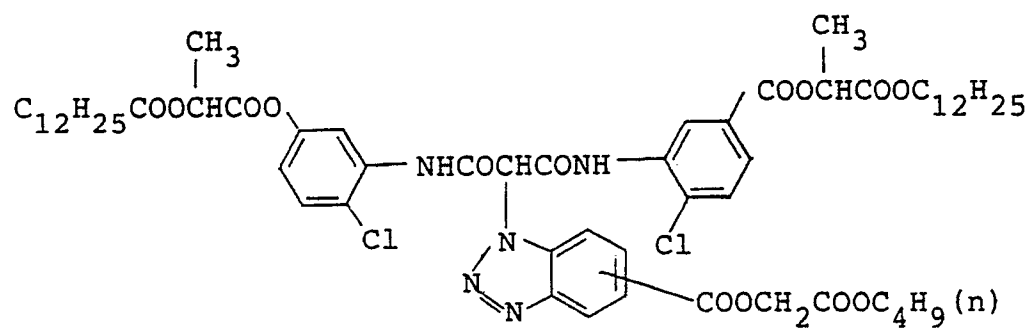
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D-50

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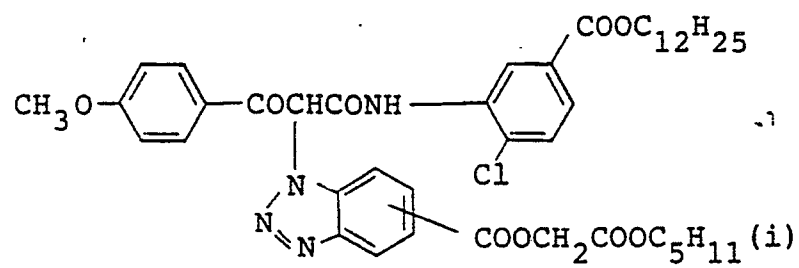
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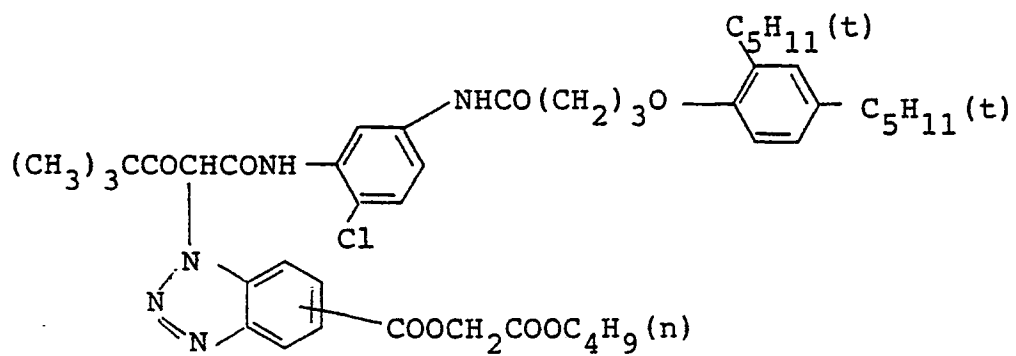
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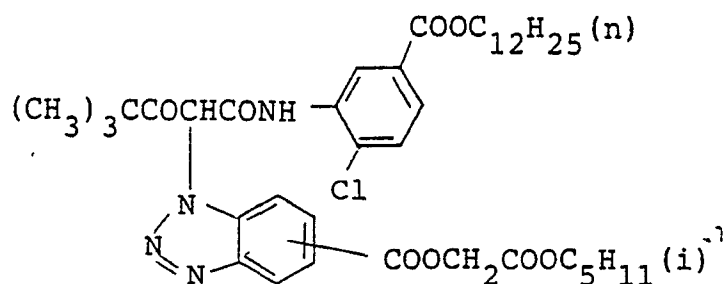
D-51



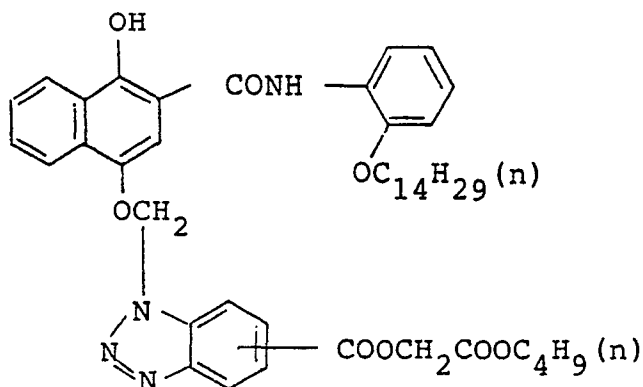
D-52



D-53



D-54



The compounds of the present invention can be synthesized according to the methods described in JP-A-54-145135, JP-A-63-37346, JP-A-56-114946, JP-A-57-154234, JP-A-58-162949 (corresponding to U.S. Patents 4,248,962, 4,861,701, 4,409,323, 4,421,845, and 4,482,629, respectively), JP-A-63-37350, JP-A-57-151944 (corresponding to U.S. Patent 4,477,563), JP-A-58-205150, JP-A-60-218645, the literature and other patent specifications.

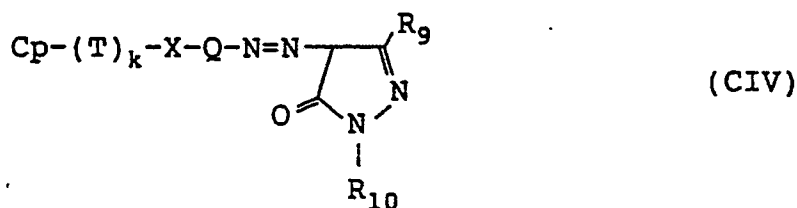
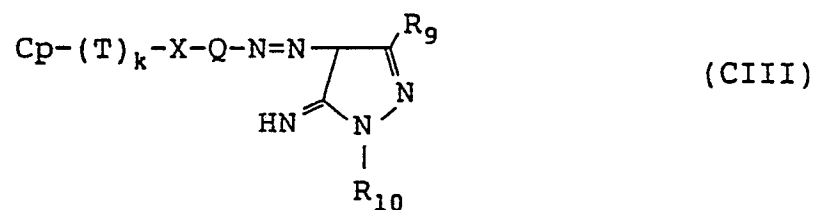
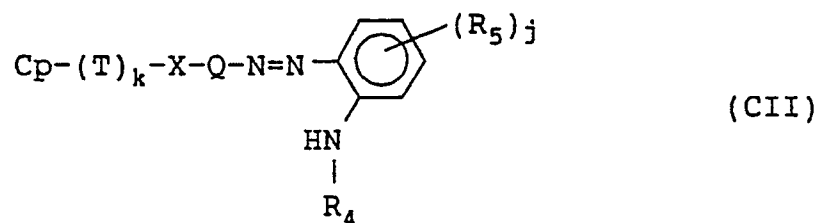
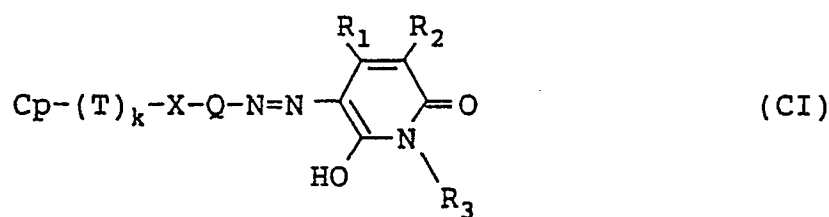
The yellow colored cyan couplers of the present invention will be described below.

The yellow colored cyan couplers of the present invention refer to cyan couplers which have an absorption maximum at 400 nm to 500 nm in the visible absorption region of the couplers and form cyan dyes having an absorption maximum at 630 nm to 750 nm in the visible absorption region by the coupling thereof with the oxidation product of an aromatic primary amine developing agent.

Among the yellow colored cyan couplers of the present invention, there are preferred cyan couplers which release a moiety of a water soluble compound having a 6-hydroxy-2-pyridone-5-ylazo group, a water-solubilizing group pyrazolone-4-ylazo group, a water-solubilizing group 2-acylamino-phenylazo group, a 2-sulfonamidophenylazogroup, and a 5-aminopyrazol-4-ylazo group by a coupling reaction with the oxidation product of an aromatic primary amine developing agent.

The water soluble compound should dissolved out from the photographic material during a development processing. The compound is preferably soluble in a developing solution of pH 9 to 12 in an amount of at least 1 g/l, more preferably at least 3 g/l at 25°C.

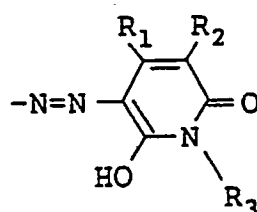
Preferably, the colored cyan couplers of the present invention can be represented by the following general formulas (CI) to (CIV).



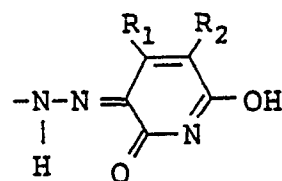
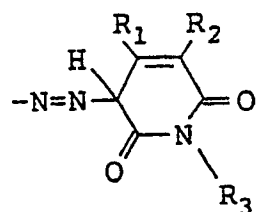
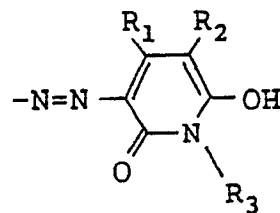
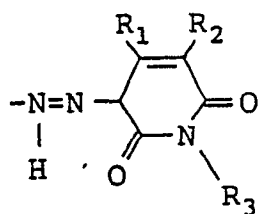
In formulas (CI) to (CIV), Cp represents a cyan coupler moiety (T is bonded to the coupling site thereof); T represents a timing group; k represents 0 or 1; X represents an N-, O- or S-containing bivalent group which is bonded to (T)_k through the N, O or S atom and which also is bonded to Q; an Q represents an arylene group or a bivalent heterocyclic group.

In formula (CI), R₁ and R₂ are independently a hydrogen atom, a carboxyl group, a sulfo group, a cyano group, an alkyl group, a cycloalkyl group, an aryl group, a heterocyclic group, a carbamoyl group, a sulfamoyl group, a carbonamido group, a sulfonamido group or an alkylsulfonyl group; R₃ is a hydrogen atom, an alkyl-group, a cycloalkyl group, an aryl group or a heterocyclic group; and at least one of T, X, Q, R₁, R₂ and R₃ has a water-soluble group (e.g., hydroxyl, carboxyl, sulfo, amino, ammonium, phosphono, phosphino, hydroxysulfonyloxy).

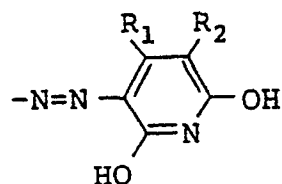
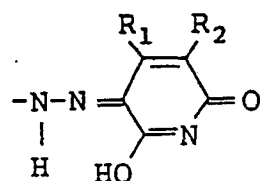
It will be understood that the group of



in formula (CI) can exist in tautomeric forms as follows. All such tautomeric structures are included within the scope of the compounds of formula (I) of the present invention.

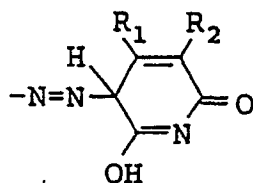


(where R₃ is hydrogen)



(where R₃ is hydrogen)

(where R₃ is hydrogen)



etc.

(where R₃ is hydrogen)

In formula (CII), R₄ is an acyl group or a sulfonyl group; R₅ is a group which can be attached to the benzene ring; j is an integer of 0 to 4; when j is 2 or greater, the two or more R₅ groups may be the same or different; and at least one of T, X, Q, R₄ and R₅ has a water-soluble group (e.g., hydroxyl, carboxyl, sulfo, phosphono, phosphino, hydroxysulfonyloxy, amino, ammonium).

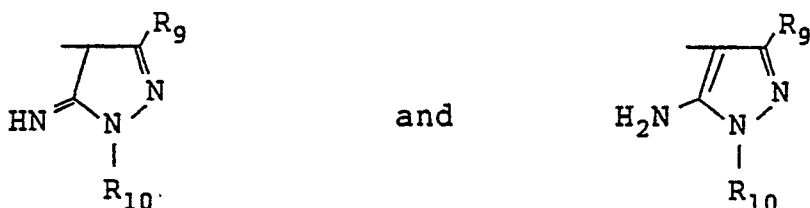
In formulas (CIII) and (CIV), R₉ is a hydrogen atom, a carboxyl group, a sulfo group, a cyano group, an alkyl group, a cycloalkyl group, an aryl group, an alkoxy group, a cycloalkyloxy group, an aryloxy group, a heterocyclic group, a carbamoyl group, a sulfamoyl group, a carbonamido group, a sulfonamido group or an

alkylsulfonyl group; R_{10} is hydrogen atom, an alkyl group, a cycloalkyl group, an aryl group or a heterocyclic group; and at least one of T, X, Q, R_9 and R_{10} has a water-soluble group (e.g., hydroxyl, carboxyl, sulfo, phosphono, phosphino, hydroxysulfonyloxy, amino, ammonium).

Further, the compounds having the following group exist in a tautomeric form.

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The compounds represented by general formulas (CI) to (CIV) will be discussed in more detail below.

Examples of the coupler moiety represented by Cp include conventional cyan coupler moieties (e.g., moieties of phenol type and naphthol type couplers).

Preferred examples of Cp are coupler moieties represented by general formulas (Cp-6), (Cp-7) and (Cp-8) among those exemplified in the description of the compounds of formula (I).

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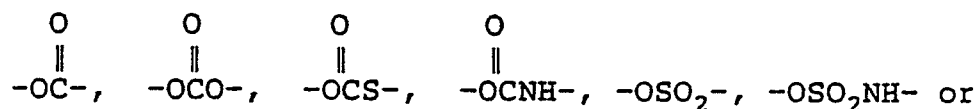
The timing group represented by T in formulas (CI) to (CIV) is a group which is cleaved from X after the cleavage of the bond between Cp and T by the coupling reaction of the couplers with an oxidation product of an aromatic primary amine developing agent. The timing group is used for various purposes, e.g., controlling of coupling reactivity, stabilizing the couplers, controlling the release timing of X, etc. Examples of the timing group include conventional timing groups represented by formulas (T-1) to (T-7) exemplified in the description of the compounds of formula (I).

25

Though k may be an integer of 0 or 1, the case where k is 0 is generally preferred, that is, Cp is directly bonded to X.

X is a bivalent group which is bonded to $(T)_k$ through an N, O or S atom. Preferably, X is -O-, -S-,

30



35

a bivalent group which is bonded to $(T)_k$ through N, such as a heterocyclic group (e.g., a group derived from pyrrolidine, piperidine, morpholine, piperazine; pyrrole, pyrazole, imidazole, 1,2,4-triazole, benzotriazole, succinimide, phthalimide, oxazolidine-2,4-dione, imidazolidine-2,4-dione, 1,2,4-triazolidine-3,5-dione or the like) or a composite group of these groups and an alkylene group (e.g., methylene, ethylene, propylene), a cycloalkylene group (e.g., 1,4-cyclohexylene), an arylene group (e.g., o-phenylene, p-phenylene), a bivalent heterocyclic group (e.g., a group derived from pyridine, thiophene or the like), -CO-, -SO₂-, -COO-, -CONH-, -SO₂NH-, -SO₂O-, -NHCO-, NHSO₂-, -NHCONH-, -NHSO₂NH- or -NHCOO-. More preferably, X is a group represented by the following general formula (II):

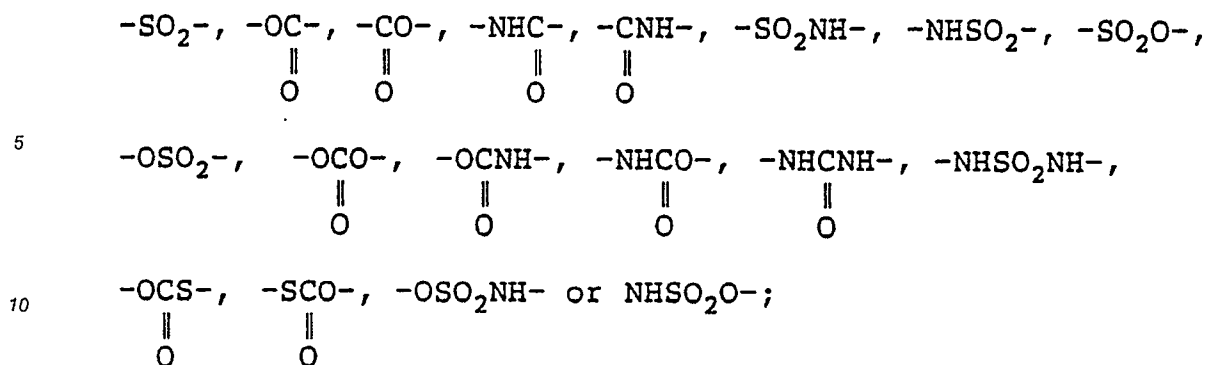
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In formula (II), the mark * represents the position where the group is bonded to $(T)_k$; the mark ** represents the position where the group is bonded to Q; X_1 represents -O- or -S-; L represents an alkylene group; X_2 represents a single bond, -O-, -S-, -CO-,

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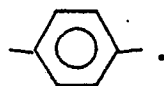
and m represents

an integer of 0 to 3. The total of carbon atoms (hereinafter referred to as the carbon number) in X is preferably 0 to 12, more preferably 0 to 8. Most preferably, X is $-\text{OCH}_2\text{CH}_2\text{O}-$.

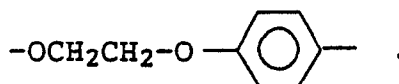
Q in formula (I) is an arylene group or a divalent heterocyclic group. When Q is an arylene group, the arylene group may be a condensed ring, and the arylene group may have one or more substituent groups (e.g., halogen atom, hydroxyl, carboxyl, sulfo, nitro, cyano, amino, ammonium, phosphono, phosphino, alkyl, cycloalkyl, aryl, carbonamido, sulfonamido, alkoxy, aryloxy, acyl, sulfonyl, carboxyl, carbamoyl, sulfamoyl). The C-number is preferably 6 to 15, more preferably 6 to 10.

When Q is a divalent heterocyclic group, the heterocyclic group is a 3-membered to 8-membered (preferably 5-membered to 7-membered) monocyclic or condensed ring heterocyclic group containing at least one hetero-atom selected from the group consisting of N, O, S, P, Se and Te as a member of the heterocyclic ring (e.g., a group derived from pyridine, thiophene, furan, pyrrole, pyrazole, imidazole, thiazole, oxazole, benzothiazole, benzoxazole, benzofuran, benzothiophene, 1,3,4-thiadiazole, indole, or quinoline). The heterocyclic group may have one or more substituent groups (examples of the substituent groups include those already described above in the definition of the substituent groups for the arylene group of Q). The C-number is preferably 2 to 15, more preferably 2 to 10.

The most preferred Q is



Therefore, the most preferred $-(T)_k\text{-X-Q-}$ is



When R_1 , R_2 or R_3 in formula (I) is an alkyl group, the alkyl group includes both straight-chain and branched chain alkyl groups which may have unsaturated bonds and one or more substituent groups (e.g., halogen, hydroxyl, carboxyl, sulfo, phosphono, phosphino, cyano, alkoxy, aryl, alkoxy carbonyl, amino, ammonium, acyl, carbonamido, sulfonamido, carbamoyl, sulfamoyl, or sulfonyl).

When R_1 , R_2 or R_3 is a cycloalkyl group, the cycloalkyl group is a 3-membered to 8-membered cycloalkyl group which may have crosslinking groups, unsaturated bonds or substituent groups (examples of the substituent groups include those already described above in the definition of the substituent groups for the alkyl group of R_1 , R_2 or R_3).

When R_1 , R_2 or R_3 is an aryl group, the aryl group may be a condensed ring and may have substituent groups (examples of the substituent groups include alkyl, cycloalkyl and those already described above in the definition of the substituent groups for the alkyl group of R_1 , R_2 or R_3).

When R_1 , R_2 or R_3 is a heterocyclic group, the heterocyclic group is a 3-membered to 8-membered (preferably 5-membered to 7-membered) monocyclic or condensed ring heterocyclic group containing at least one hetero-atom selected from the group consisting of N, S, O, P, Se and Te as a member of the heterocyclic ring. Examples of the heterocyclic group include imidazolyl, thienyl, pyrazolyl, thiazolyl, pyridyl and quinolyl. The heterocyclic group may have one or more substituent groups (examples of the

substituent groups are the same as those for the aryl group of R_1 , R_2 or R_3).

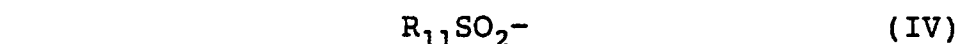
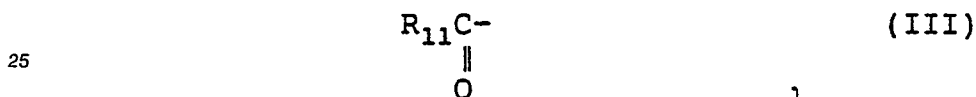
The carboxyl group includes a carboxylate group; the sulfo group includes a sulfonato group; the phosphino group includes a phosphinato group; and the phosphono group includes a phosphonato group. Those groups may include any counter ions, including Li^+ , Na^+ , K^+ or ammonium.

5 Preferably, R_1 is a hydrogen atom, a carboxyl group, an alkyl group having 1 to 10 carbon atoms (e.g., methyl, t-butyl, sulfomethyl, 2-sulfoethyl, carboxymethyl, 2-carboxyethyl, 2-hydroxyethyl, benzyl, ethyl, isopropyl) or an aryl group having 6 to 12 carbon atoms (e.g., phenyl, 4-methoxyphenyl, 4-sulfophenyl) with a hydrogen atom, a methyl group or a carboxyl group being particularly preferred.

10 Preferably, R_2 is a cyano group, carboxyl group, a carbamoyl group having 1 to 10 carbon atoms, a sulfamoyl group having 0 to 10 carbon atoms, a sulfo group, an alkyl group having 1 to 10 carbon atoms (e.g., methyl, sulfomethyl), a sulfonyl group having 1 to 10 carbon atoms (e.g., methylsulfonyl, phenylsulfonyl), a carbonamido group having 1 to 10 carbon atoms (e.g., acetamido, benzamido) or a sulfonamido group having 1 to 10 carbon atoms (e.g., methanesulfonamido, toluenesulfonamido) with a cyano group, carbamoyl group or carboxyl group being particularly preferred.

15 Preferably, R_3 is a hydrogen atom, an alkyl group having 1 to 12 carbon atoms (e.g., methyl, sulfomethyl, carboxyethyl, 2-sulfoethyl, 2-carboxyethyl, ethyl, n-butyl, benzyl, 4-sulfobenzyl) or an aryl group having 6 to 15 carbon atoms (e.g., phenyl, 4-carboxyphenyl, 3-carboxyphenyl, 4-methoxyphenyl, 2,4-dicarboxyphenyl, 2-sulfophenyl, 3-sulfophenyl, 4-sulfophenyl, 2,4-disulfophenyl, 2,4-disulfophenyl). More preferably, R_3 is an alkyl group having 1 to 7 carbon atoms or an aryl group having 6 to 10 carbon atoms.

20 Preferably, R_4 is an acyl group represented by the following general formula (III) or a sulfonyl group represented by the following general formula (IV):



30 When R_{11} is an alkyl group, the alkyl group includes both straight-chain and branched groups, and may contain unsaturated bonds and may have one or more substituent groups (examples of the substituent groups include halogen atom, hydroxyl, carboxyl, sulfo, phosphono, phosphino, cyano, alkoxy, aryl, alkoxy carbonyl, amino, ammonium, acyl, carbonamido, sulfonamido, carbamoyl, sulfamoyl, sulfonyl).

35 When R_{11} is a cycloalkyl group, the cycloalkyl group is a 3-membered to 8-membered cycloalkyl group which may contain crosslinking groups and unsaturated bonds and may have one or more substituent groups (examples of the substituent groups being those described above in the description of the substituent groups for the alkyl group of R_{11}).

40 When R_{11} is an aryl group, the aryl group may be a condensed ring or may have one or more substituent groups (examples of the substituent groups include an alkyl group, a cycloalkyl group and those described above in the description of the substituent groups for the alkyl group of R_{11}).

45 When R_{11} is a heterocyclic group, the heterocyclic group is a 3-membered to 8-membered (preferably 5-membered to 7-membered) monocyclic or condensed ring heterocyclic group containing at least one hetero-atom selected from the group consisting of N, S, O, P, Se and Te as a member of the heterocyclic ring (e.g., imidazolyl, thienyl, pyrazolyl, thiazolyl, pyridyl, quinolynyl) and may have one or more substituent groups (examples of the substituent groups being those described above in the description of the substituent groups for the aryl group of R_{11}).

Note that in this description, carboxyl group may include carboxylate group, sulfo group may include sulfonato group, phosphino group may include phosphinato group, and phosphono group may include phosphonato group. Counter ions are Li^+ , Na^+ , K^+ , ammonium, etc.

50 Preferably, R_{11} is an alkyl group having 1 to 10 carbon atoms (e.g., methyl, carboxymethyl, sulfoethyl, cyanoethyl), a cycloalkyl group having 5 to 8 carbon atoms (e.g., cyclohexyl, 2-carboxycyclohexyl) or an aryl group having 6 to 10 carbon atoms (e.g., phenyl, 1-naphthyl, 4-sulfophenyl) among which an alkyl group having 1 to 3 carbon atoms and an aryl group having 6 carbon atoms are particularly preferred.

55 R_5 is a group which can be substituted and is preferably an electron donative group. Particularly preferably, R_5 is a group of $-NR_{12}R_{13}$ or $-OR_{14}$ which is preferably attached to the 4-position. R_{12} , R_{13} and R_{14} are each a hydrogen atom, an alkyl group, a cycloalkyl group, an aryl group or a heterocyclic group and hence each has the same meaning as R_{11} . R_{12} and R_{13} may be combined together to form a ring. As

the ring to be formed, an alicyclic nitrogen-containing heterocyclic ring is preferred.

j is an integer of 0 to 4, preferably 1 to 2, particularly preferably 1.

When R_9 or R_{10} is an alkyl group, the alkyl group may be any of a straight chain alkyl group and a branched alkyl group, may contain unsaturated bonds, and may have one or more substituent groups (e.g.,
5 halogen atom, hydroxyl, carboxyl, sulfo, phosphono, phosphino, cyano, alkoxy, aryl, alkoxy carbonyl, amino, ammonium, acyl, carbonamido, sulfonamido, carbamoyl, sulfamoyl, sulfonyl).

When R_9 or R_{10} is a cycloalkyl group, the cycloalkyl group is a 3-membered to 8-membered cycloalkyl group which may have crosslinking groups, unsaturated bonds or substituent groups (examples of the substituent groups being those described above in the description of the substituent groups for the alkyl
10 group of R_9 or R_{10}).

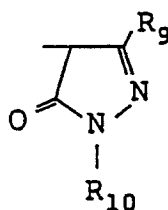
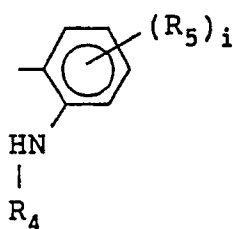
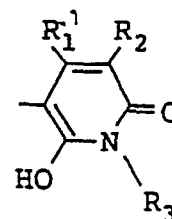
When R_9 or R_{10} is an aryl group, the aryl group may be a condensed ring or may have one or more substituent groups (examples of the substituent groups being an alkyl group, a cycloalkyl group and those described above in the definition of the substituent groups for the alkyl group of R_9 or R_{10}).

When R_9 or R_{10} is a heterocyclic group, the heterocyclic group is a 3-membered to 8-membered
15 (preferably 5-membered to 7-membered) monocyclic or condensed ring heterocyclic group containing at least one hetero-atom selected from the group consisting of N, S, O, P, Se and Te as a member of the heterocyclic ring (e.g., imidazolyl, thienyl, pyrazolyl, thiazolyl, pyridyl, quinolyl) and may have one or more substituent groups (examples of the substituent groups being those described above in the description of the substituent groups for the aryl group of R_9 or R_{10}).

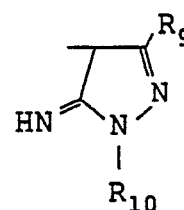
Note that in this description, carboxyl group may include carboxylato group, sulfo group may include sulfonato group, phosphino group may include phosphinato group and phosphono group may include
20 phosphonato group. Counter ions are Li^+ , Na^+ , K^+ , ammonium, etc.

Preferably, R_9 is a cyano group, a carboxyl group, a carbamoyl group having 1 to 10 carbon atoms, an alkoxy carbonyl group having 2 to 10 carbon atoms, an aryloxy carbonyl group having 7 to 11 carbon atoms,
25 a sulfamoyl group having 0 to 10 carbon atoms, a sulfo group, an alkyl group having 1 to 10 carbon atoms (e.g., methyl, carboxymethyl, sulfomethyl), a sulfonyl group having 1 to 10 carbon atoms (e.g., methylsulfonyl, phenylsulfonyl), a carbonamido group having 1 to 10 carbon atoms (e.g., acetamido, benzamido), a sulfonamido group having 1 to 10 carbon atoms (e.g., methanesulfonamido, toluenesulfonamido), an alkyloxy group (e.g., methoxy, ethoxy) or an aryloxy group (e.g., phenoxy), among which a cyano group, a
30 carbamoyl group, an alkoxy carbonyl group and a carboxyl group are particularly preferred.

Preferably, R_{10} is a hydrogen atom, an alkyl group having 1 to 12 carbon atoms (e.g., methyl, sulfomethyl, carboxymethyl, ethyl, 2-sulfoethyl, 2-carboxyethyl, 3-sulfopropyl, 3-carboxypropyl, 5-sulfopen-
35 tyl, 5-carboxypentyl, 4-sulfobenzyl, or an aryl group having 6 to 15 carbon atoms (e.g., phenyl, 4-carboxyphenyl, 3-carboxyphenyl, 2,4-dicarboxyphenyl, 4-sulfophenyl, 3-sulfophenyl, 2,5-disulfophenyl, 2,4-diulfophenyl) among which an alkyl group having 1 to 7 carbon atoms or an aryl group having 6 to 10 carbon atoms is more preferred.



and

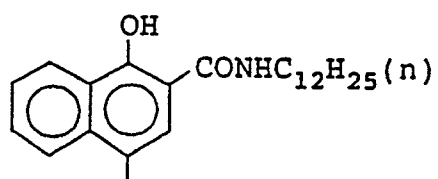


Specific examples of Cp, X, Q,

in formulas (CI) to (CIV) include the following groups:

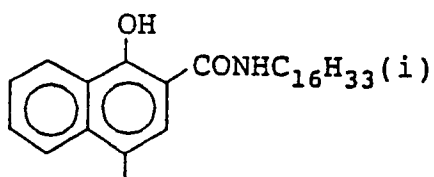
(Examples of Cp)

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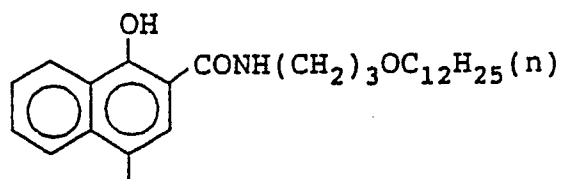
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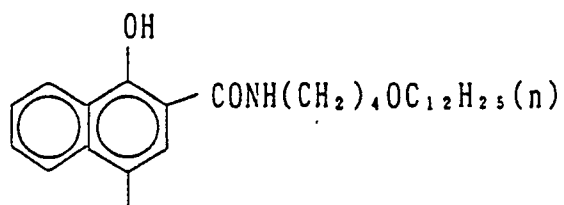
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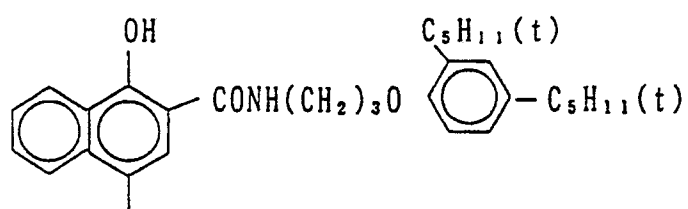


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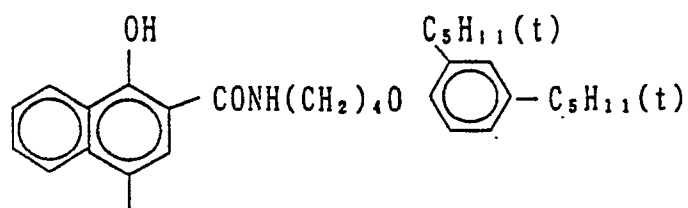
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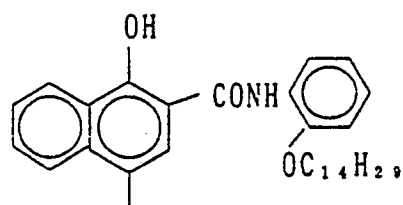


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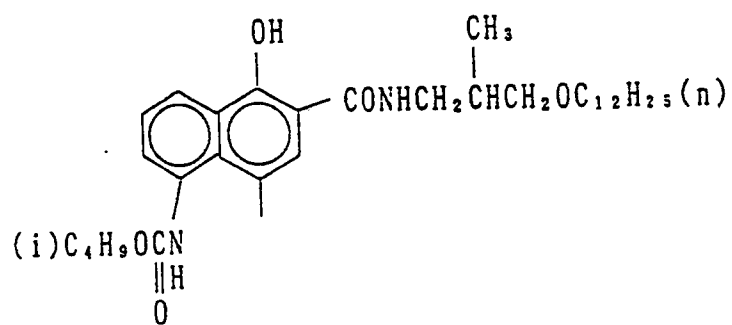
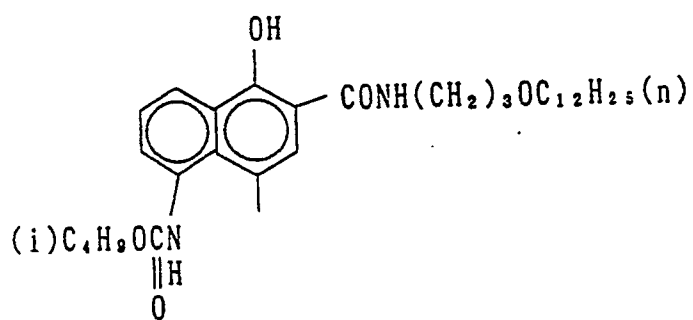
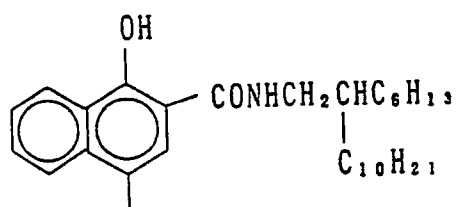
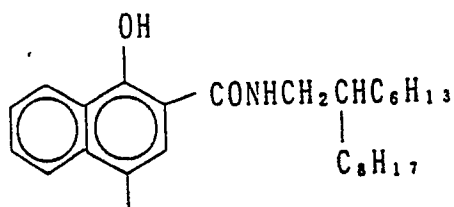
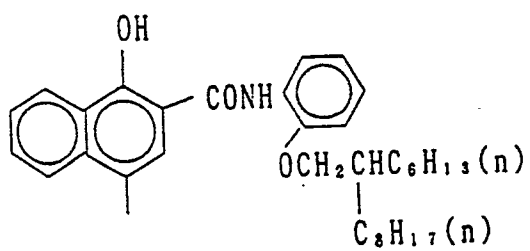


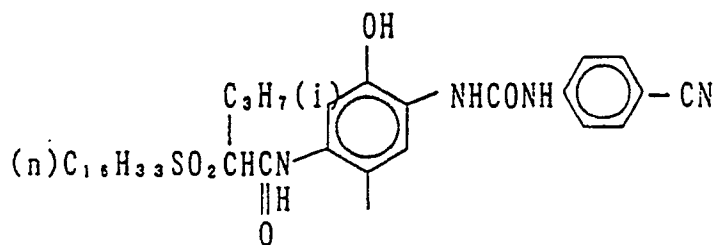
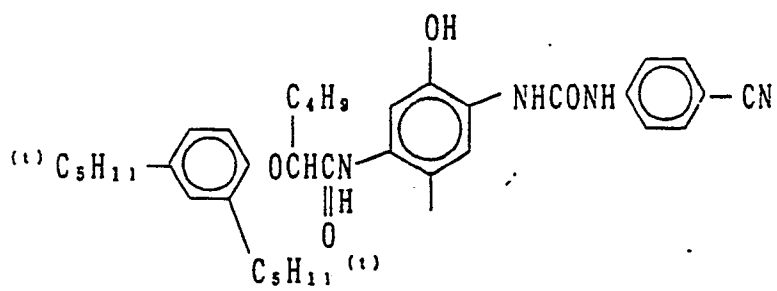
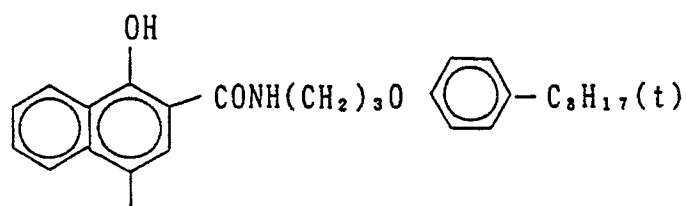
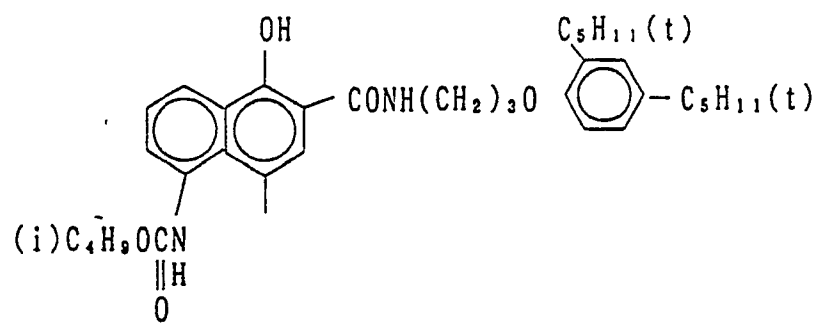
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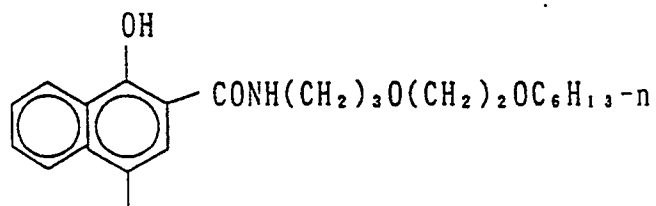
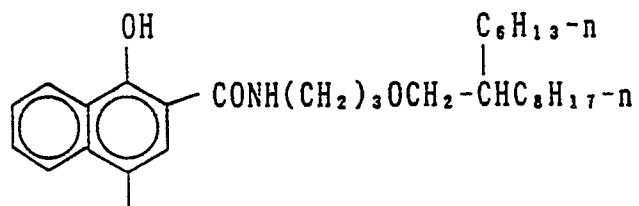
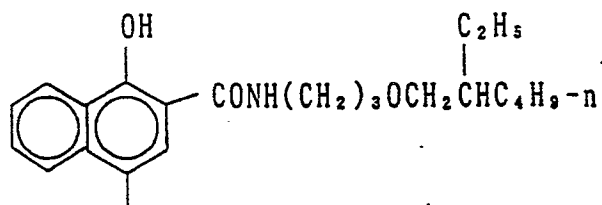
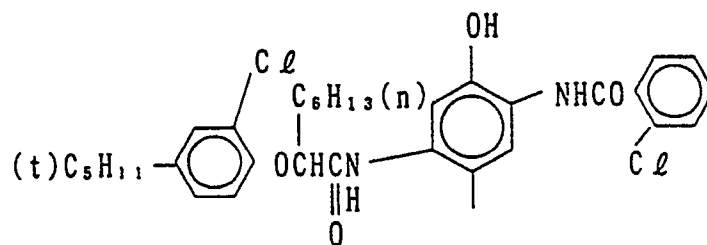
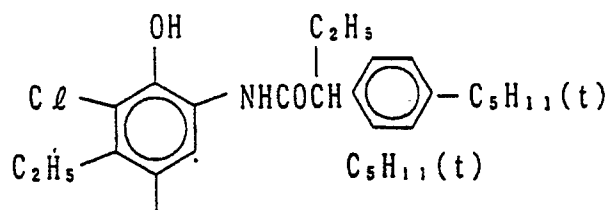
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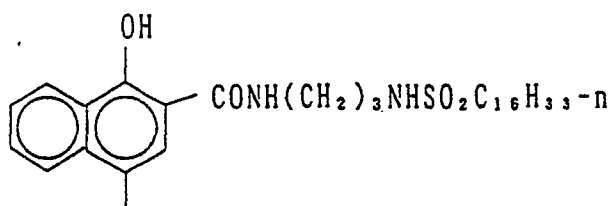
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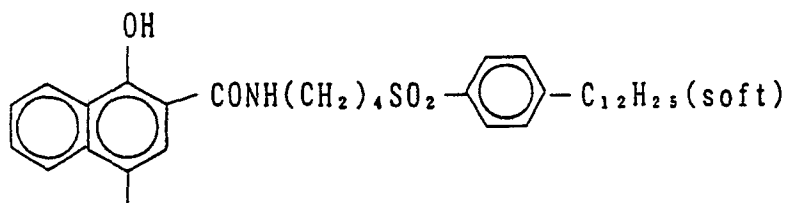




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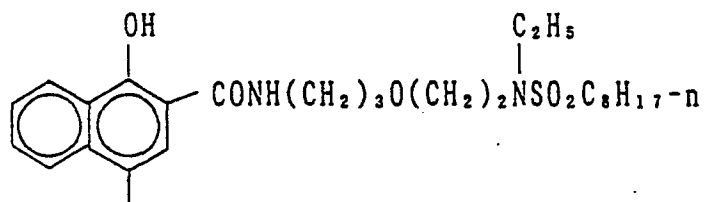


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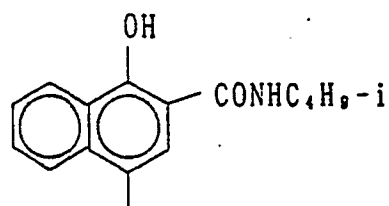
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(Examples of X)

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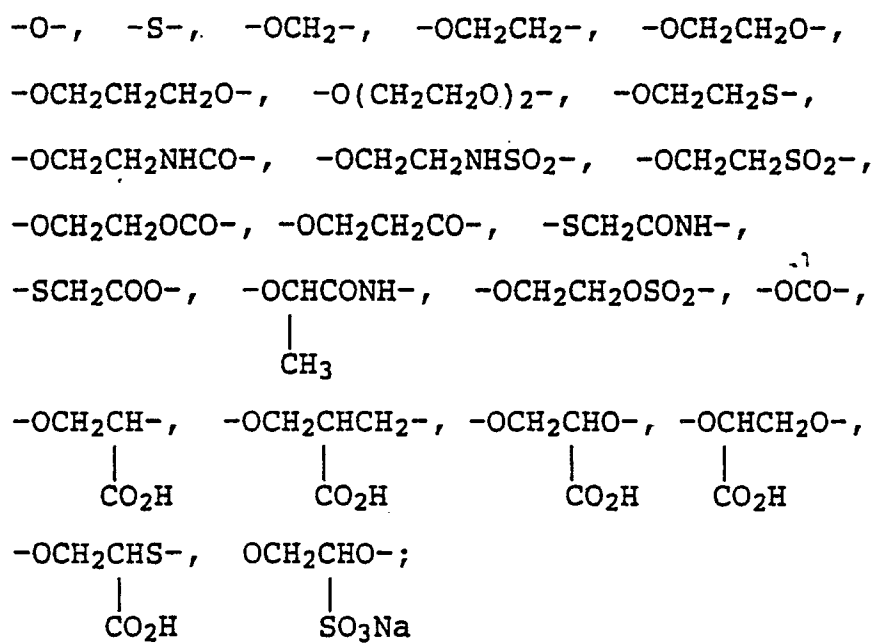
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25 (Examples of Q)

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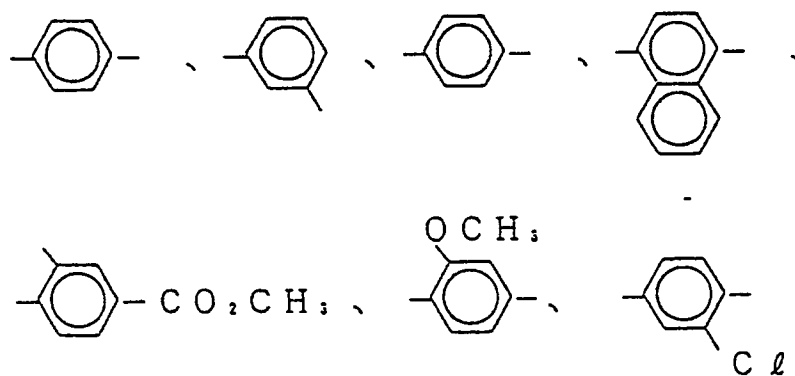
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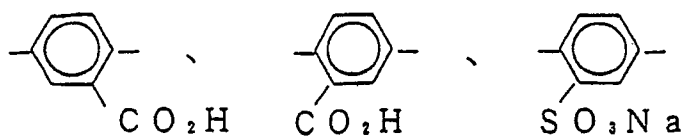
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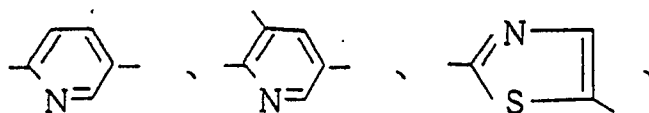
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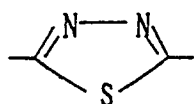
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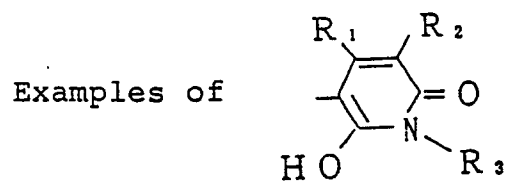
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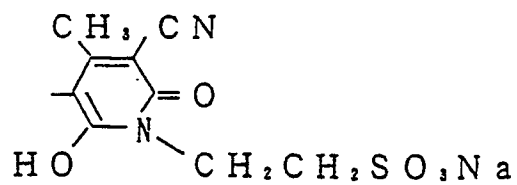


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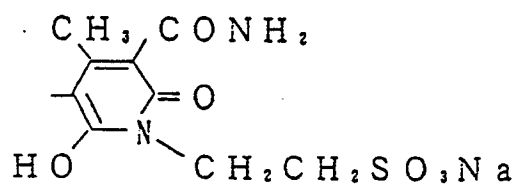


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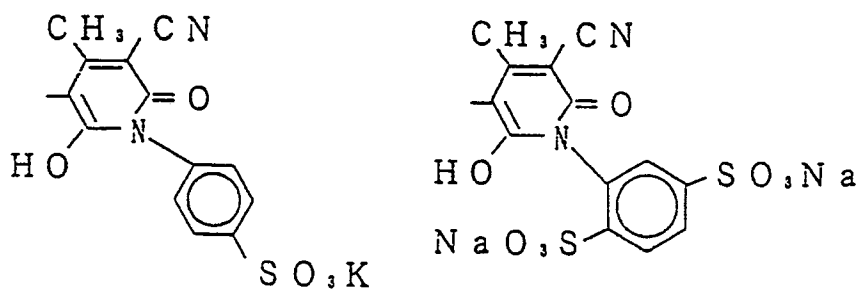
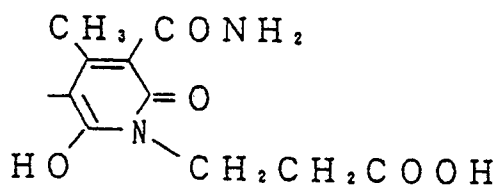
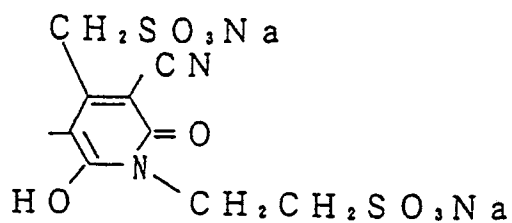
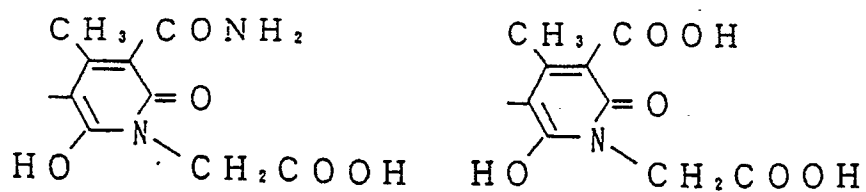


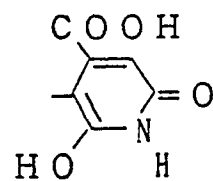
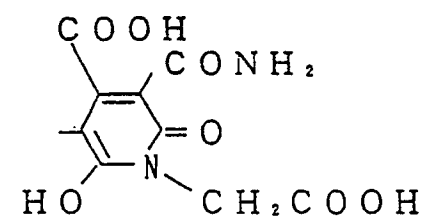
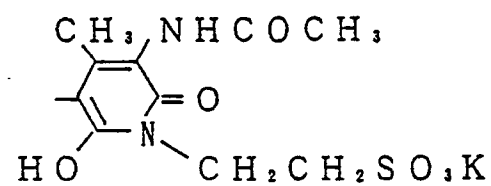
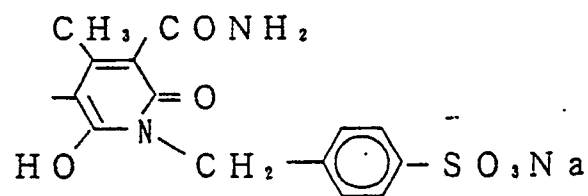
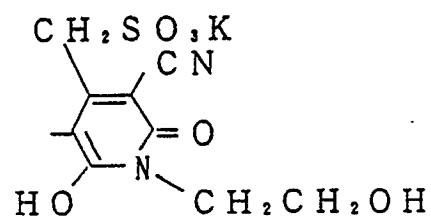
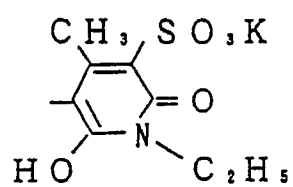
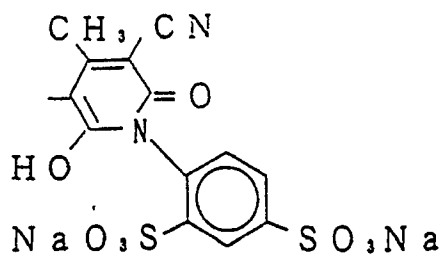
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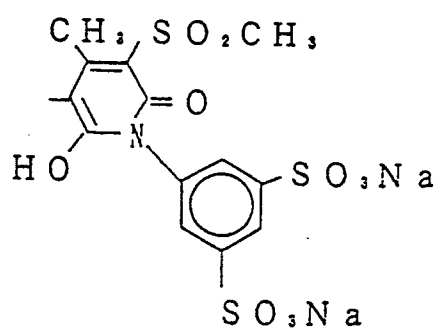
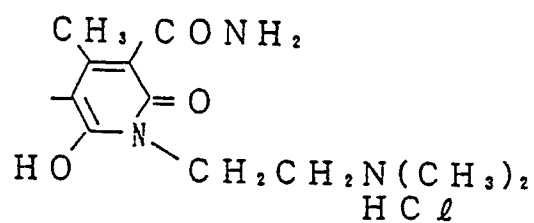
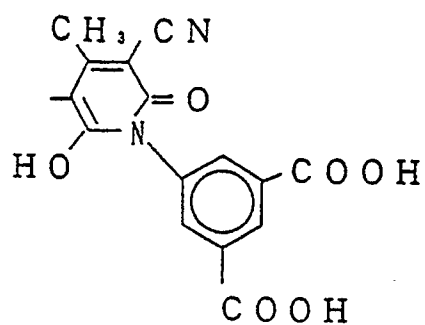
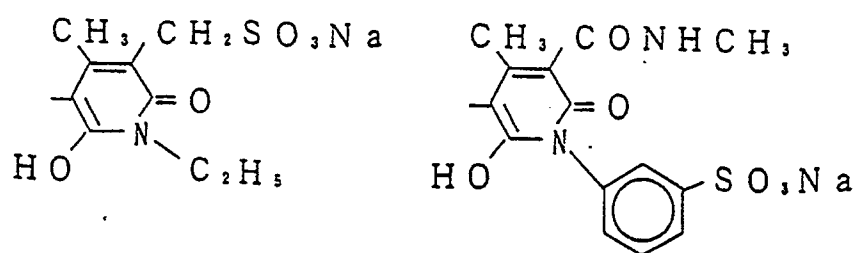
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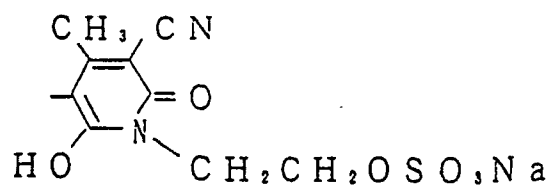
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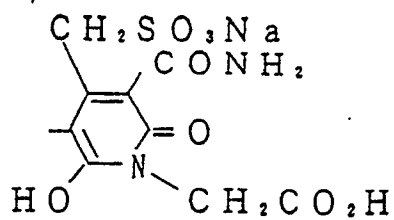




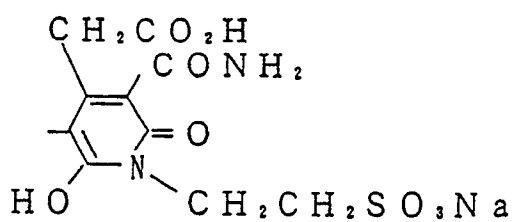
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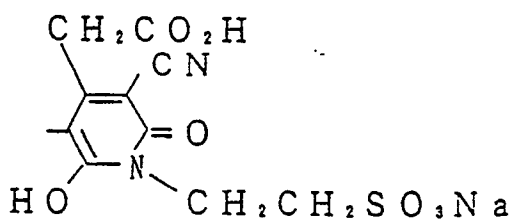


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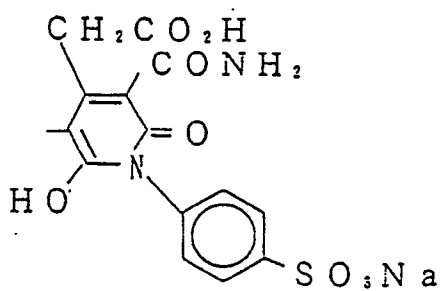


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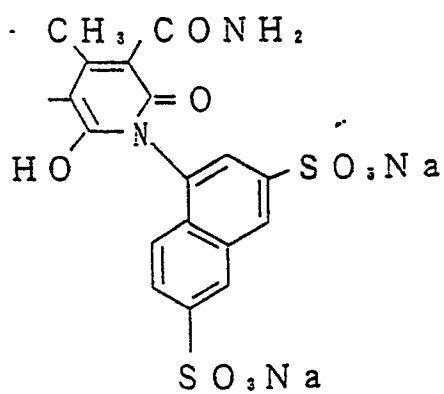
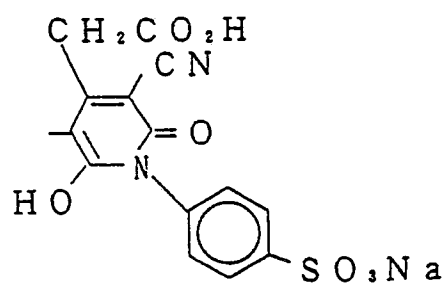
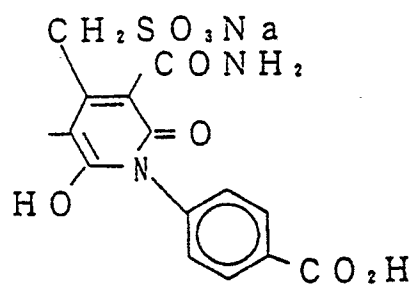
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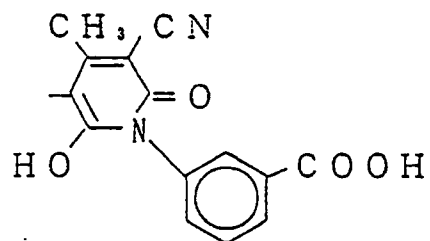
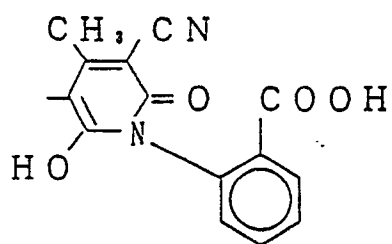
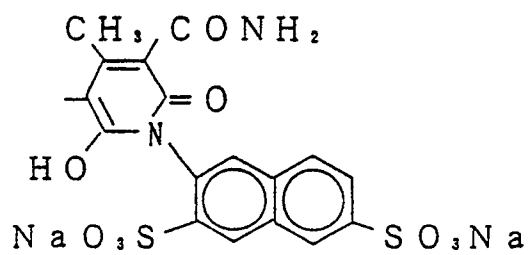
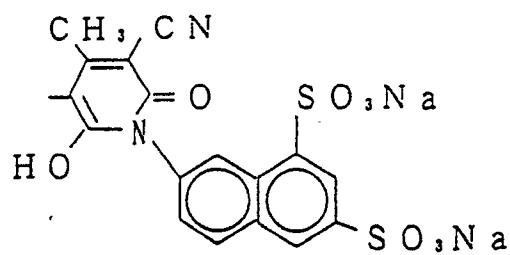
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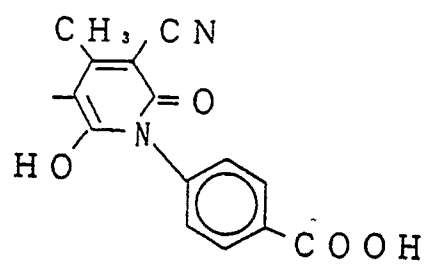
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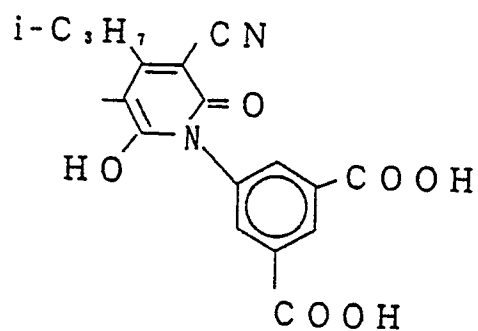




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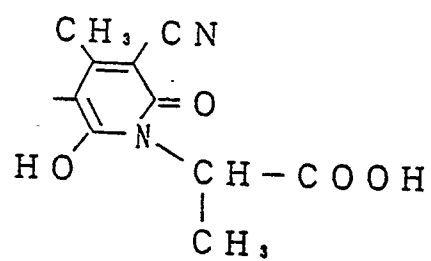
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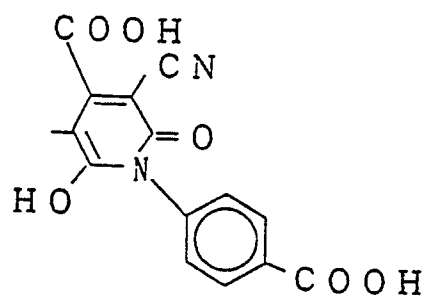
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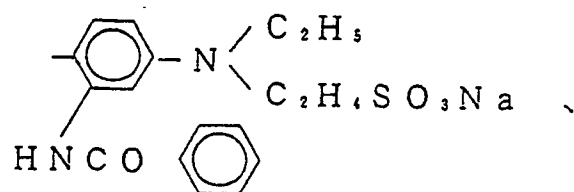
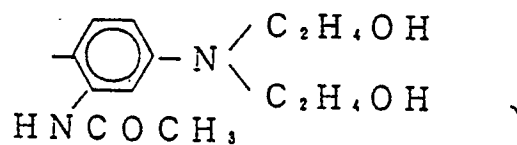
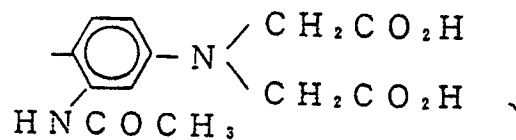
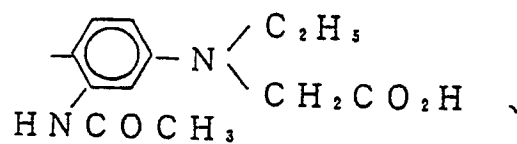
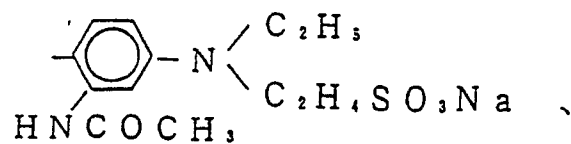
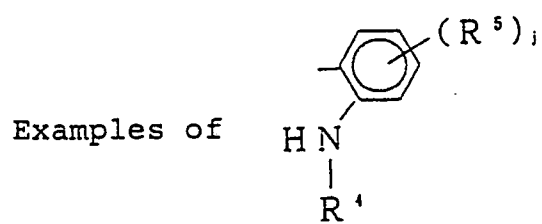


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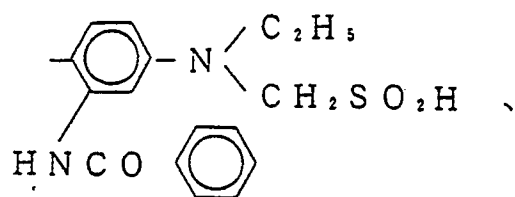
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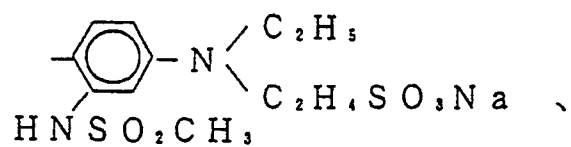
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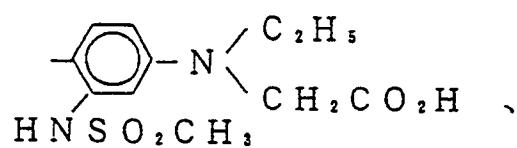


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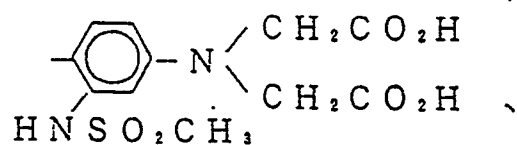


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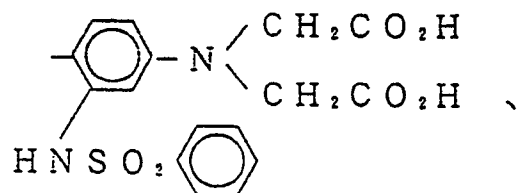
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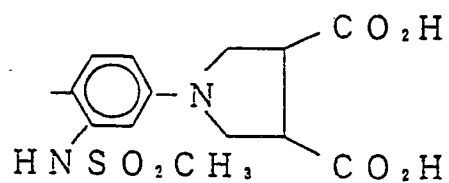


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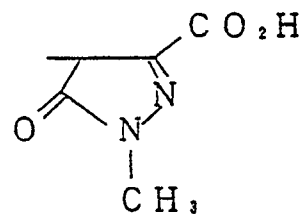
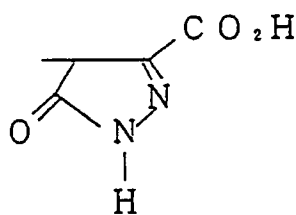
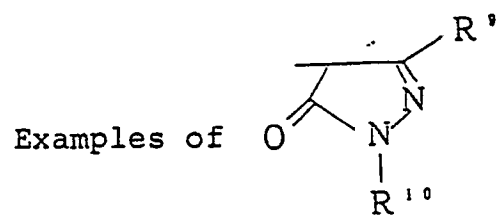
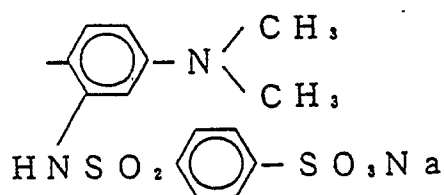
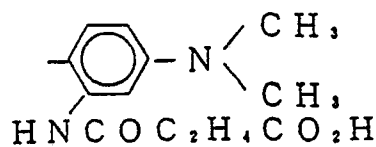
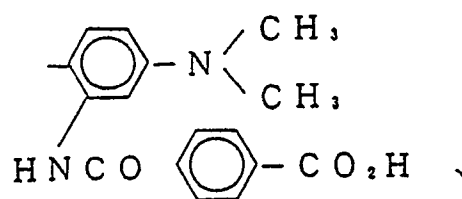
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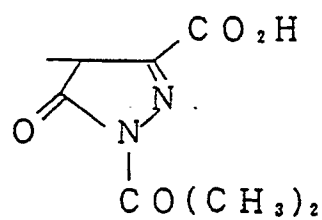
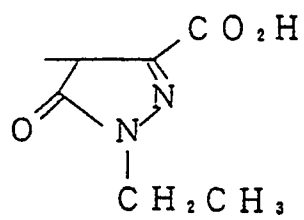
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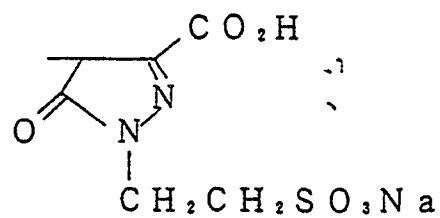
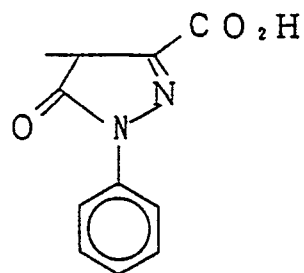
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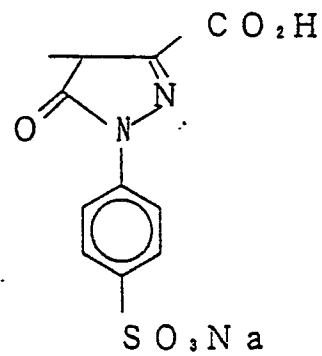
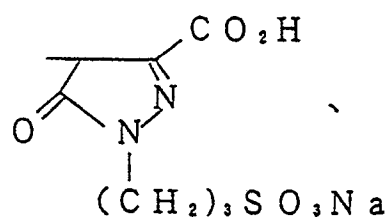


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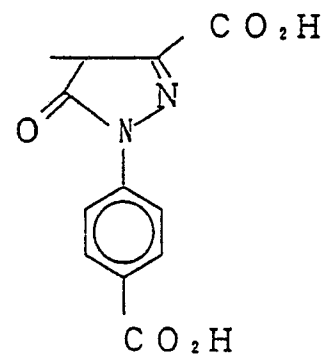
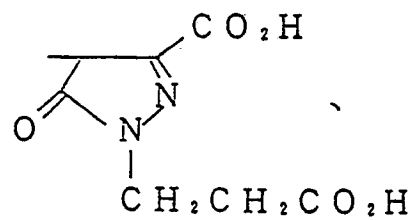
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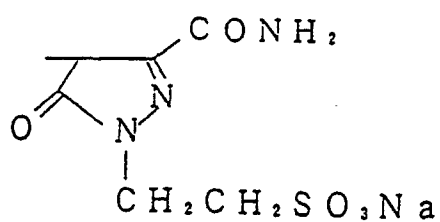
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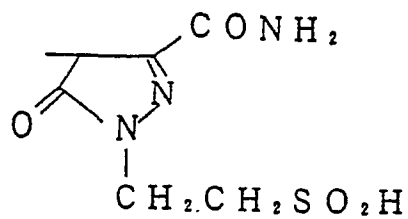
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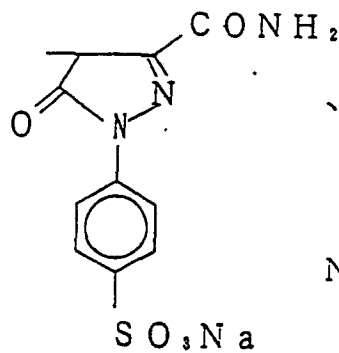


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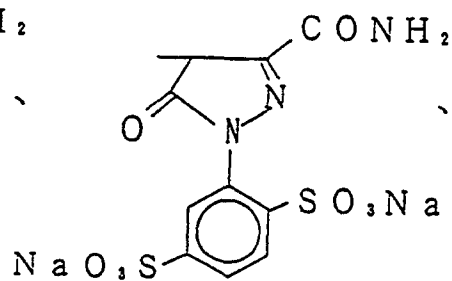


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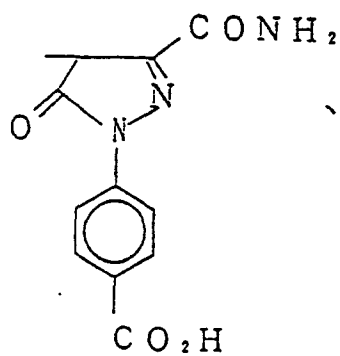


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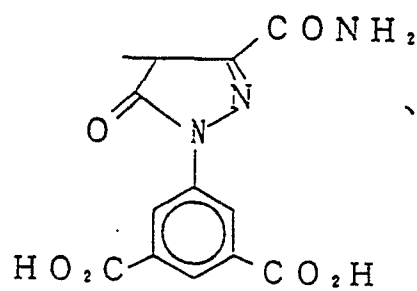


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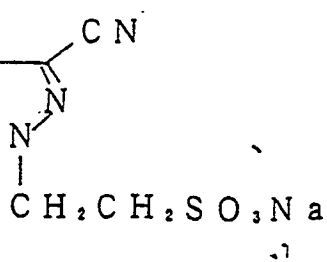
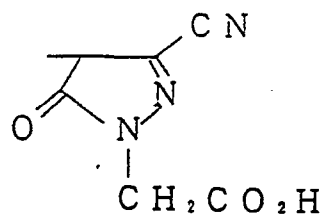


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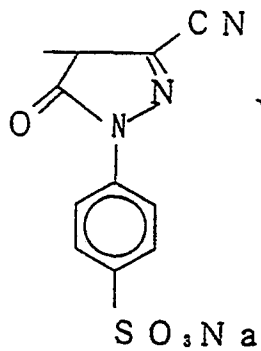
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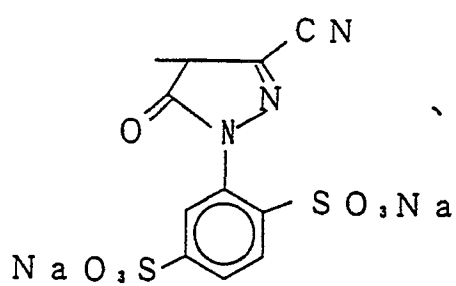
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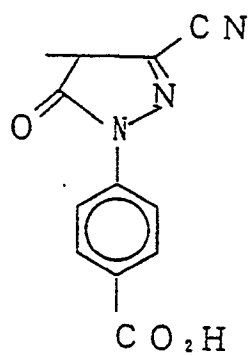


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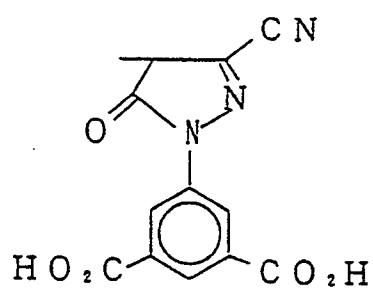


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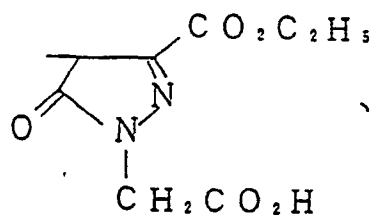
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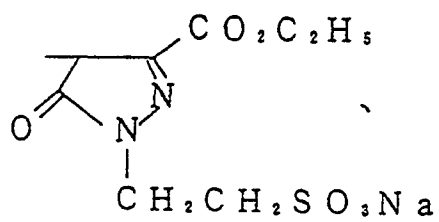
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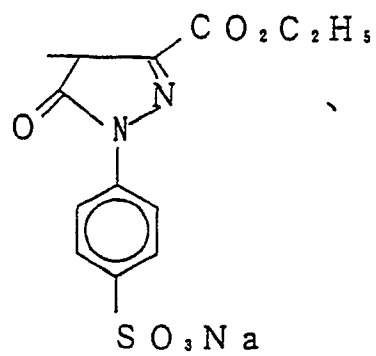


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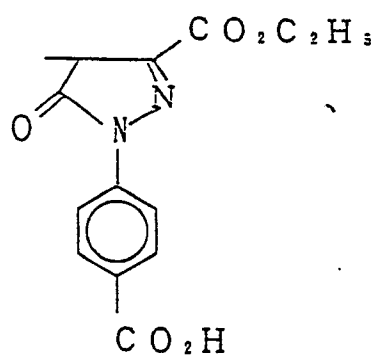
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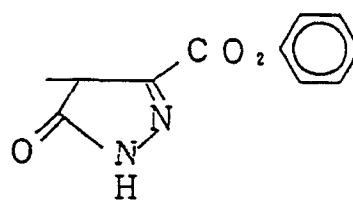
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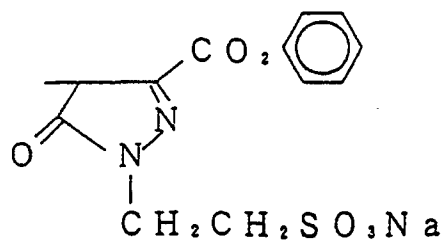
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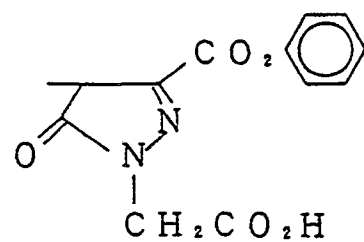
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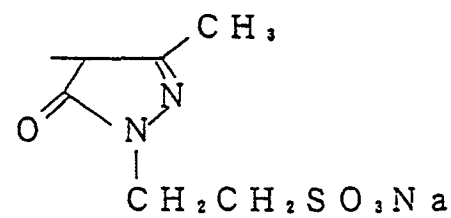
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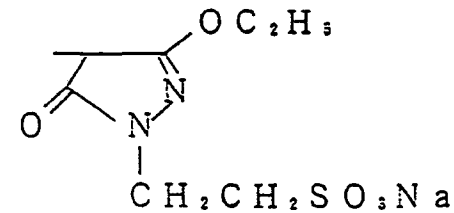
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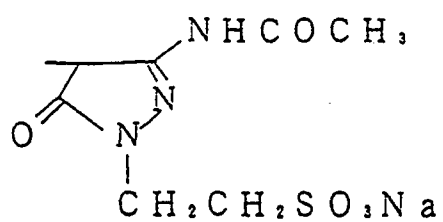
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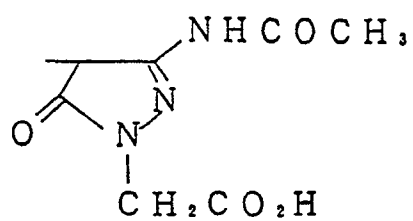
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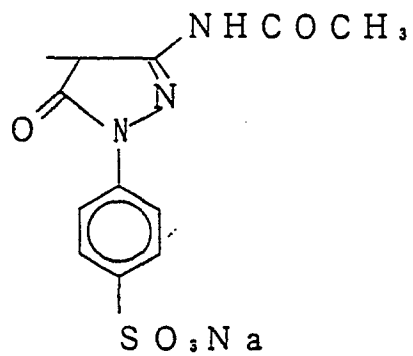


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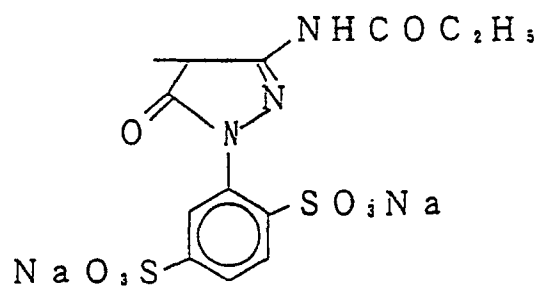
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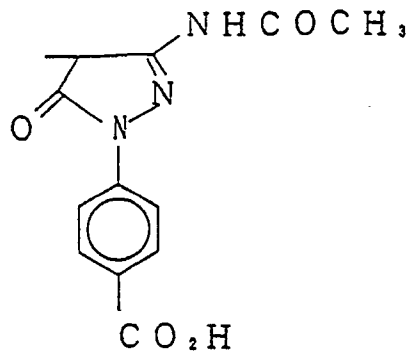
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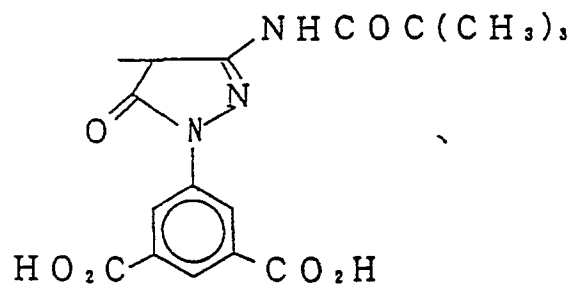
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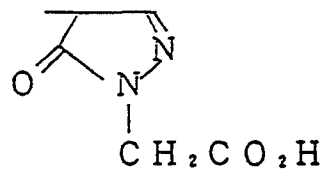
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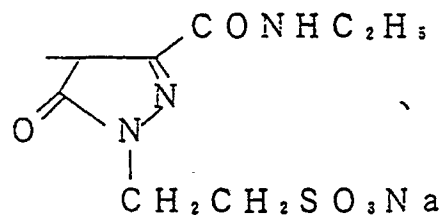
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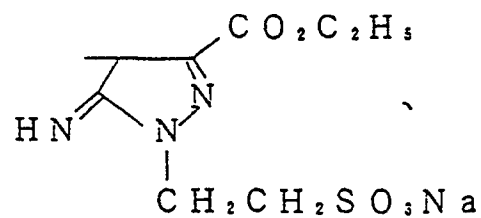
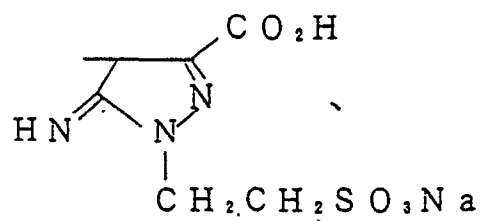
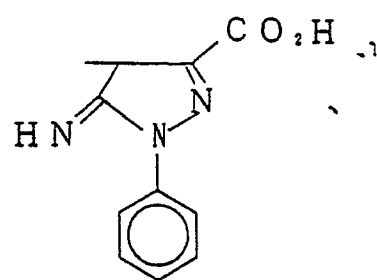
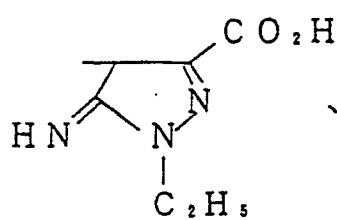
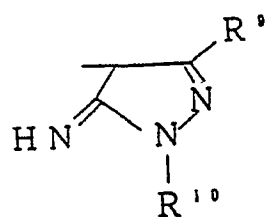
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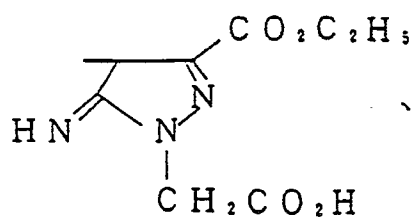
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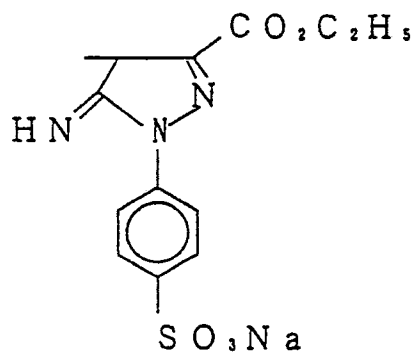
Examples of



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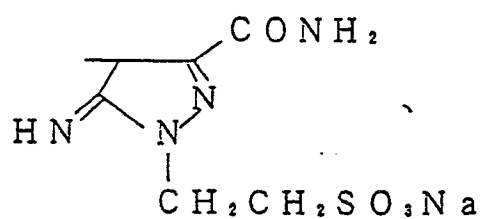
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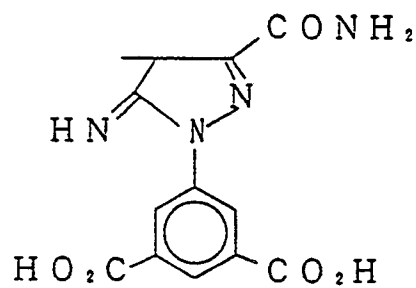
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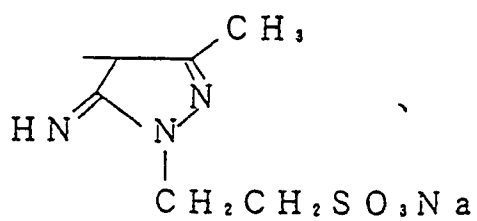
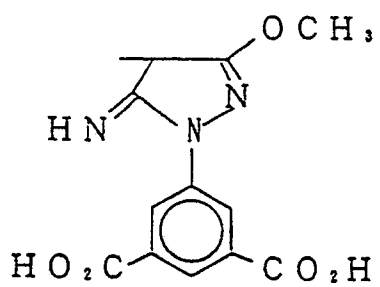
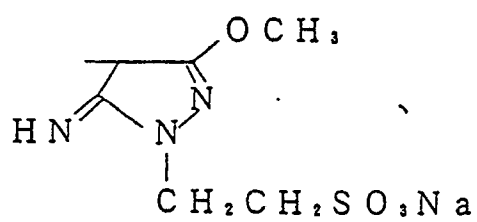
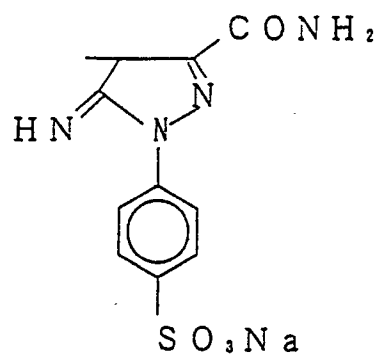


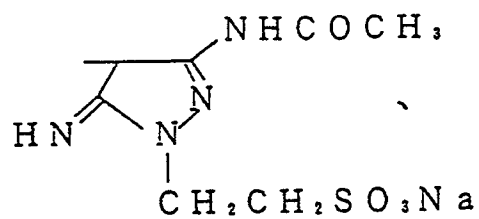
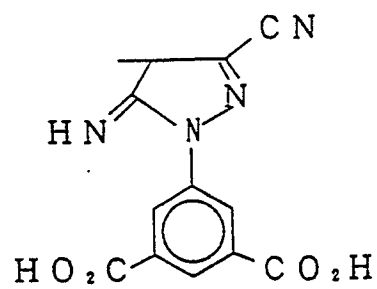
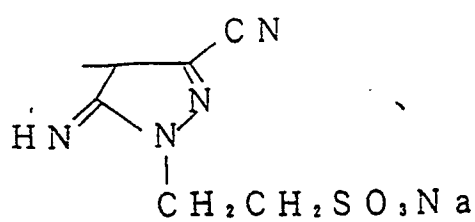
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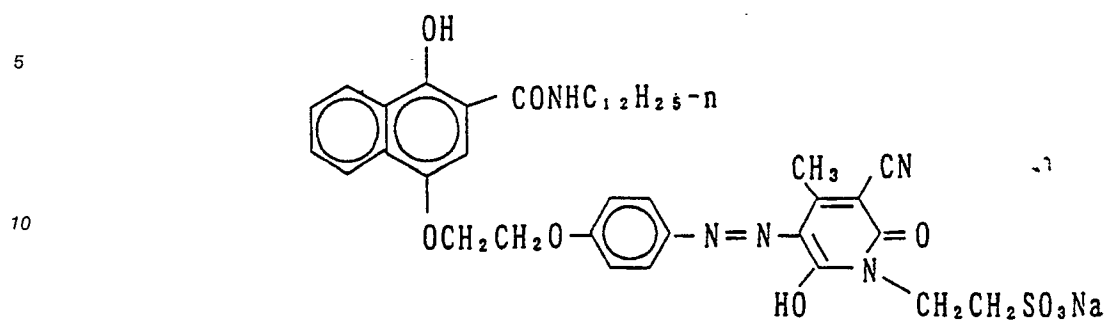
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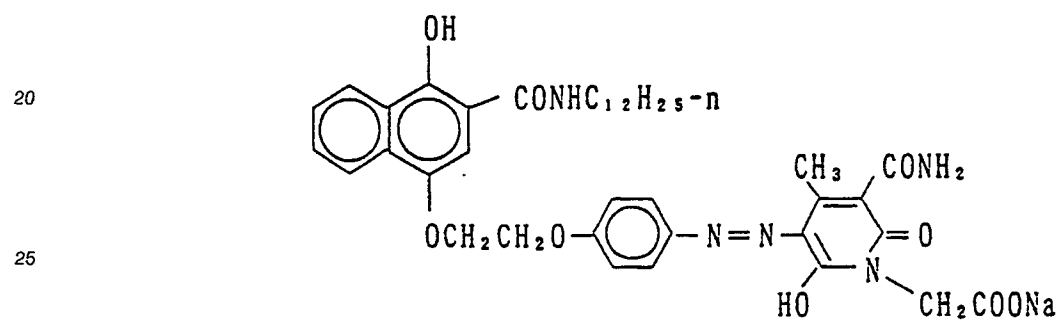


Examples of Colored Couplers of the Invention

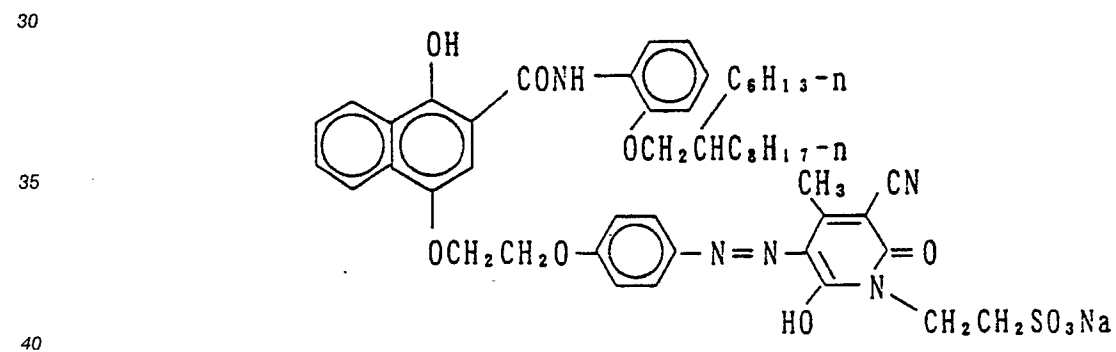
(Y C - 1)



(Y C - 2)



(Y C - 3)

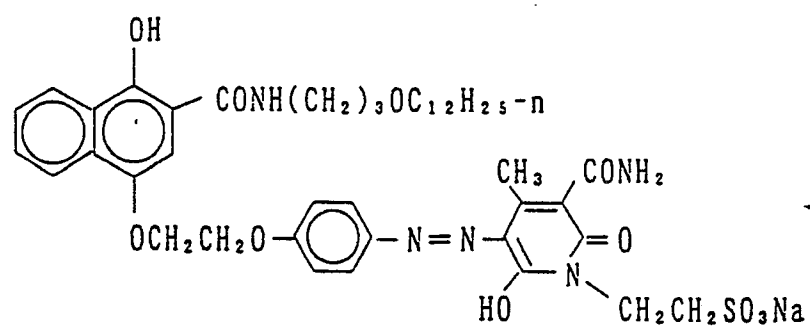


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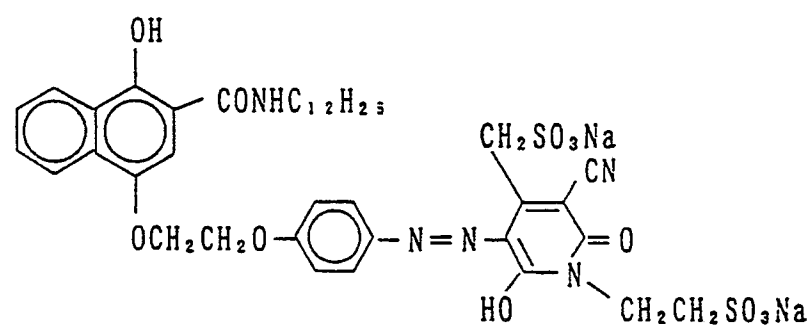
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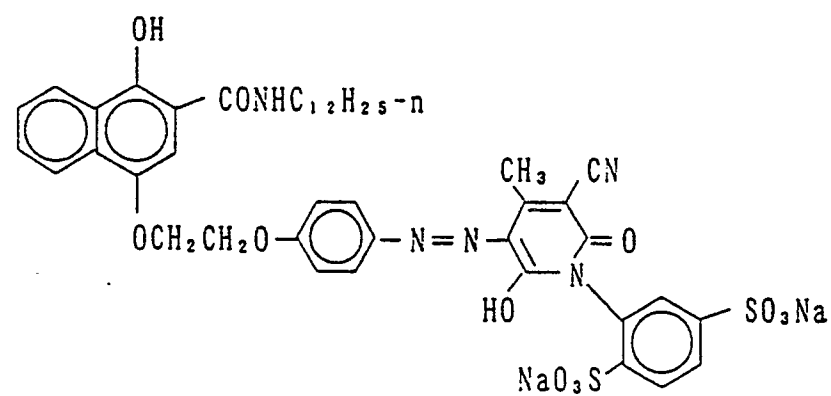
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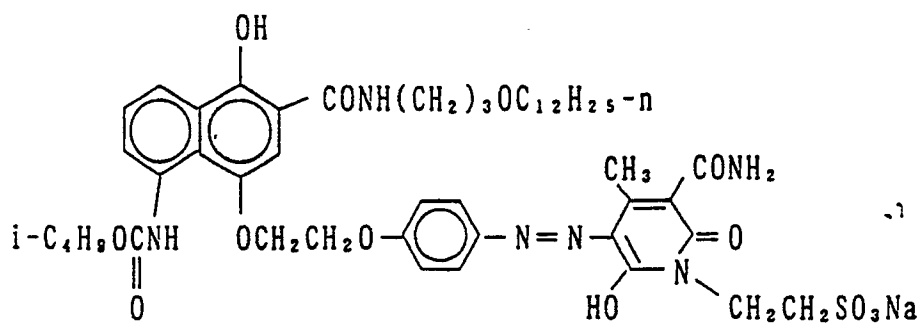
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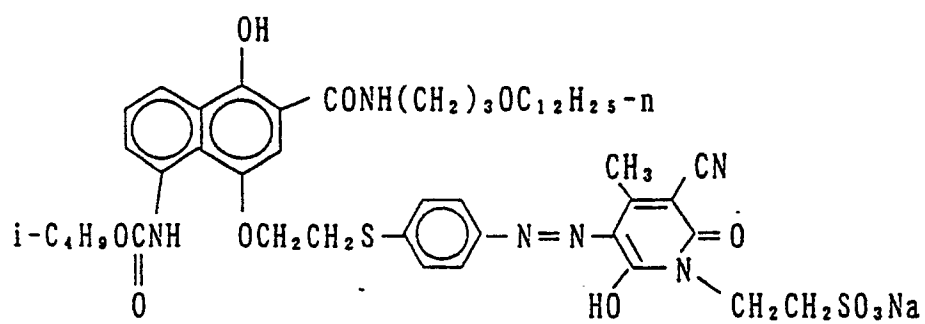
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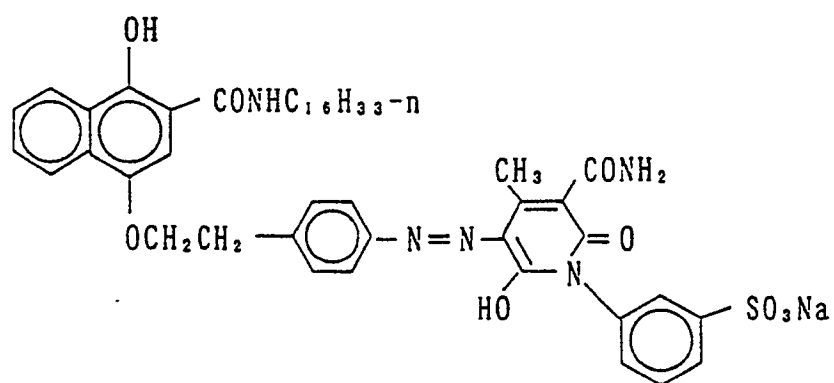
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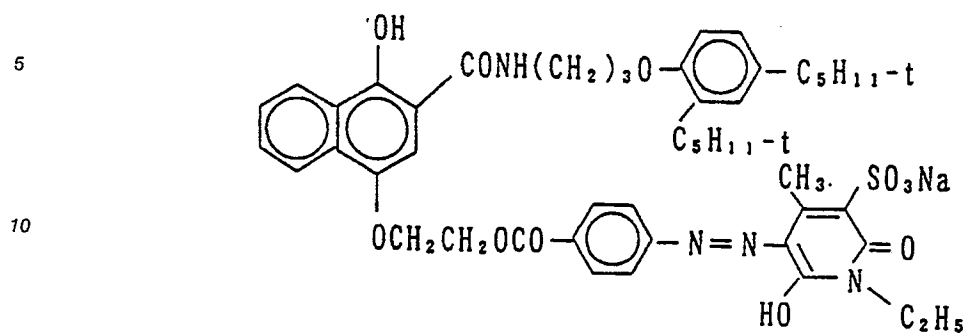
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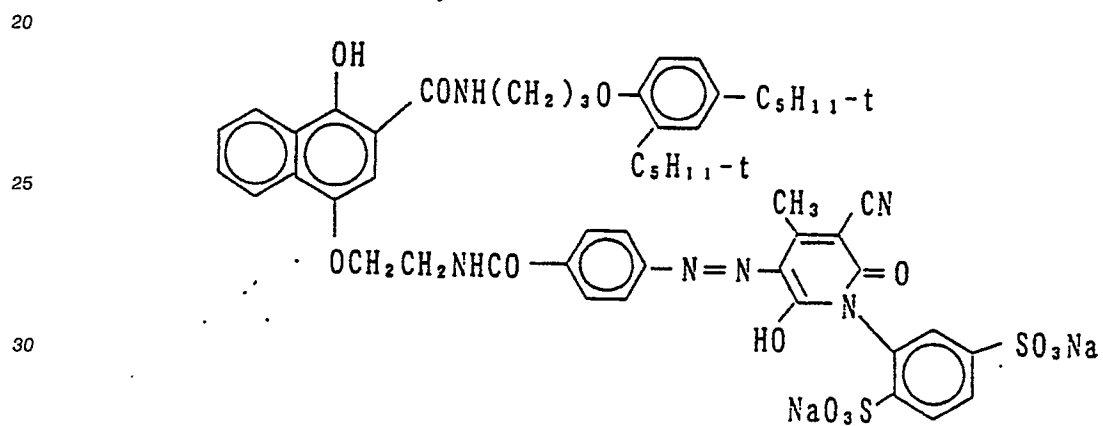
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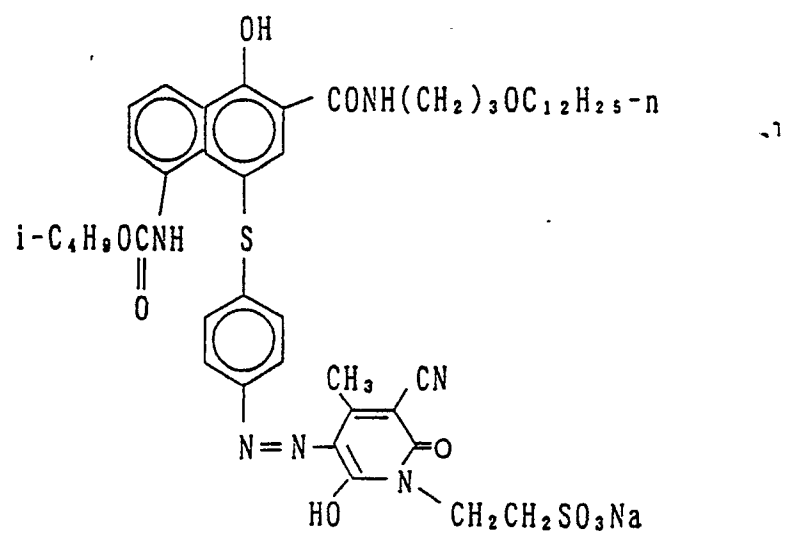
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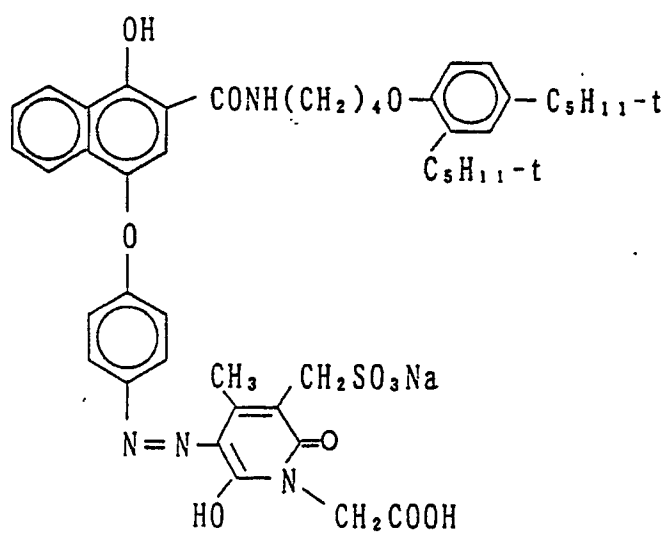
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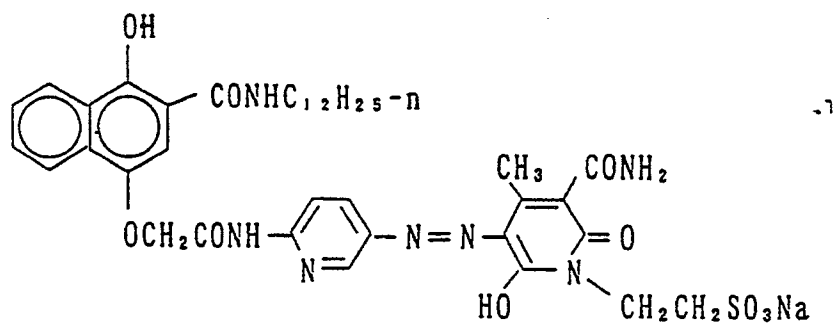
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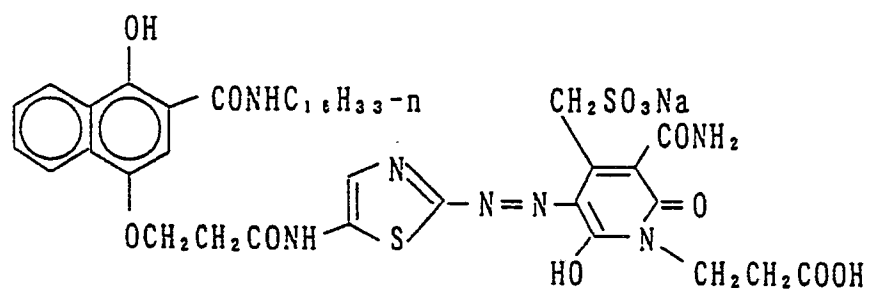
(Y C - 1 3)



(Y C - 1 4)

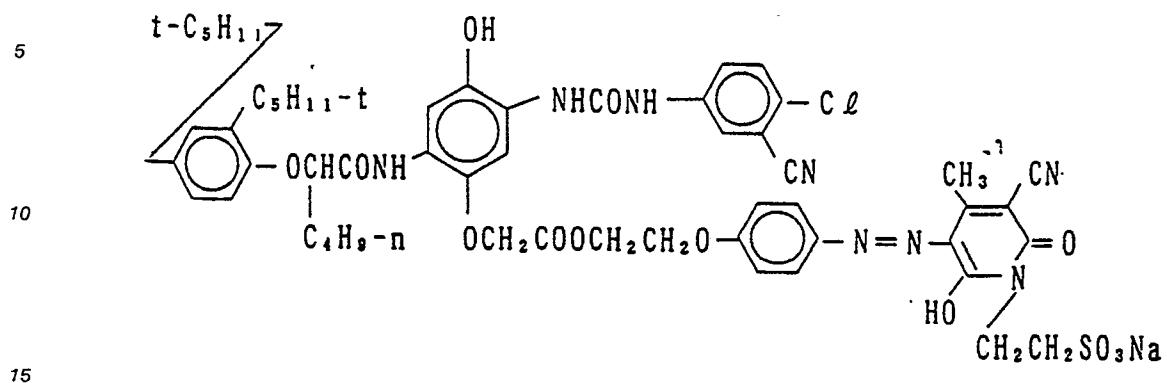


(Y C - 1 5)

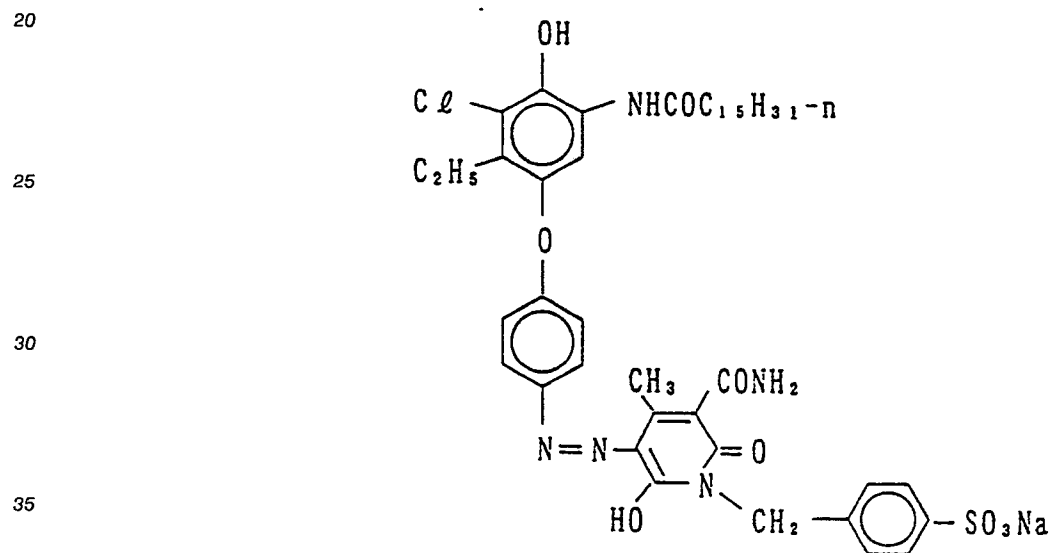


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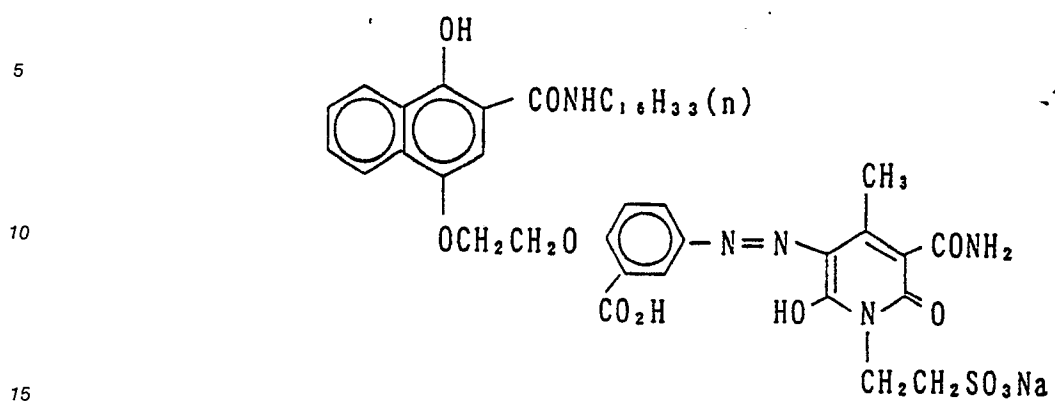
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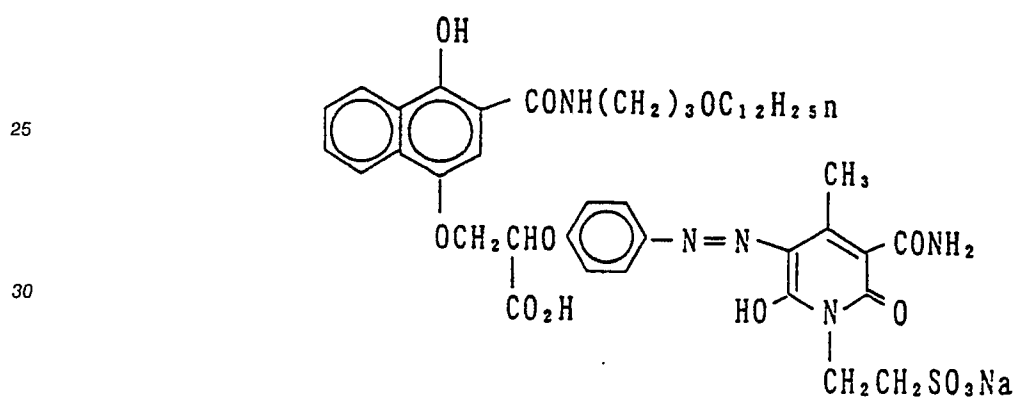
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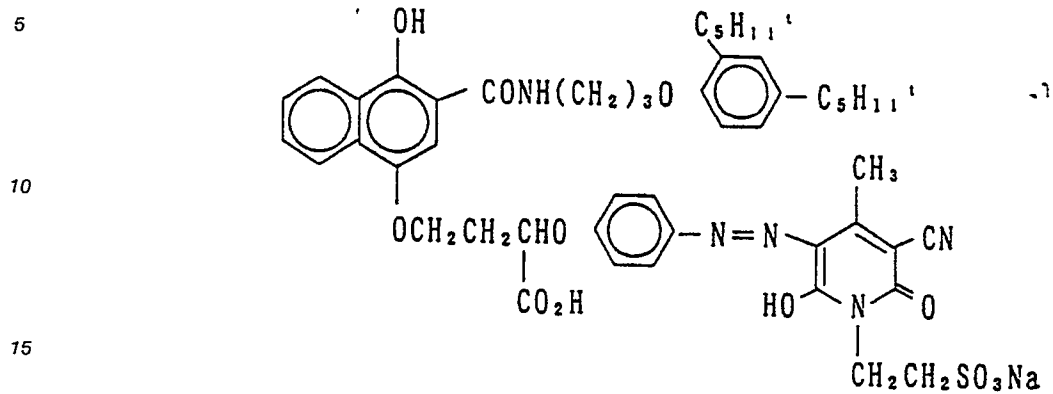
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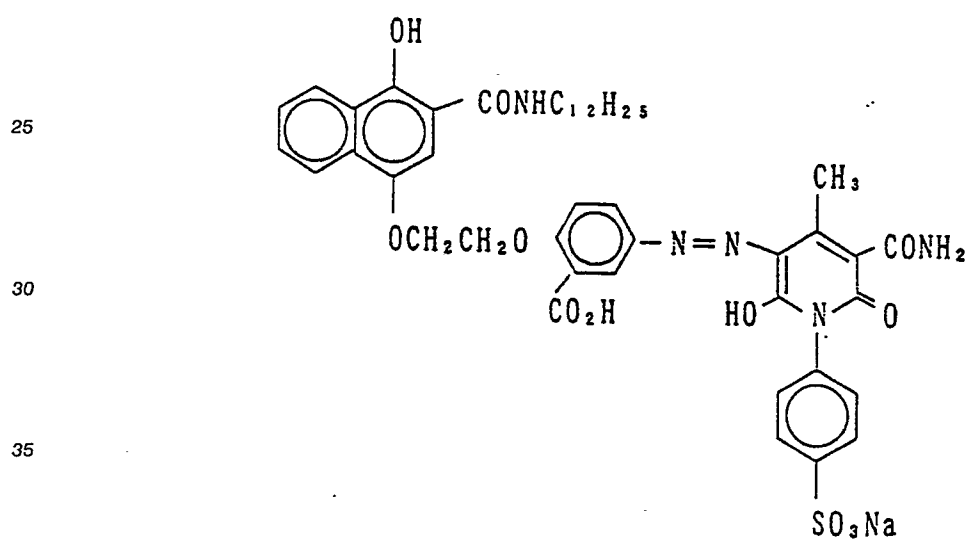
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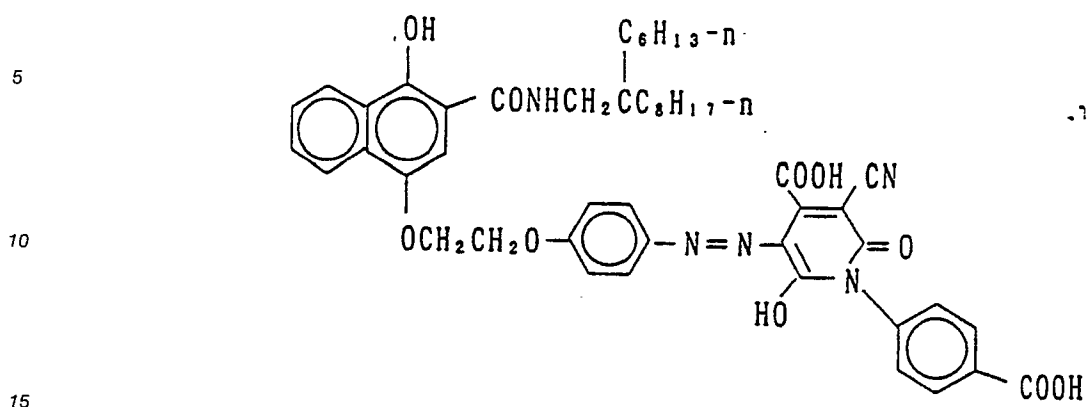
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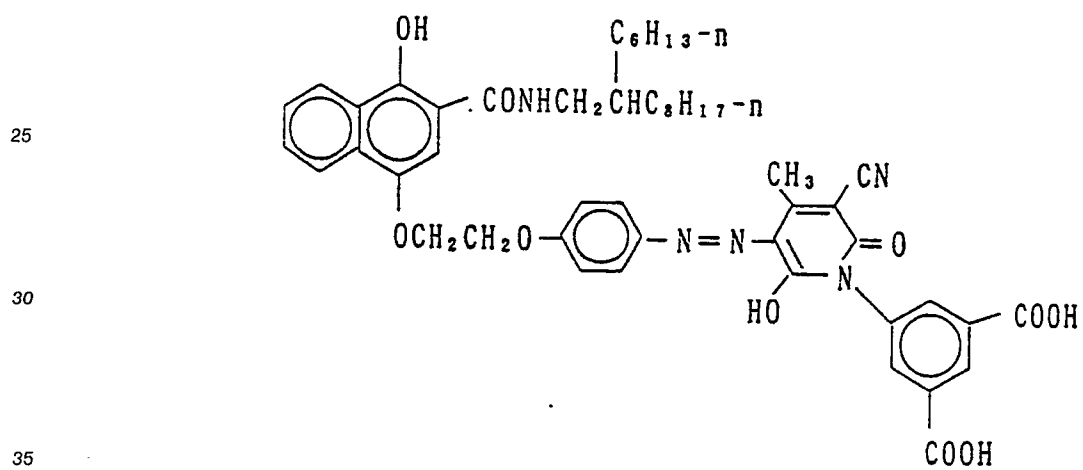
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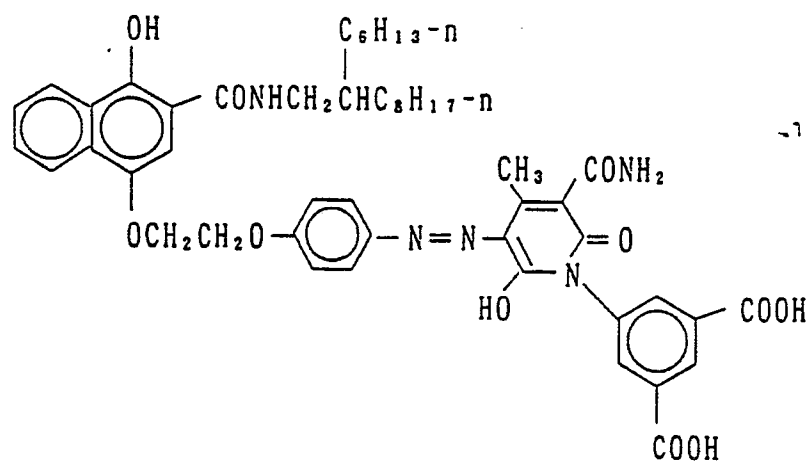
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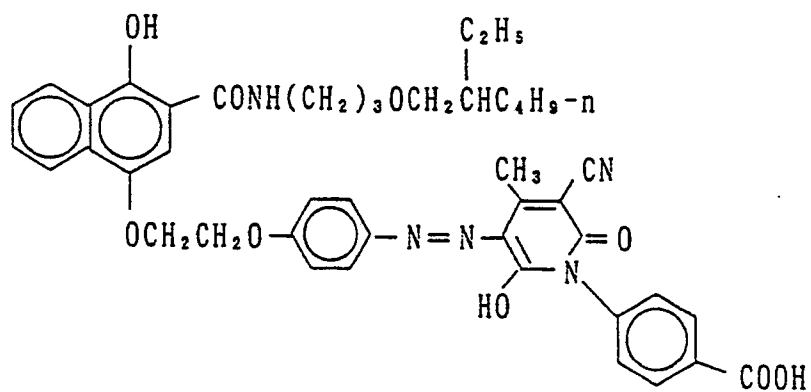
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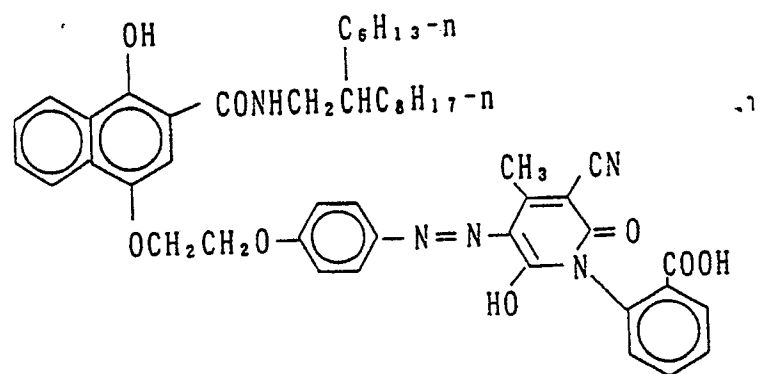
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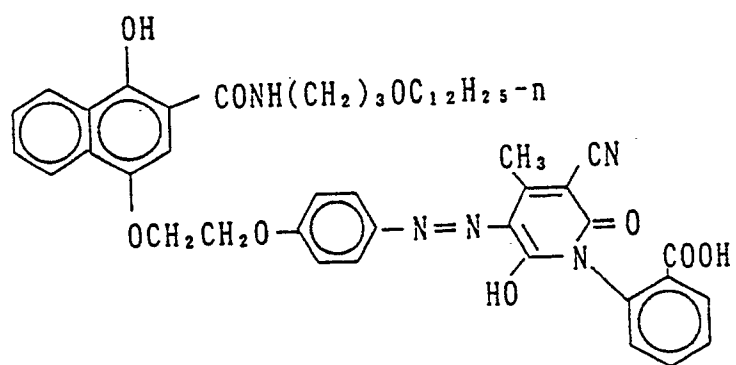
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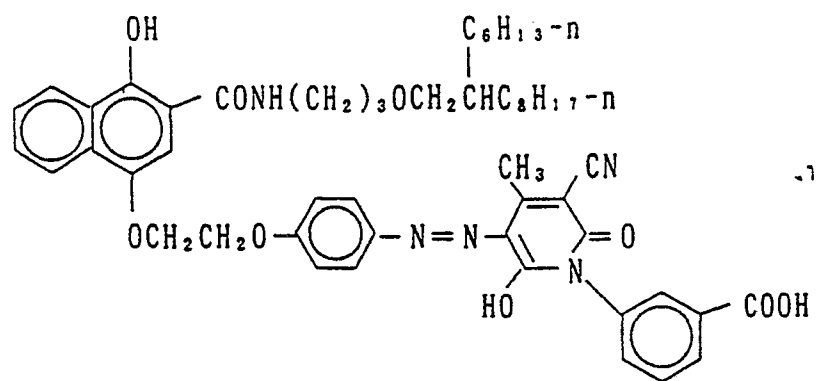
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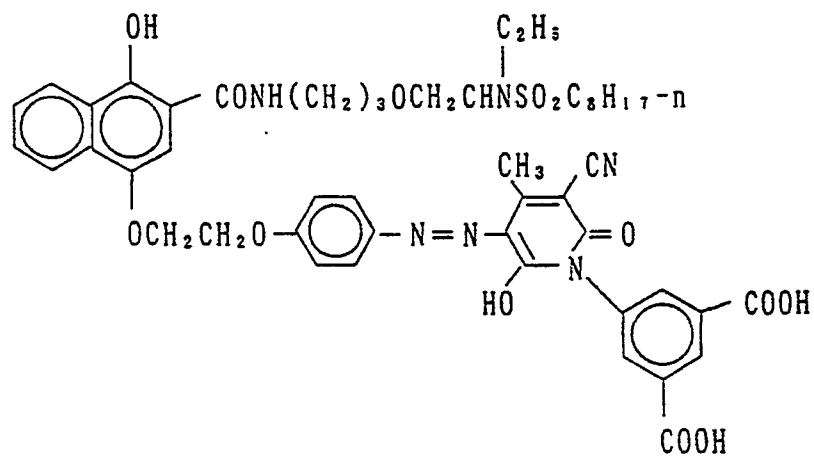
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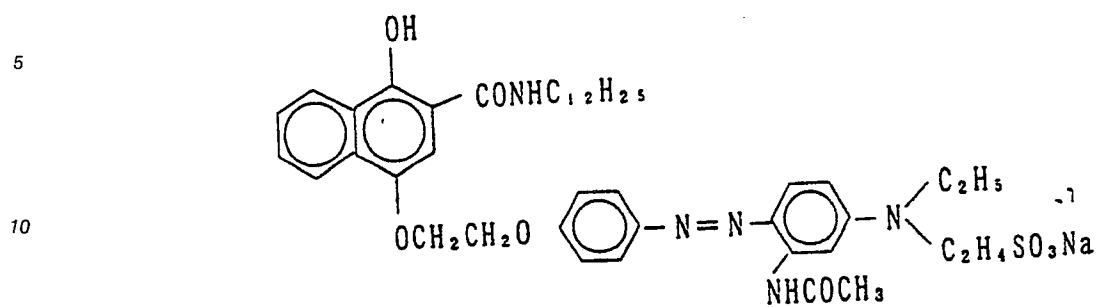
(Y C - 3 0)



(Y C - 3 1)

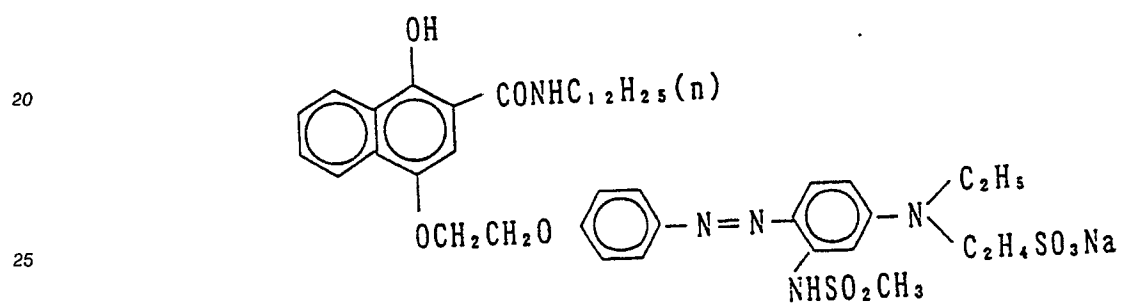


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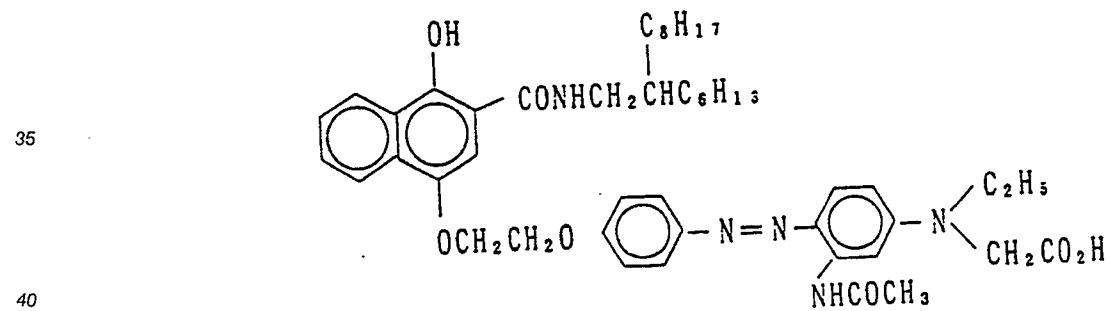
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(Y C - 3 3)



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(Y C - 3 4)

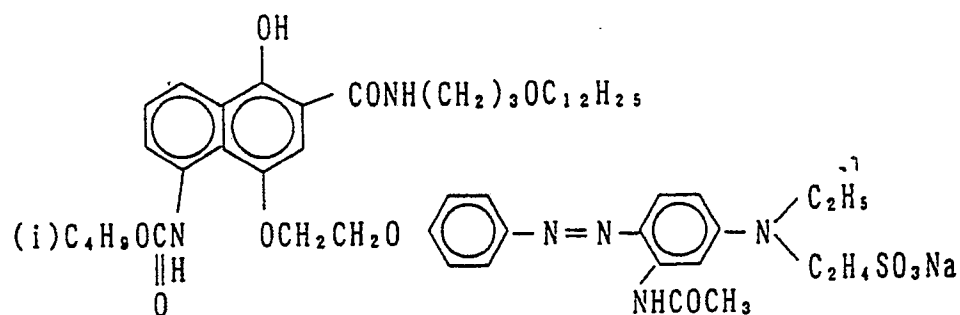


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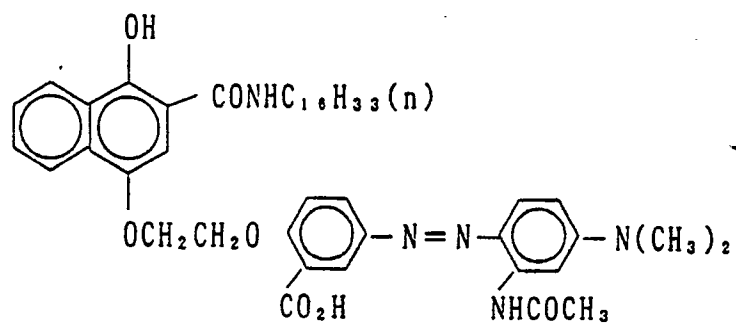
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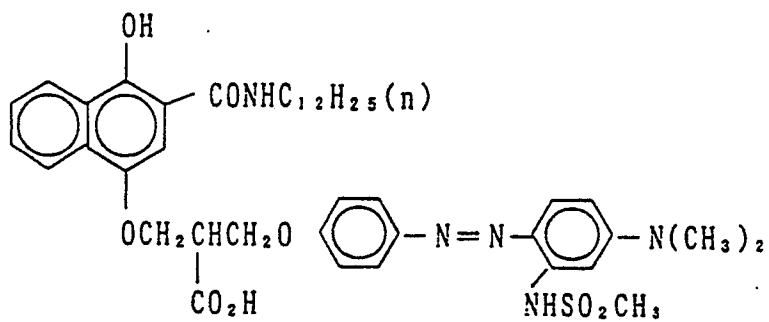
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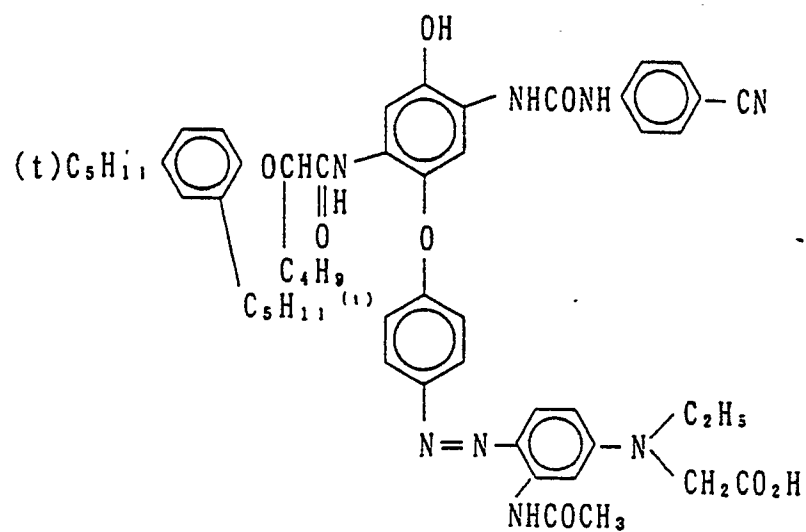
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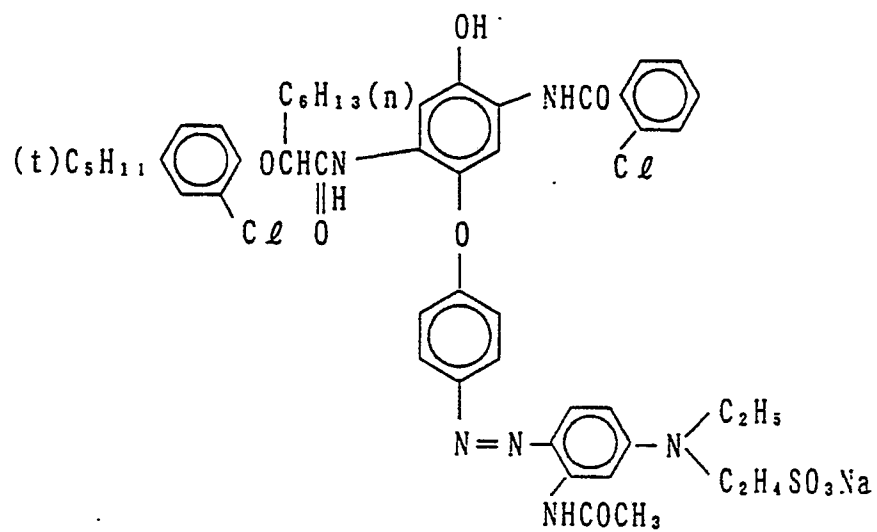
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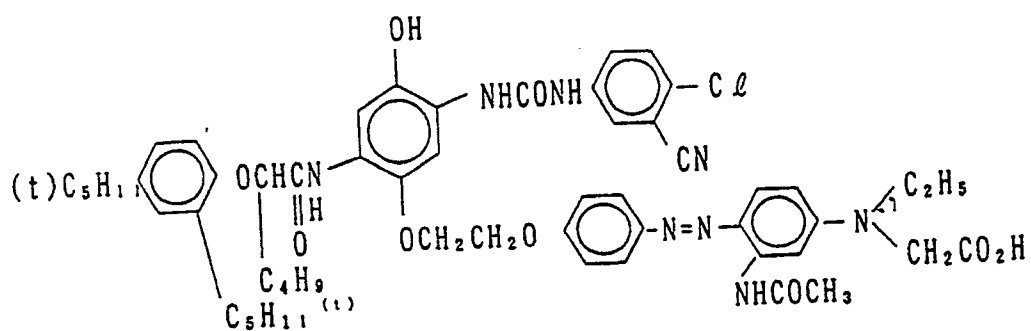
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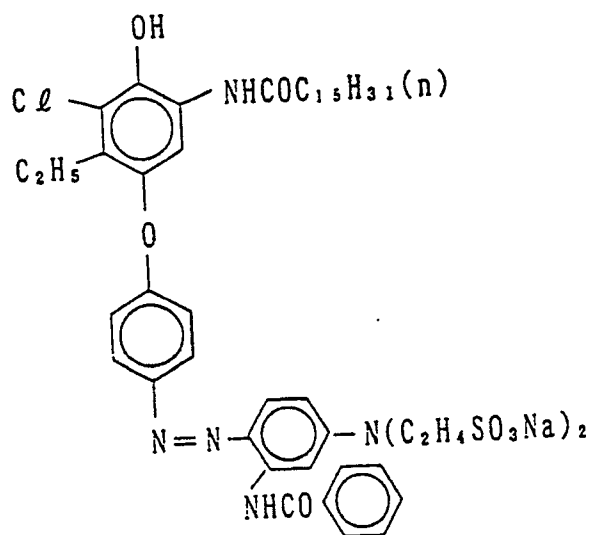
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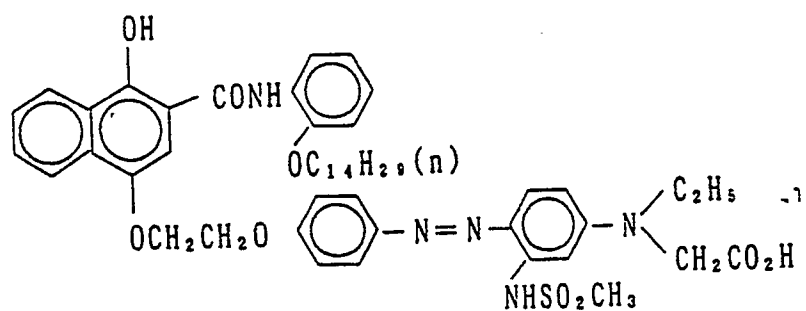
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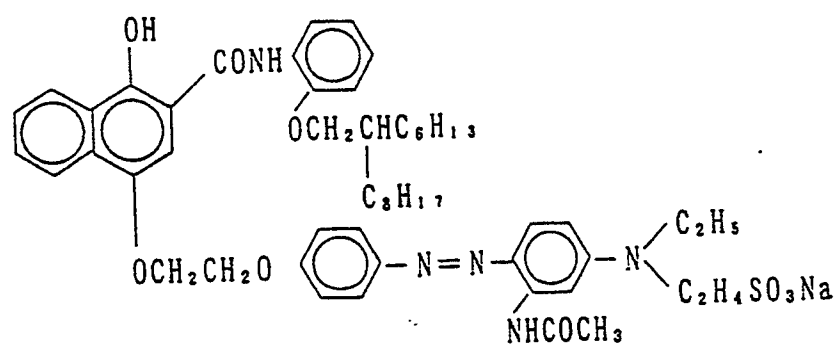
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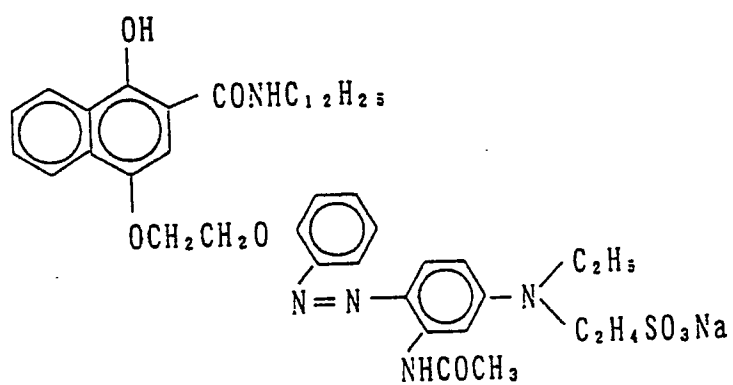
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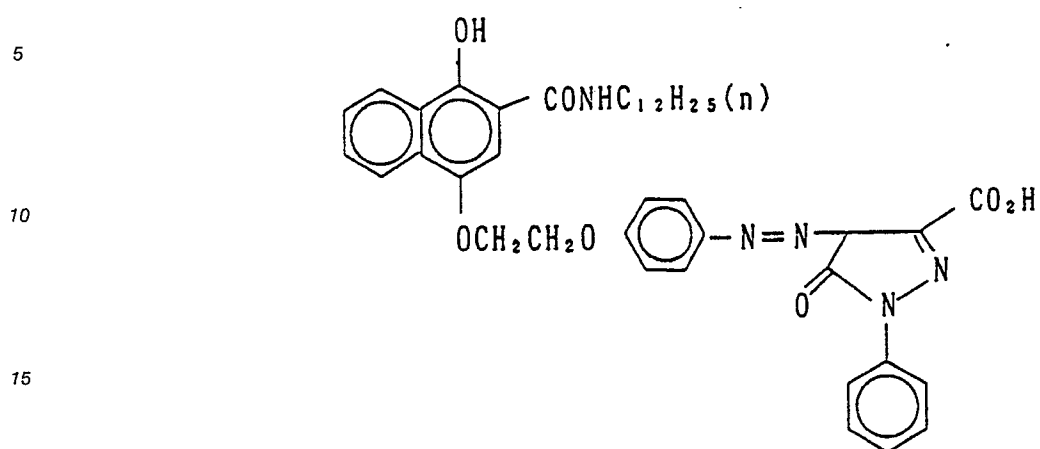
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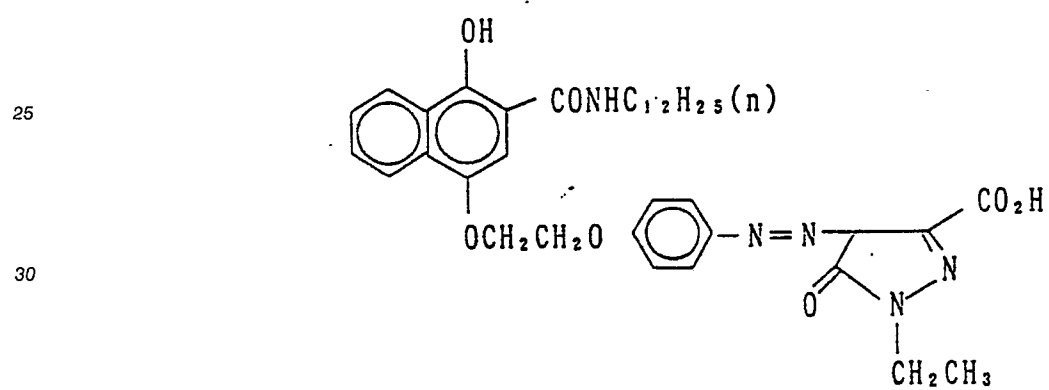


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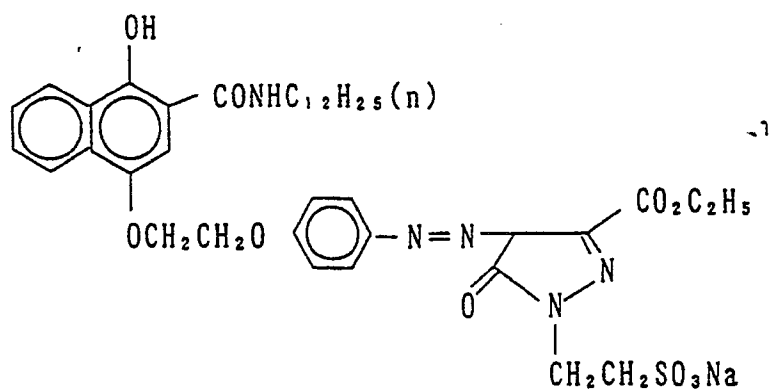


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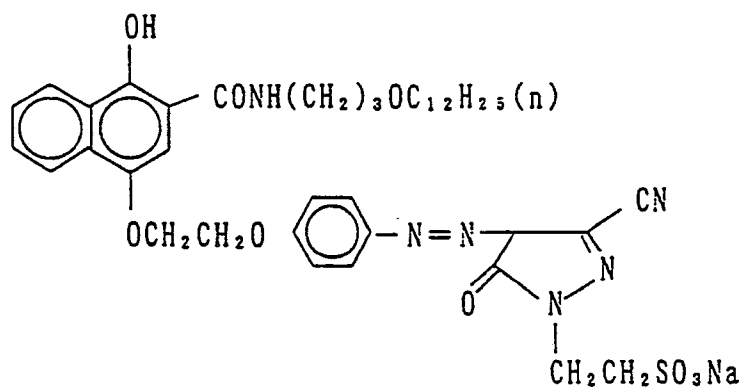
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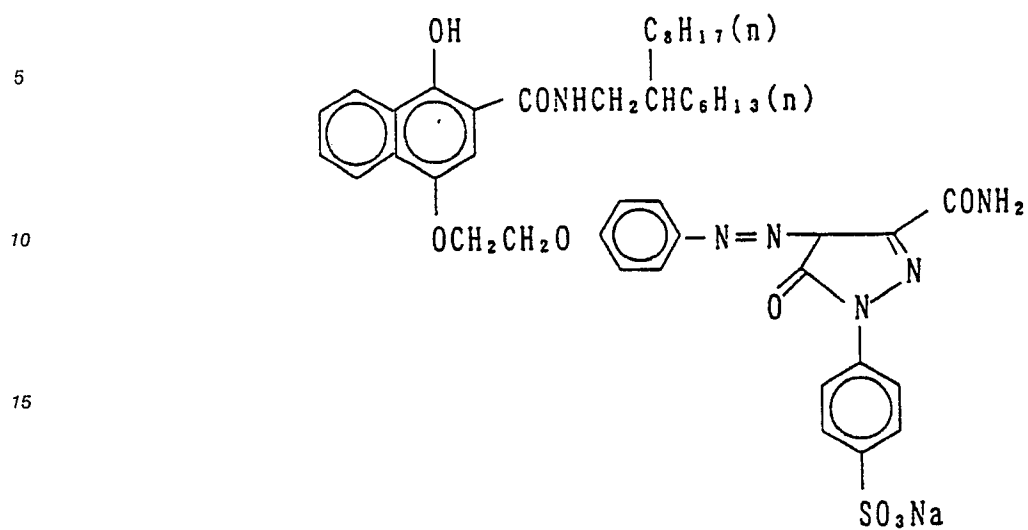
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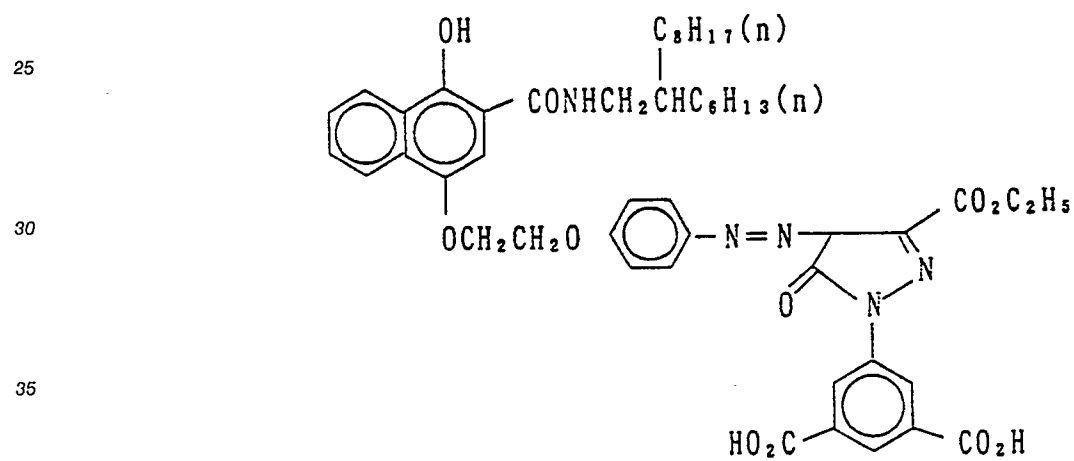
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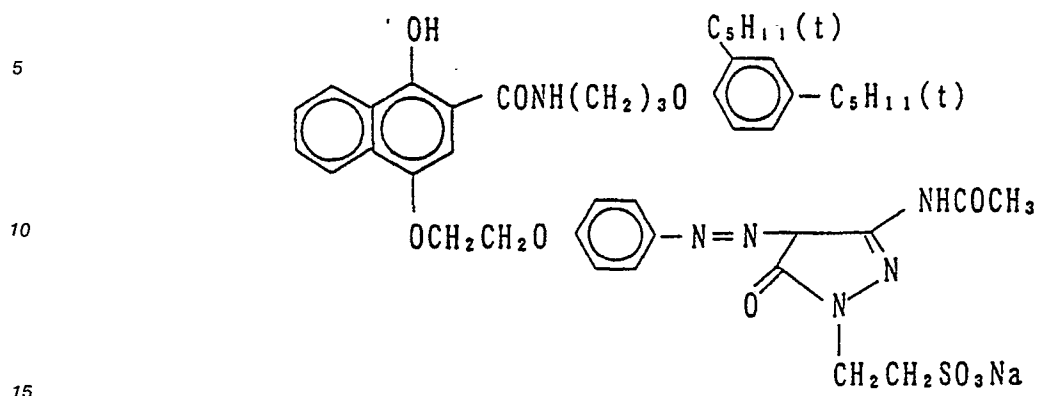
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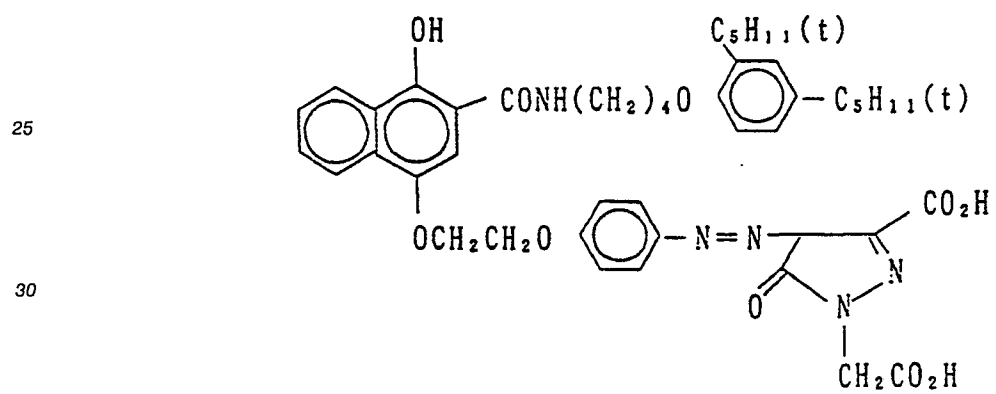
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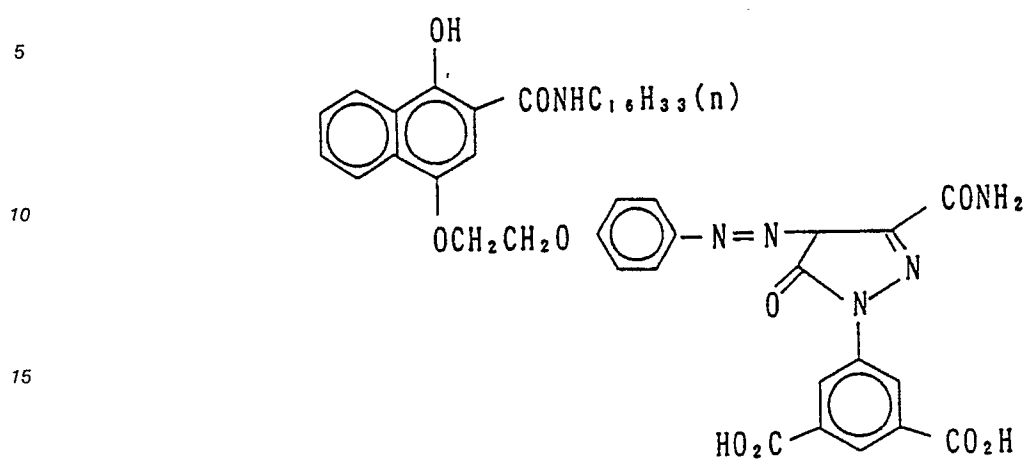
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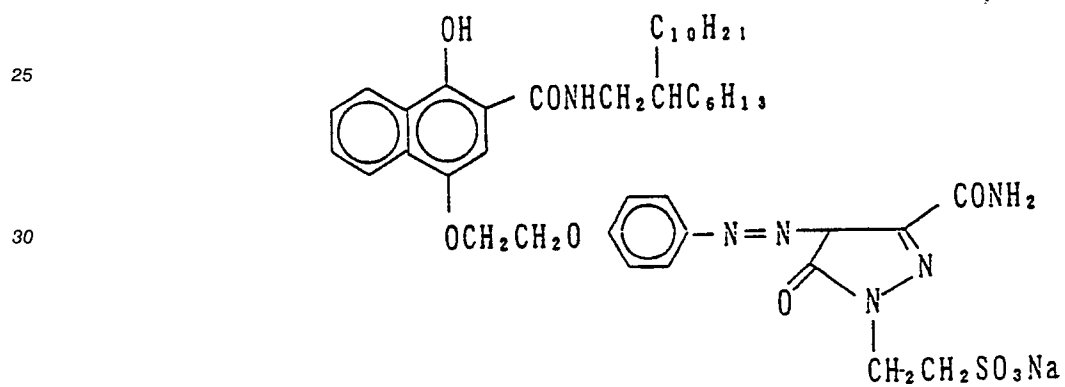
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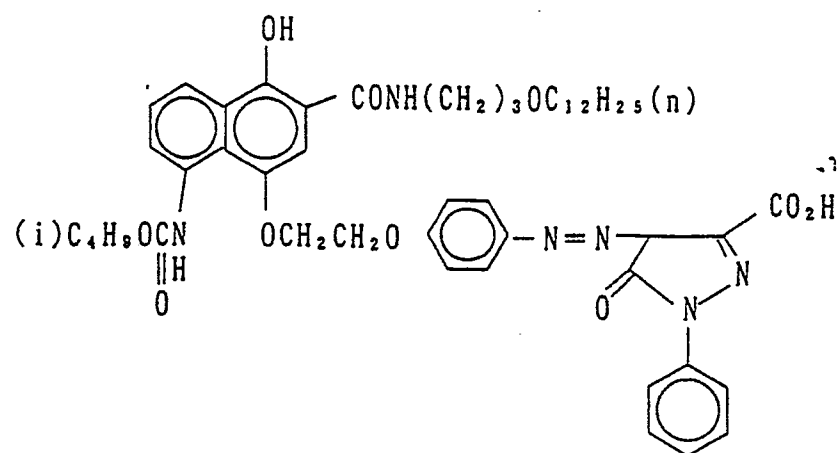
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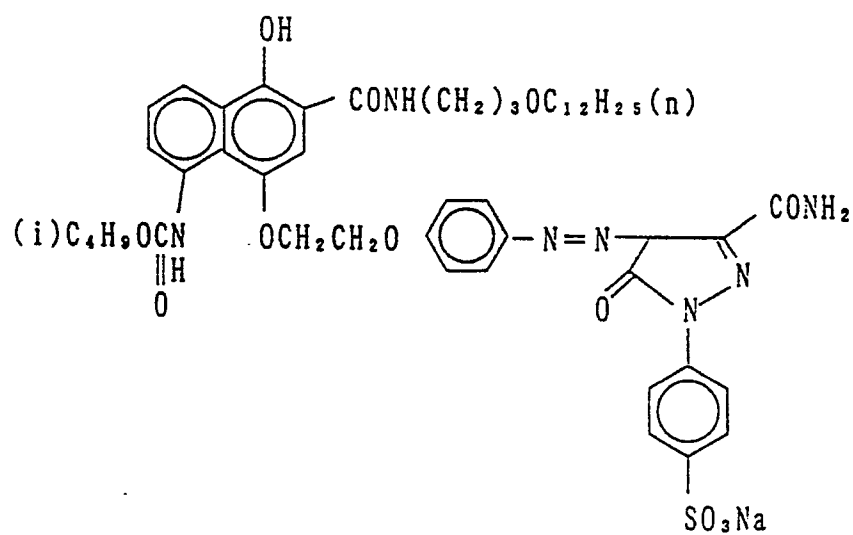
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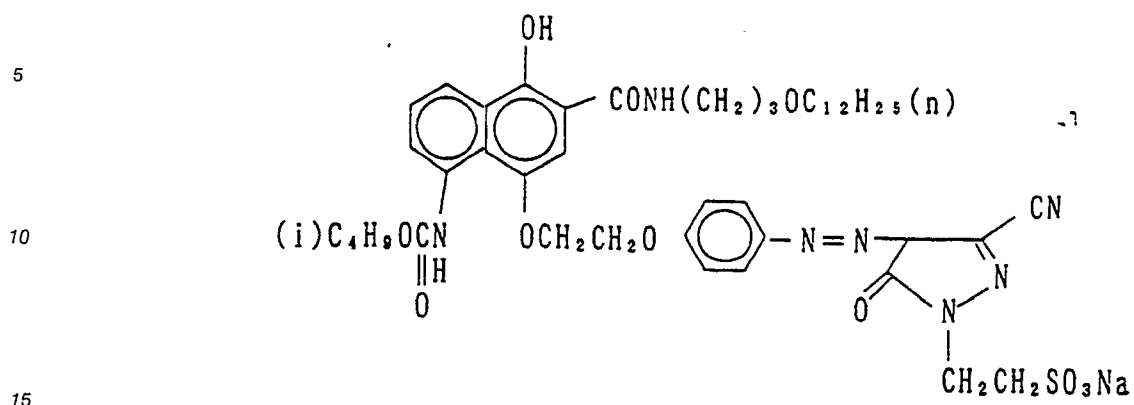
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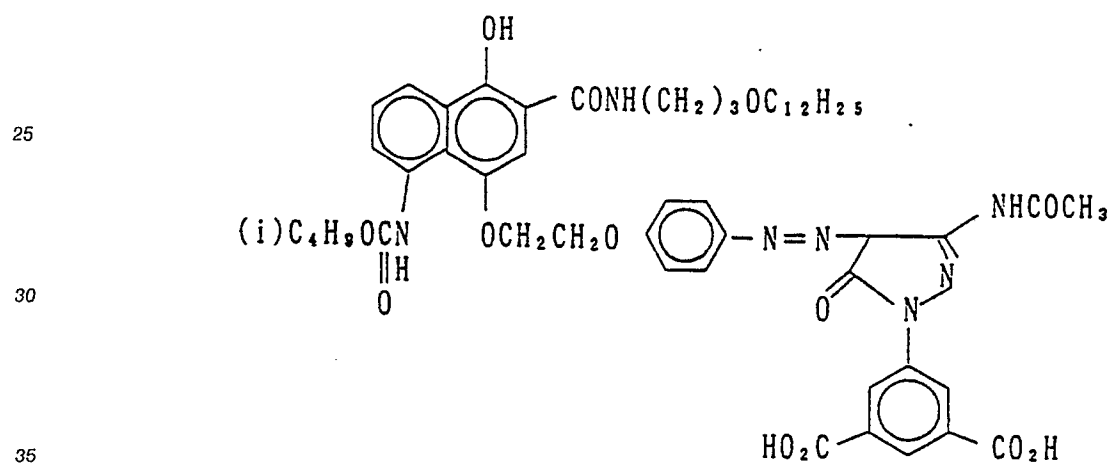
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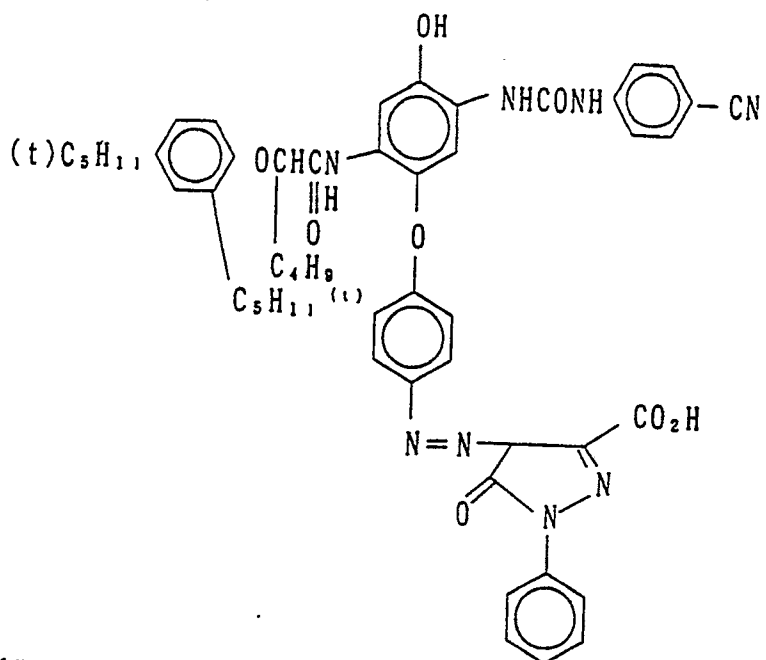
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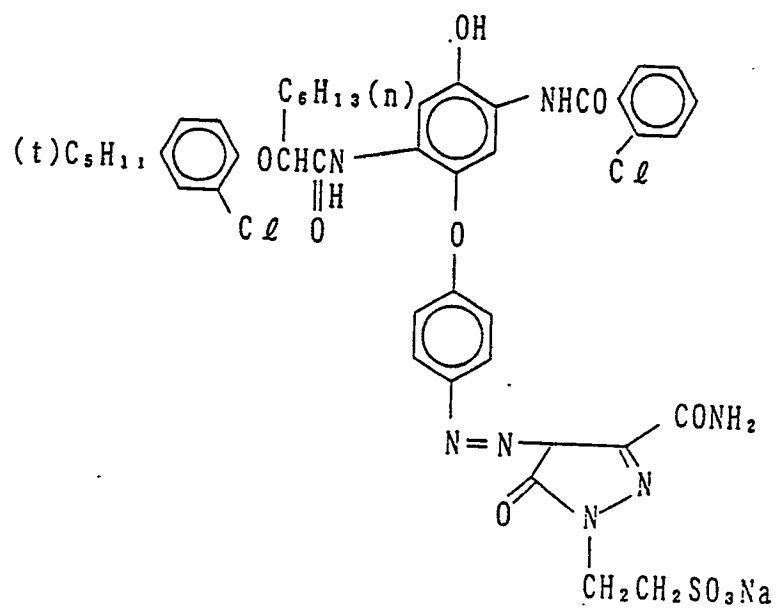
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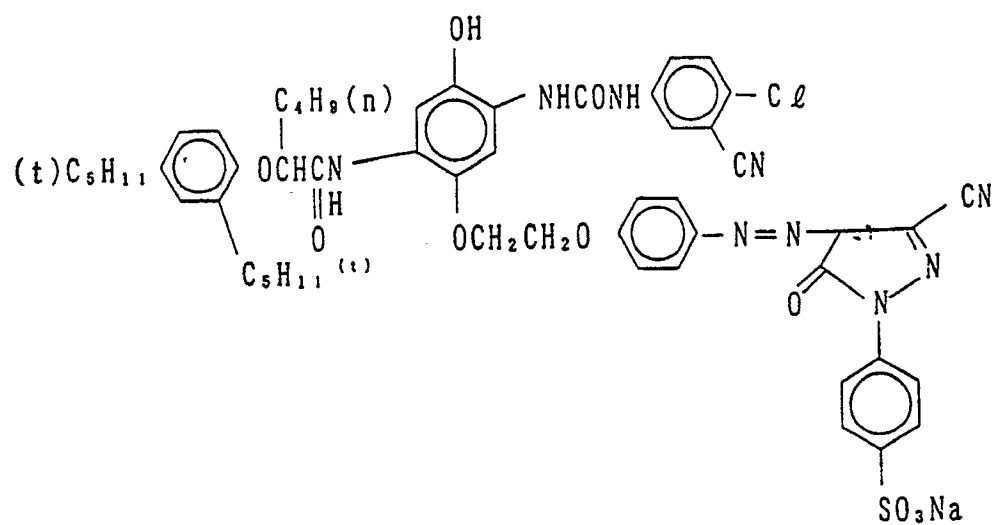
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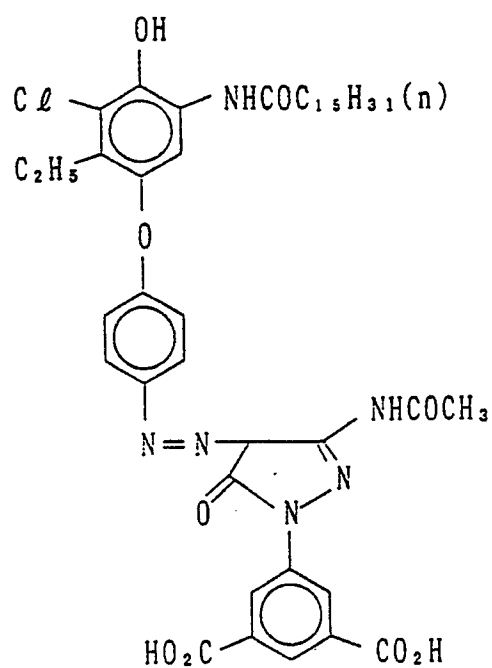
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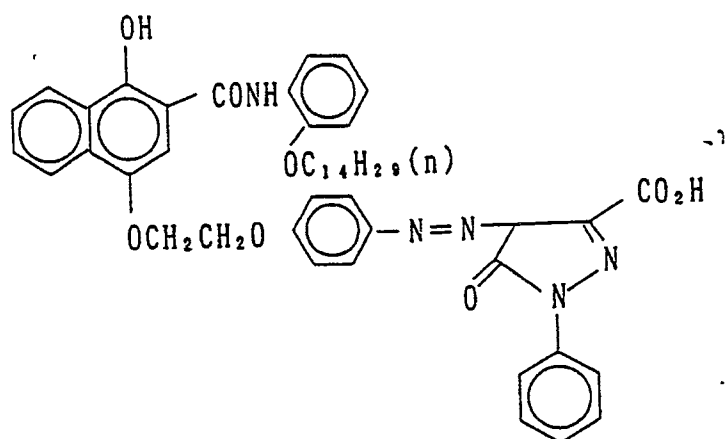


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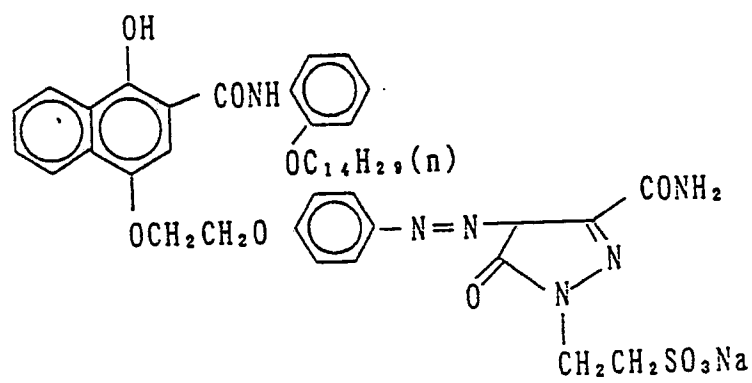


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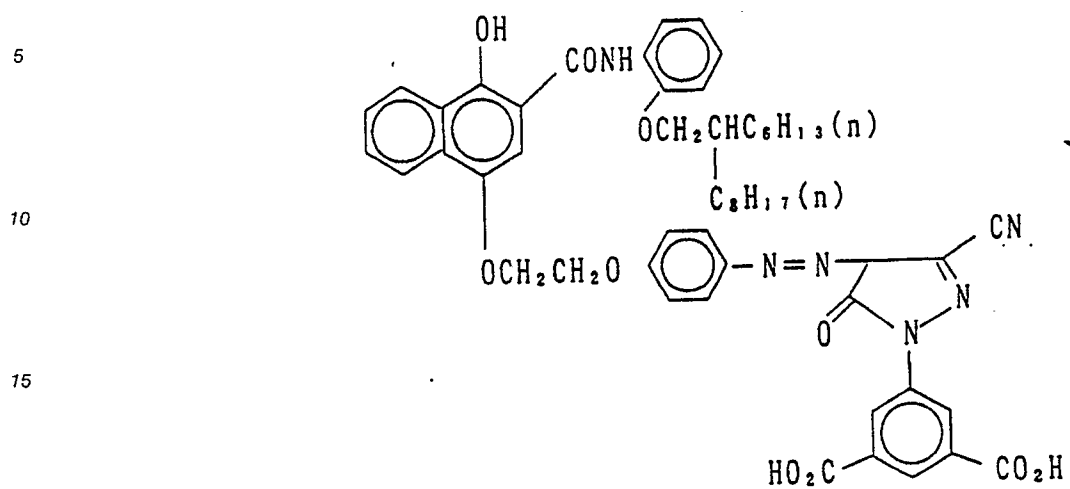




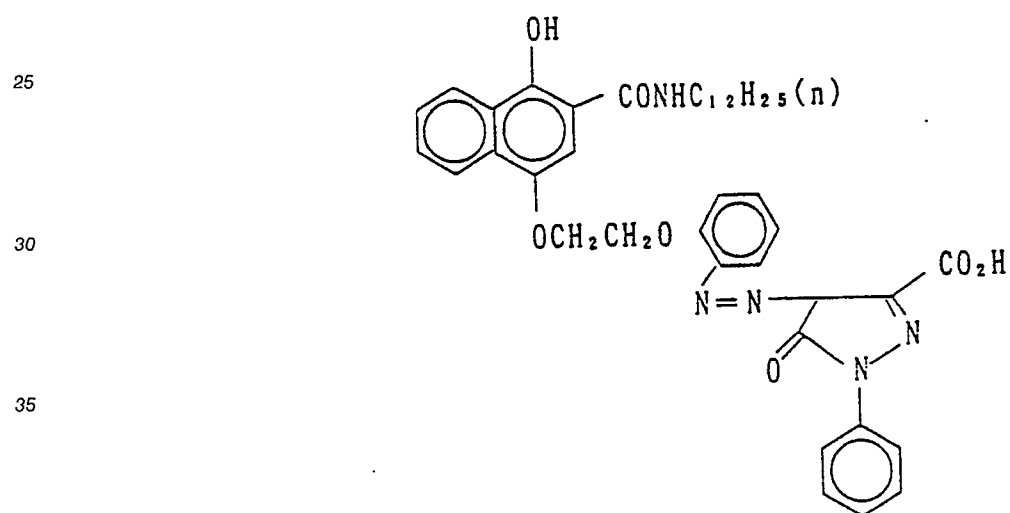
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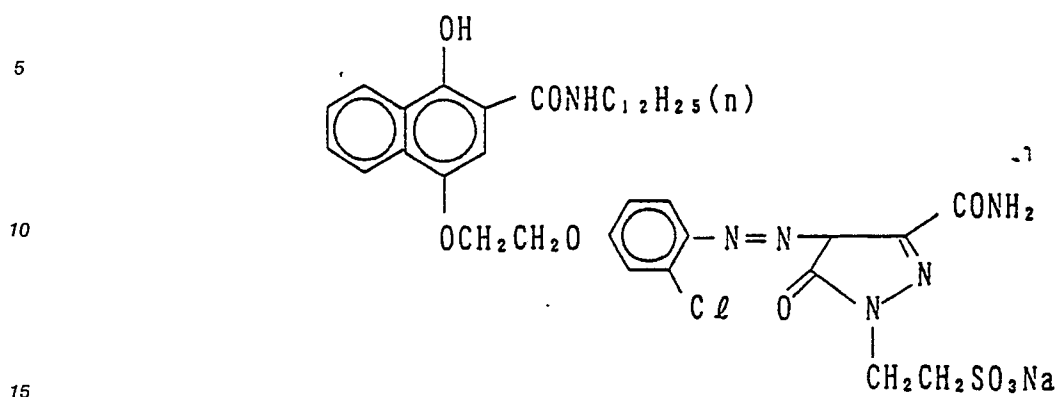
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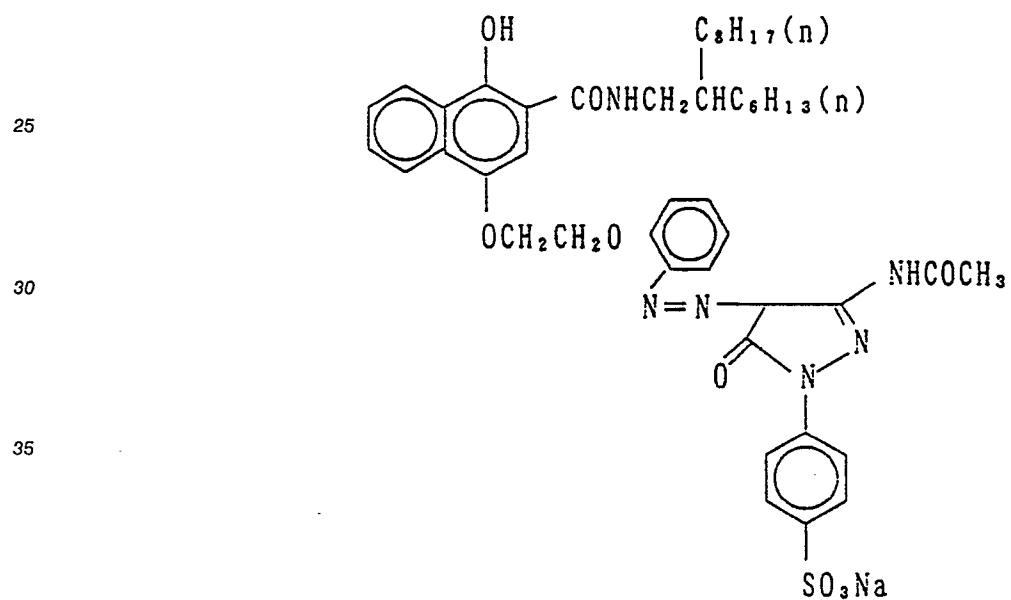
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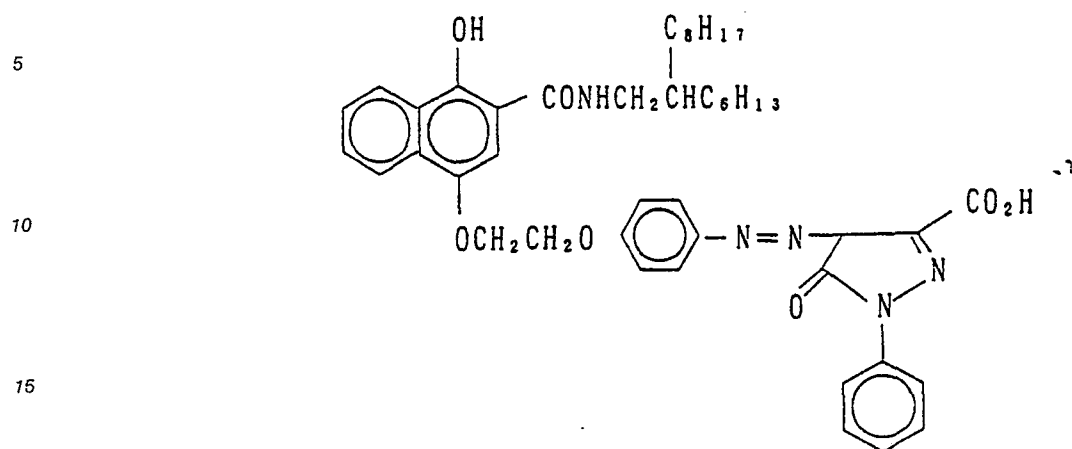
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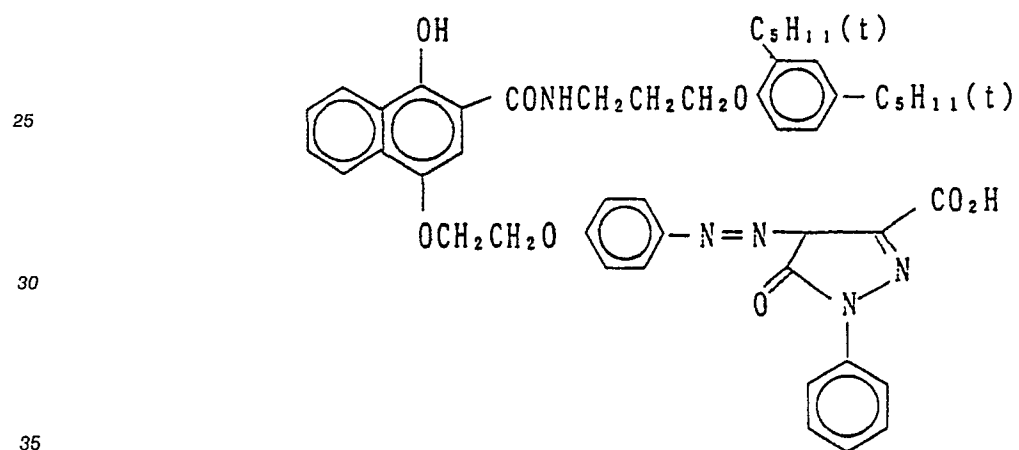
(Y C - 7 0)



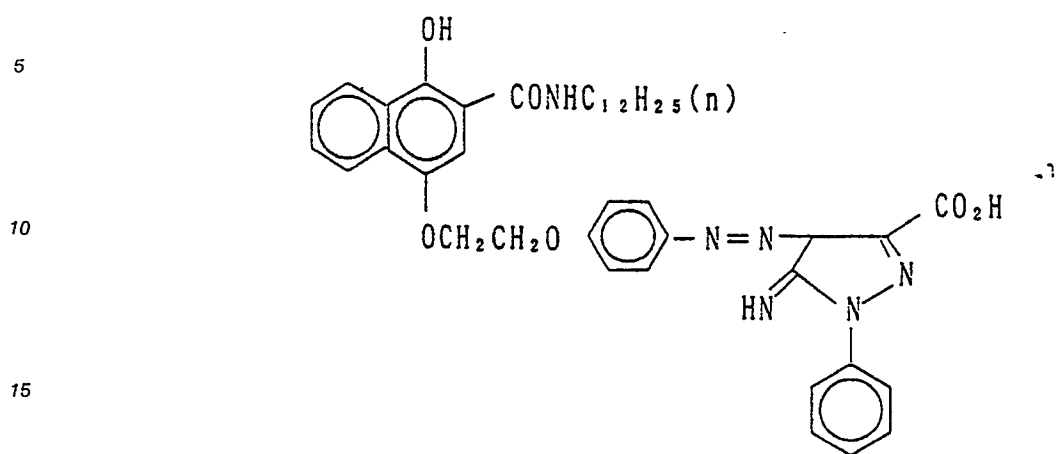
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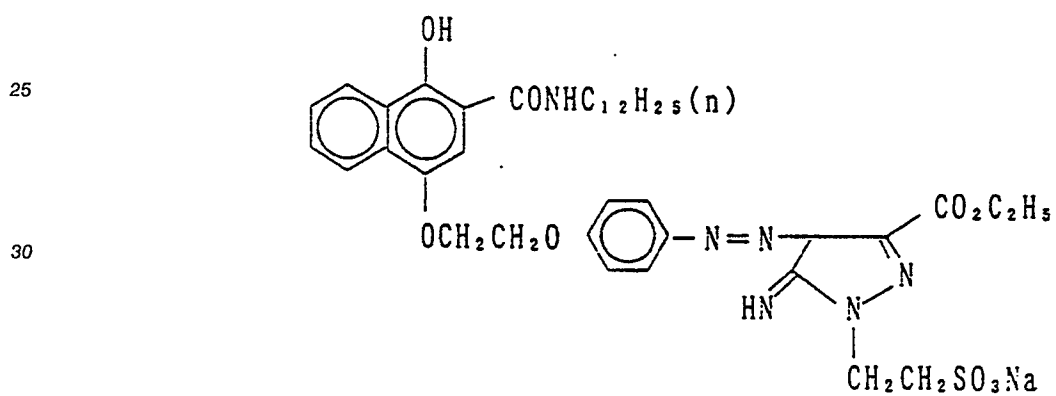
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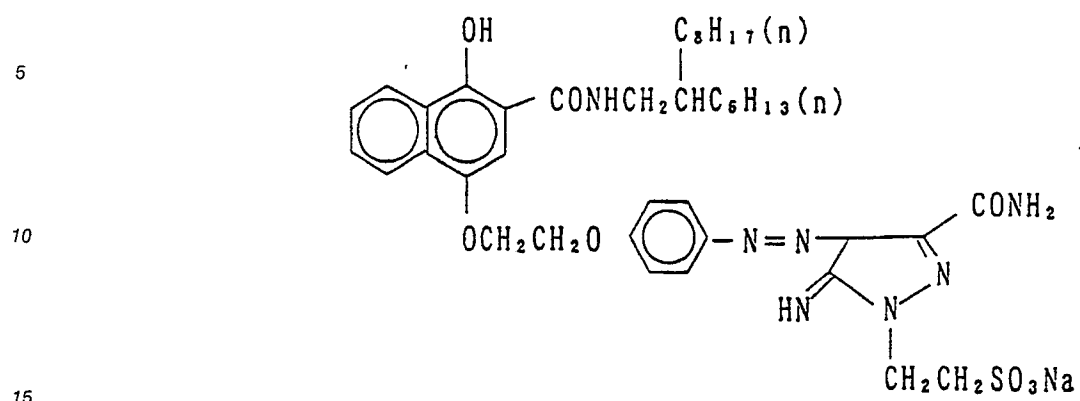
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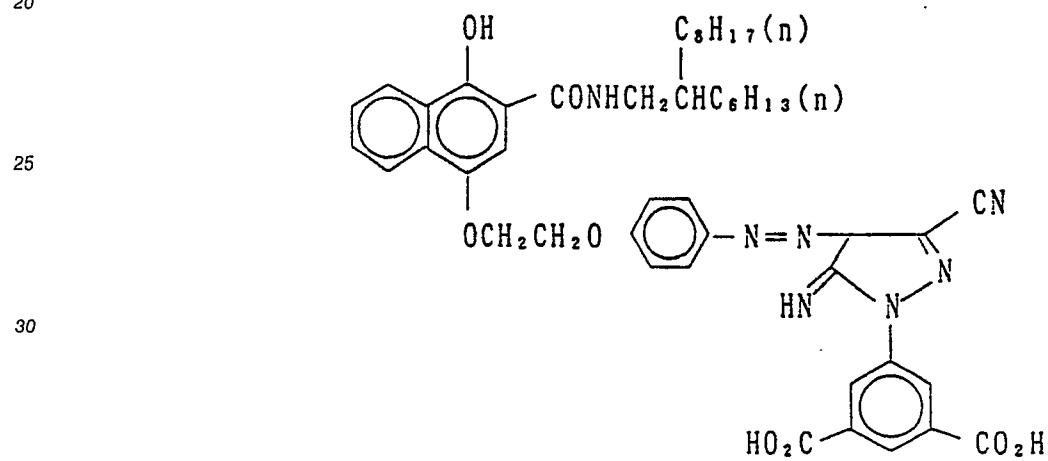
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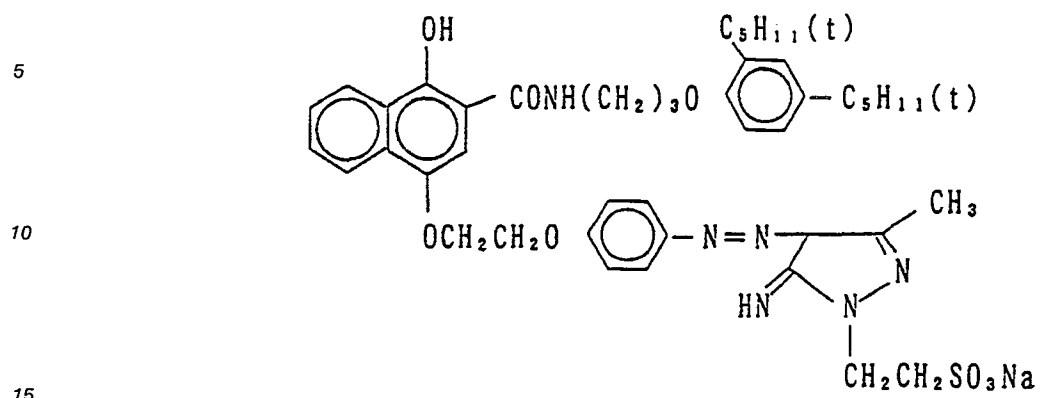
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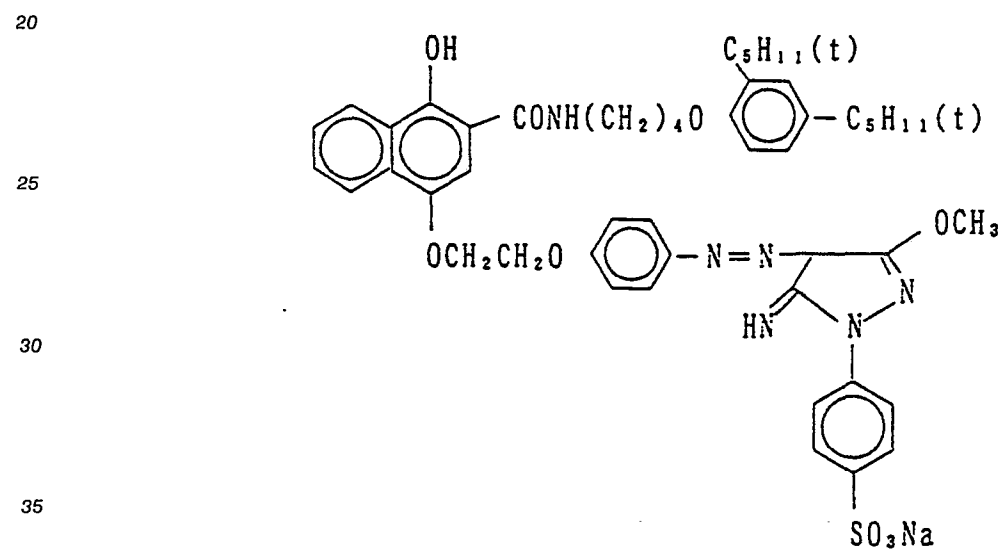
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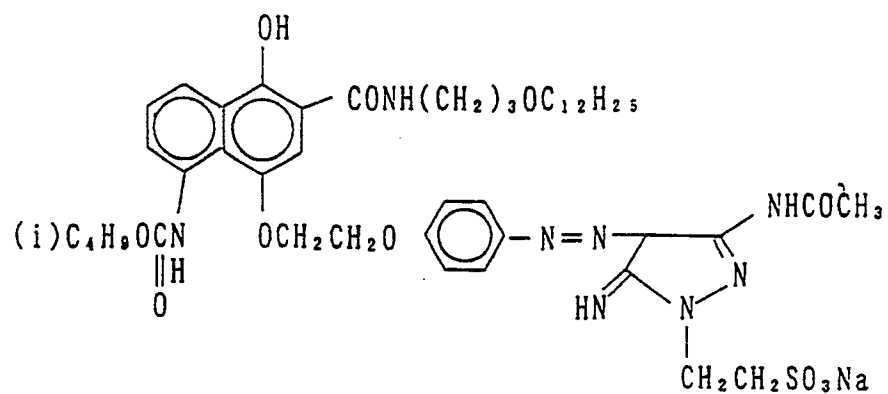
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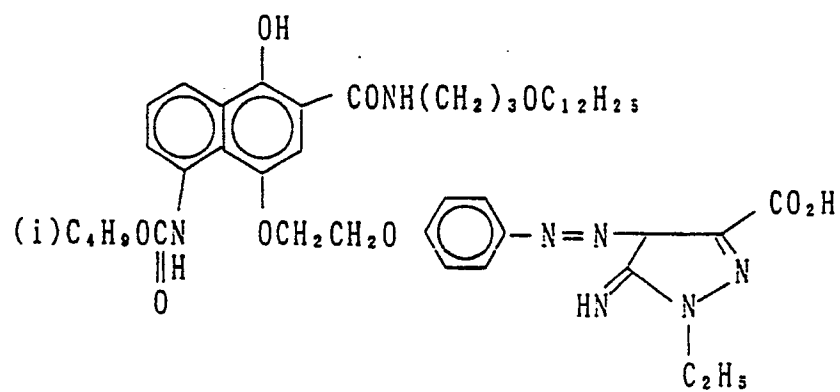
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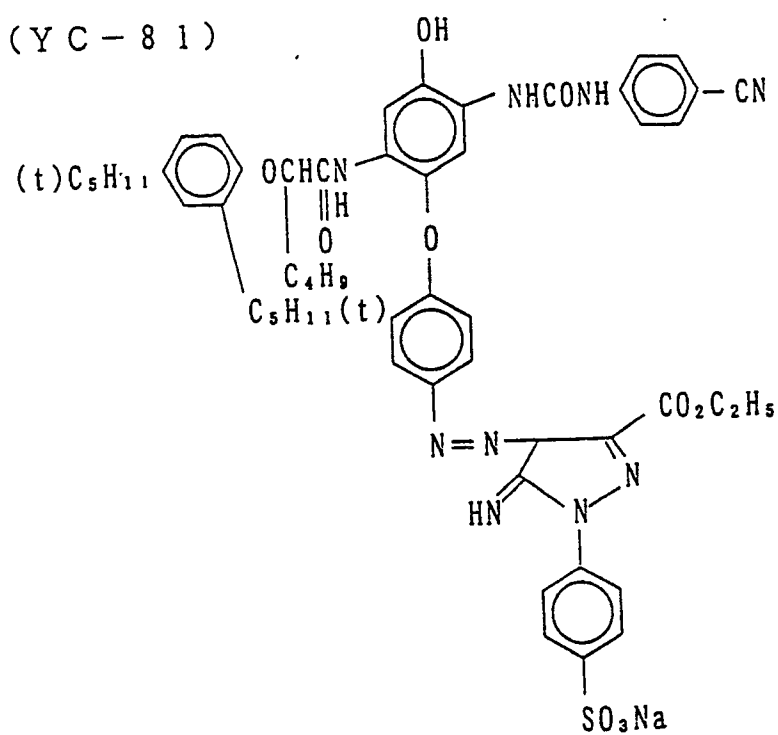
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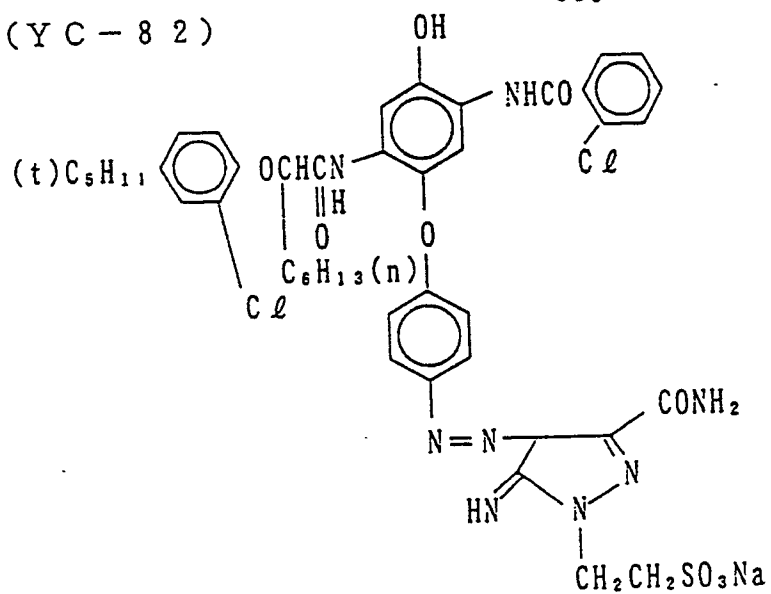
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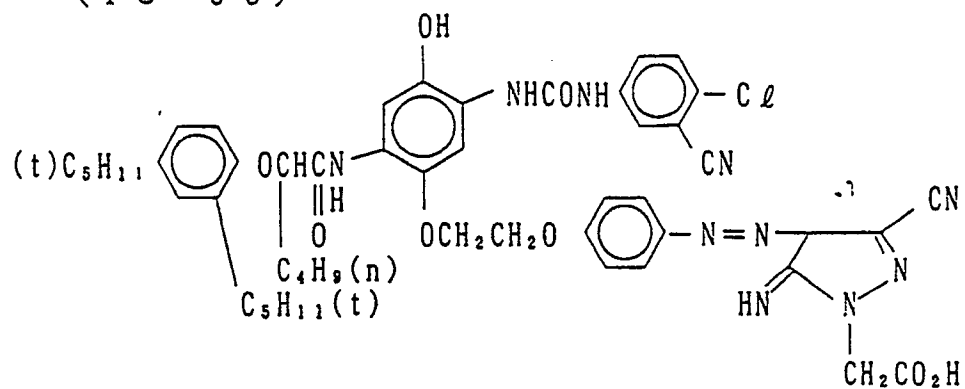
(Y C - 8 1)



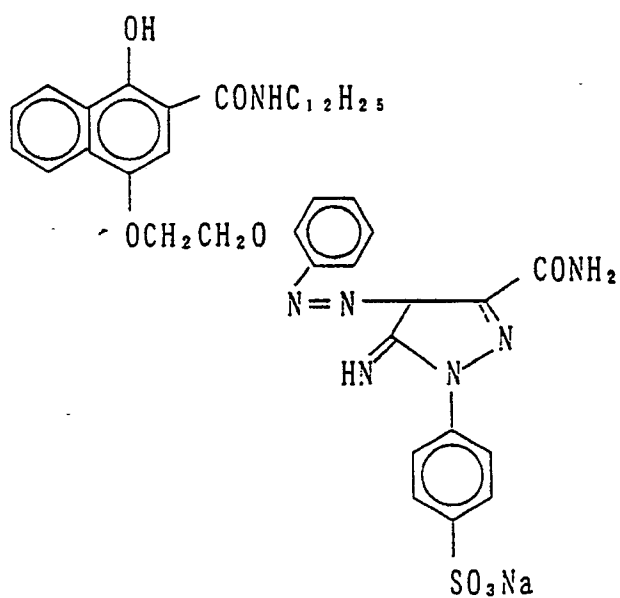
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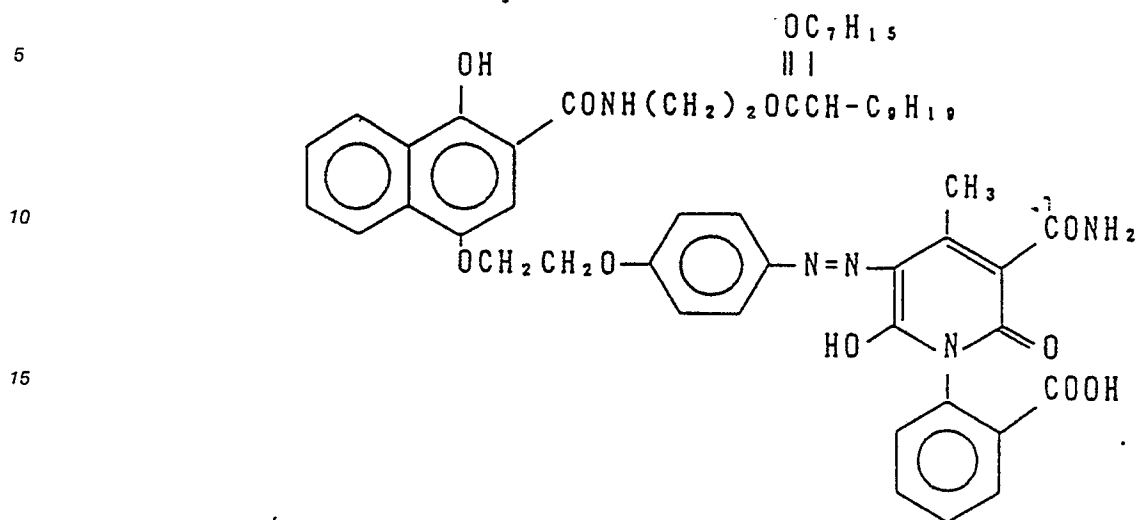
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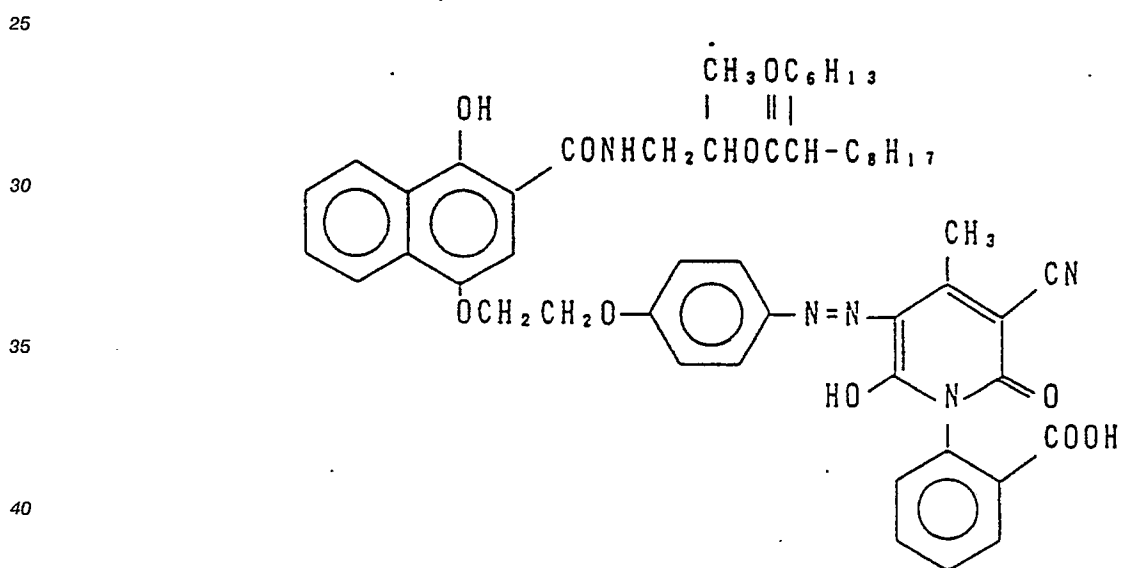
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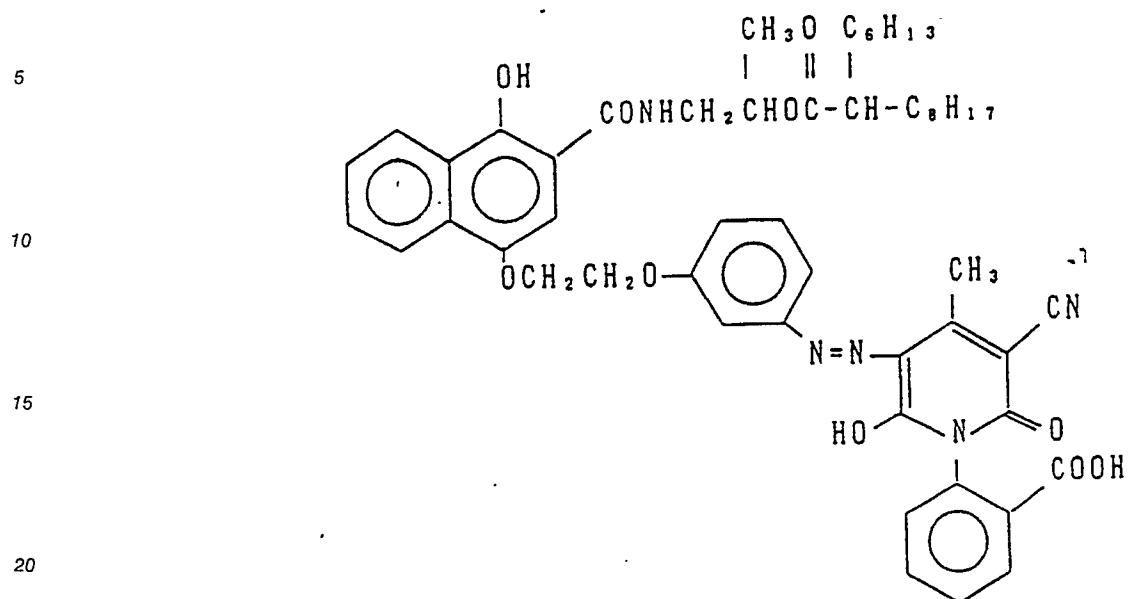
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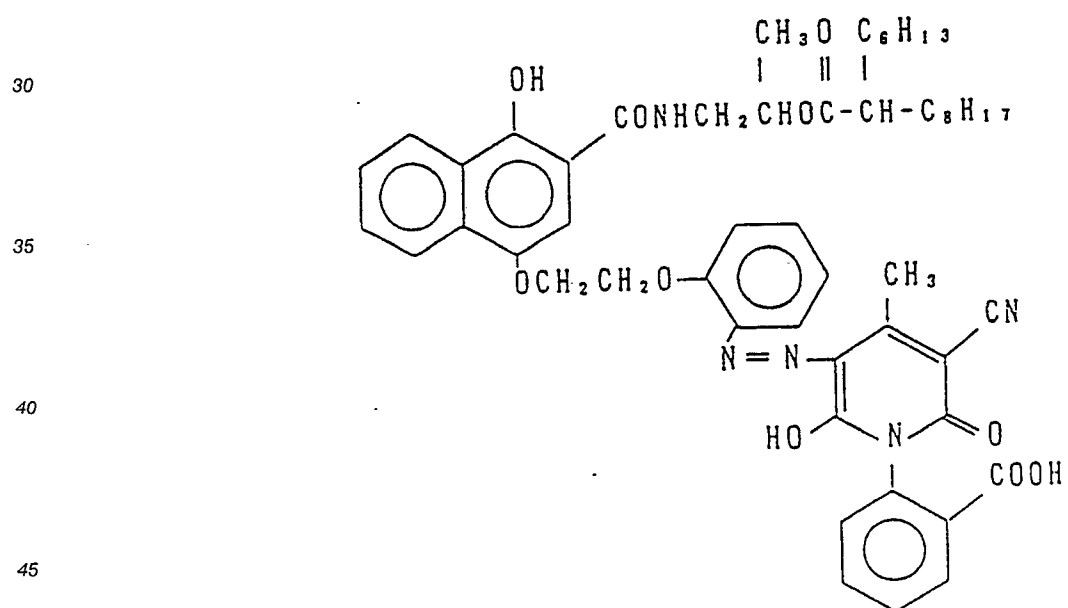
(Y C - 8 6)



(Y C - 8 7).



(Y C - 8.8)



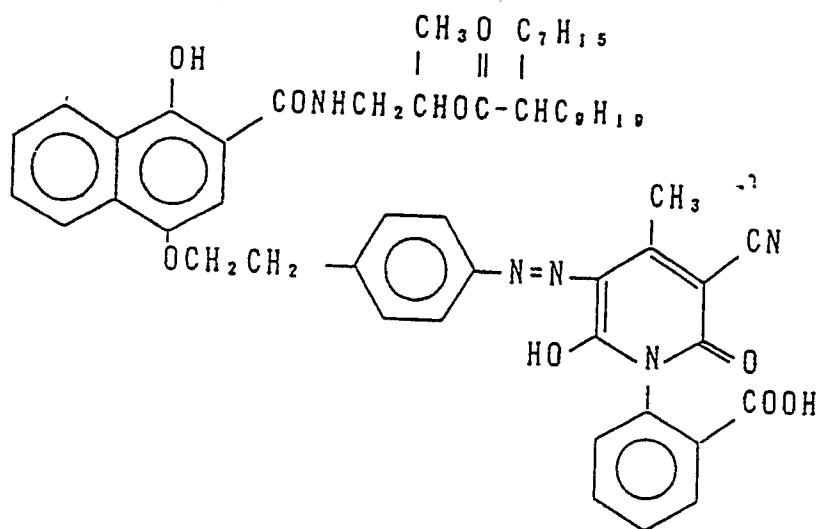
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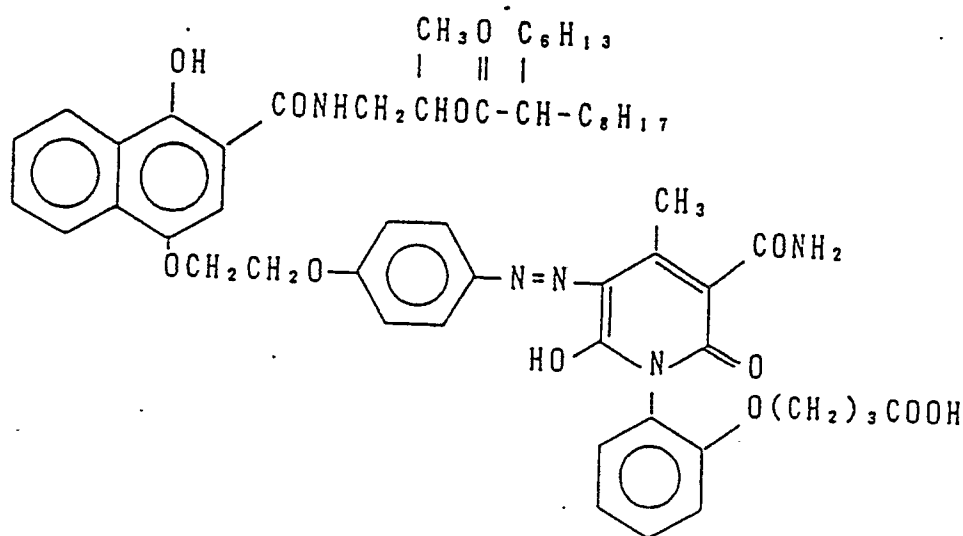
(Y C - 9 0)

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The colored couplers represented by formula (CI) of the present invention can be generally synthesized by the diazo coupling reaction of a 6-hydroxy-2-pyridone compound with an aromatic diazonium salt or heterocyclic diazonium salt having a coupler structure.

The former 6-hydroxy-2-pyridone compounds can be synthesized by methods described in Klinsberg, *Heterocyclic Compound - Pyridine and Its Derivatives*, Part 3 (Interscience 1962); J. Am. Chem. Soc., Vol. 65, page 449 (1943); J. Chem. Tech. Biotechnol., Vol. 36, page 410 (1986); Tetrahedron, Vol. 22, page 445 (1966); JP-B-61-52827 (the term "JP-B" as used herein means an "examined Japanese patent publication"); West German Patents 2,162,612, 2,349,709 and 2,902,486; and U.S. Patent 3,763,170.

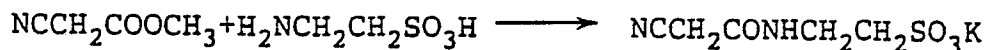
The latter diazonium salts can be synthesized according to the methods described in U.S. Patents 4,004,929 and 4,138,258, JP-A-61-72244 and JP-A-61-273543. The diazo coupling reaction of the 6-hydroxy-2-pyridone compounds with the diazonium salts can be carried out in a solvent such as methanol, ethanol, methyl cellosolve, acetic acid, N,N-dimethylformamide, N,N-dimethylacetamide, tetrahydrofuran, dioxane, water or the like or a mixture thereof. In this reaction, sodium acetate, potassium acetate, sodium

carbonate, potassium carbonate, sodium hydrogencarbonate, sodium hydroxide, potassium hydroxide, pyridine, triethylamine, tetramethylurea, or tetramethyl guanidine can be used as a base. The reaction temperature is generally from -78 to +60 °C, preferably from -20 to +30 °C.

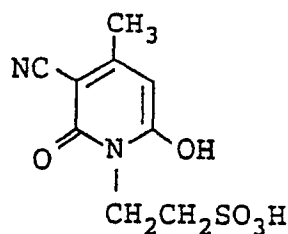
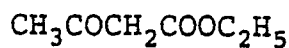
Synthesis examples of the colored couplers of the present invention are described below.

Synthesis Example 1

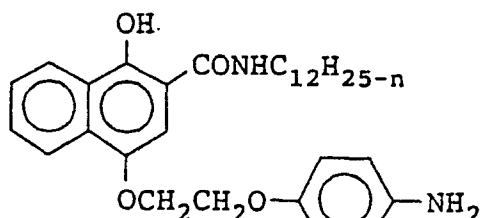
Synthesis of Coupler (YC-1)



a



b



c



Synthesis of Compound a

125.2 g of taurine and 66 g of potassium hydroxide were added to 500 ml of methanol. The mixture was stirred with heat-refluxing. 110 g of methyl cyanoacetate was added dropwise thereto over a period of about one hour. The mixture was heated to reflux for 5 hours and then left to stand overnight. The precipitated crystal was recovered by filtration, washed with ethanol and dried to give 202.6 g of the compound a as a crystal.

Synthesis of Compound b

11.5 g of the compound a and 3.5 g of potassium carbonate were added to 11.5 ml of water. While heating the mixture on a steam bath with stirring, 7.8 g of ethyl acetoacetate was added dropwise thereto. The mixture was stirred for 7 hours and then allowed to cool. 9.2 ml of concentrated hydrochloric acid was added thereto, whereby a crystal was precipitated. The crystal was recovered by filtration, washed with methanol and dried to give 10.4 g of the compound b as a crystal.

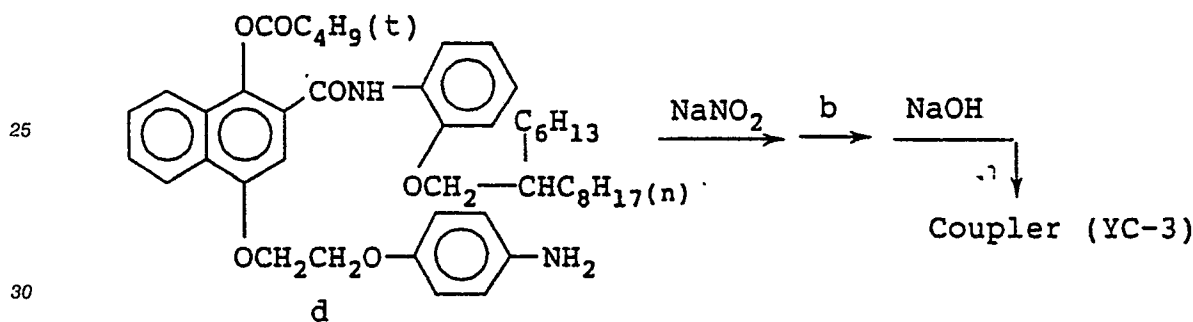
Synthesis of Coupler (YC-1)

10.1 g of compound c synthesized by the method described in U.S. Patent 4,138,258 was dissolved in 60 ml of N,N-dimethylformamide and 60 ml of methyl cellosolve. While cooling the resulting solution with ice, 4.3 ml of concentrated hydrochloric acid was added thereto and a solution of 1.84 g of sodium nitrite in 5 ml of water was added dropwise thereto to prepare a diazonium solution. 60 ml of methyl cellosolve and 20 ml of water were added to 7.8 g of the compound b and 8.2 g of sodium acetate. While stirring the resulting solution under ice cooling, the above diazonium solution was added dropwise thereto. After dropwise addition, the mixture was stirred for one hour and then at room temperature for 2 hours. The precipitated crystal was recovered by filtration, washed with water, dried and dispersed in 500 ml of methanol. The dispersion was heated to reflux for one hour and then allowed to stand to cool it. The crystal was recovered by filtration, washed with methanol and dried to give 13.6 g of the desired coupler (YC-1) as a red crystal with a melting point of 269 to 272 °C (decomposition). The structure of the compound was confirmed by ¹HNMR spectrum, mass spectrum and elemental analysis. The compound exhibited a maximum absorption wavelength in methanol at 457.7 nm and had an molecular extinction coefficient of 41300. The compound was found to have good spectral absorption characteristics as a yellow colored coupler.

Synthesis Example 2

Synthesis of Coupler (YC-3)

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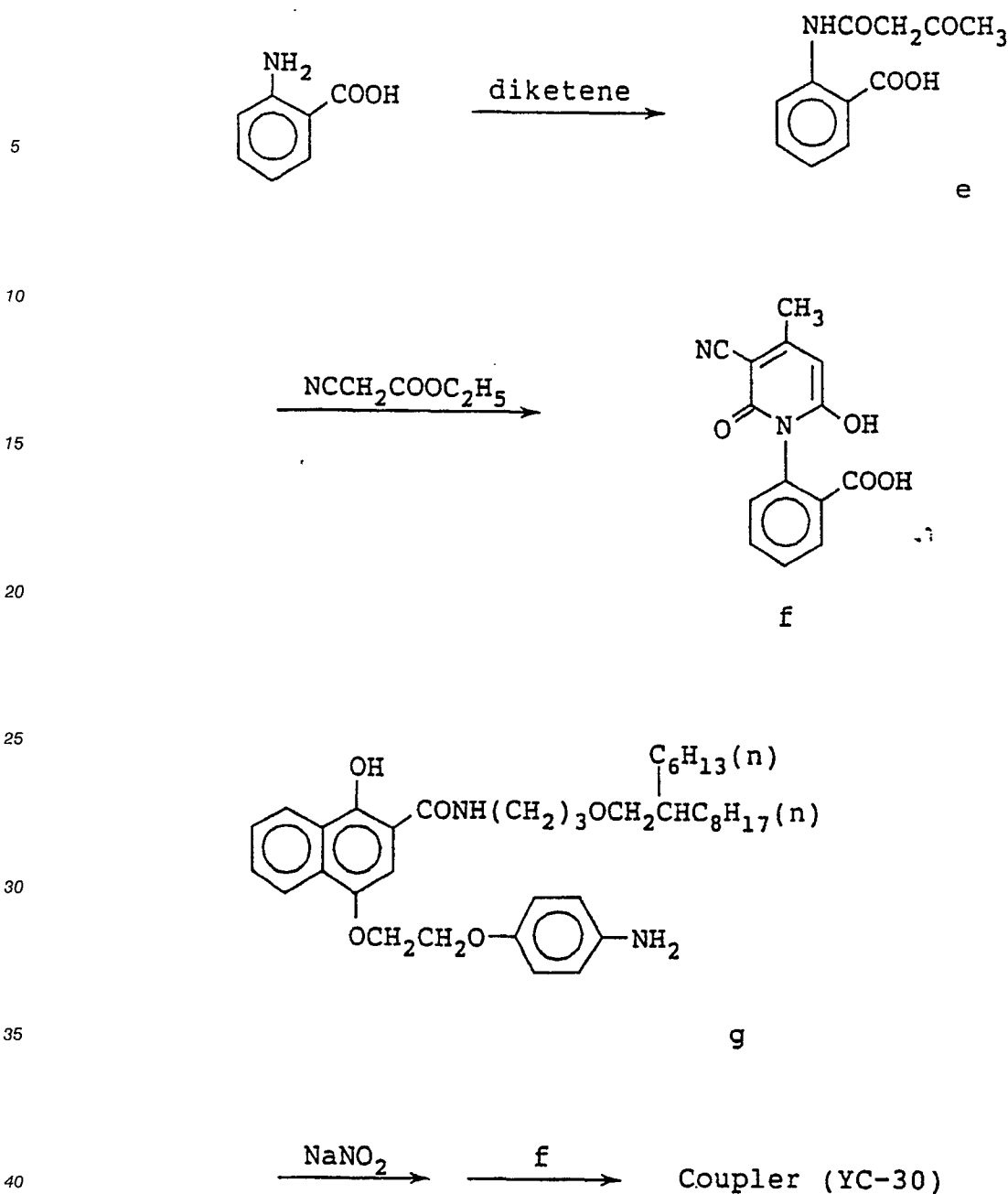


75 ml of N,N-dimethylformamide and 75 ml of methyl cellosolve were added to 19.2 g of compound d synthesized by the method described in JP-A-62-85242 (U.S. Patent 4,837,136) to dissolve it. While stirring the resulting solution under ice cooling, 5.6 ml of concentrated hydrochloric acid was added thereto and a solution of 2.5 g of sodium nitrite in 5 ml of water was then added dropwise thereto. After dropwise addition, the mixture was stirred for one hour and then at room temperature for one hour to prepare a diazonium solution.

75 ml of methyl cellosolve and 26 ml of water were added to 10.1 g of the compound b and 10.7 g of sodium acetate. While stirring the resulting solution under ice cooling, the above diazonium solution was added dropwise thereto. After dropwise addition, the mixture was stirred for one hour and then at room temperature for 2 hours. The precipitated crystal was recovered by filtration and dispersed in 200 ml of methanol. A solution of 2.2 g of sodium hydroxide in 10 ml of water was added dropwise thereto. The mixture was stirred for 3 hours and neutralized with concentrated hydrochloric acid. The precipitated crystal was washed with water and then methanol and dried. The resulting crude crystal was purified from hot methanol in the same manner as in Synthesis Example 1 to give 14.8 g of the desired coupler (YC-3) with a melting point of 246 to 251 °C (decomposition). The structure of the compound was confirmed by ¹HNMR spectrum, mass spectrum and elemental analysis. The compound exhibited a maximum absorption wavelength in methanol at 457.6 nm and had a molecular extinction coefficient of 42700. The compound was found to have good spectral absorption characteristics as a yellow colored coupler.

Synthesis Example 3

Synthesis of Coupler (YC-30)



Synthesis of Compound e

137.1 g of anthranilic acid was added to 600 ml of acetonitrile. The mixture was heat-refluxed with stirring. 92.5 g of diketene was added dropwise thereto over a period of about one hour. The mixture was heated to reflux for one hour and cooled to room temperature. The precipitated crystal was recovered by filtration, washed with acetonitrile and dried to obtain 200.5 g of the compound e as a crystal.

Synthesis of Compound f

199.1 g of the compound e, 89.2 g of ethyl cyanoacetate and 344 g of 28% sodium methoxide were added to 0.9 l of methanol. The mixture was reacted at 120°C in an autoclave for 8 hours. After the reaction mixture was left to stand overnight, the reaction mixture was concentrated under reduced pressure. 700 ml of water was added thereto and the mixture was acidified with 230 ml of concentrated hydrochloric acid. The precipitated crystal was recovered by filtration. The resulting crude crystal was washed with a mixed solvent of ethyl acetate and acetonitrile with heating to give 152 g of the compound f.

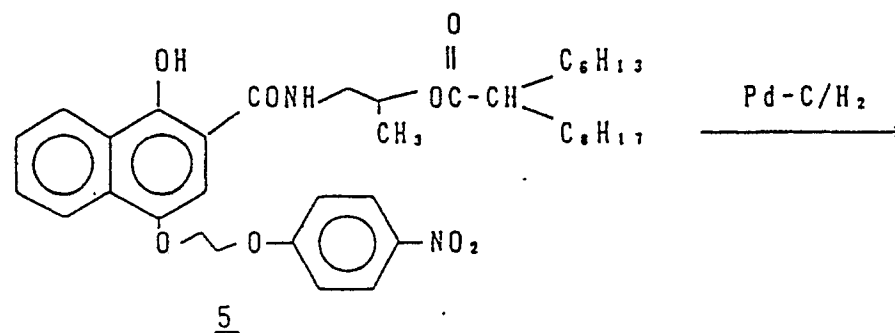
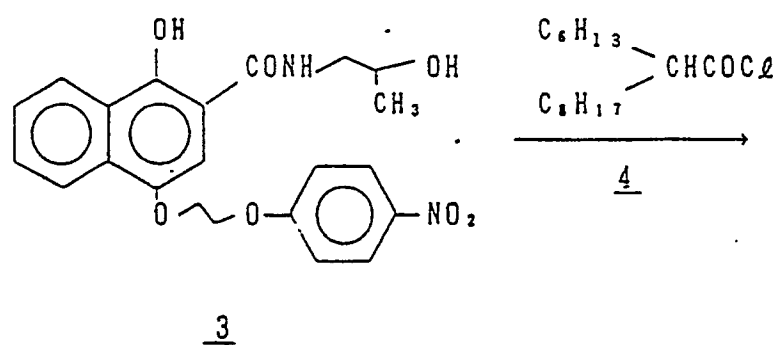
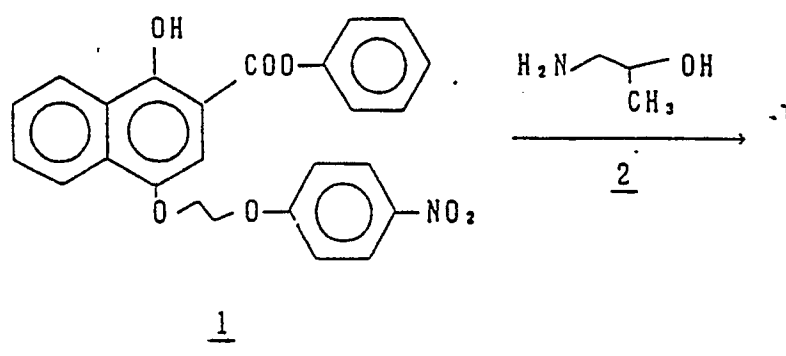
Synthesis of Coupler (YC-30)

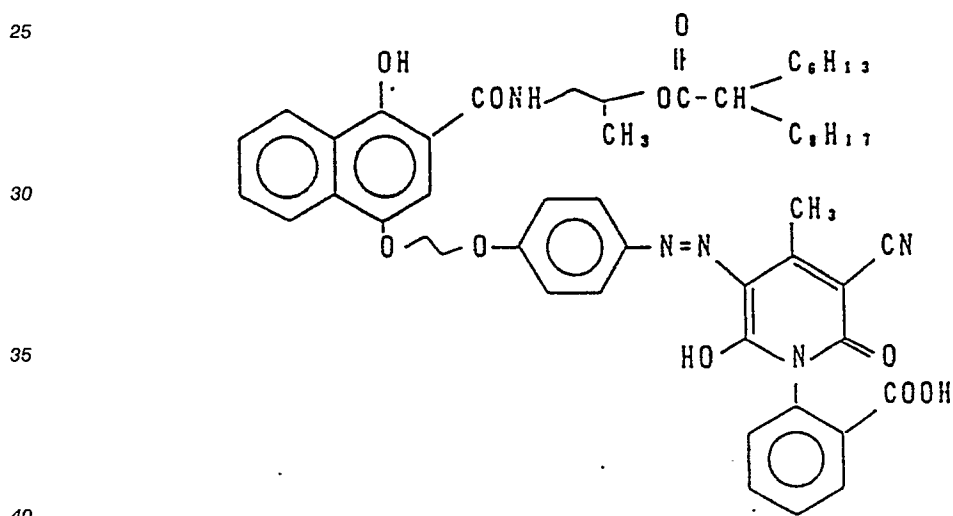
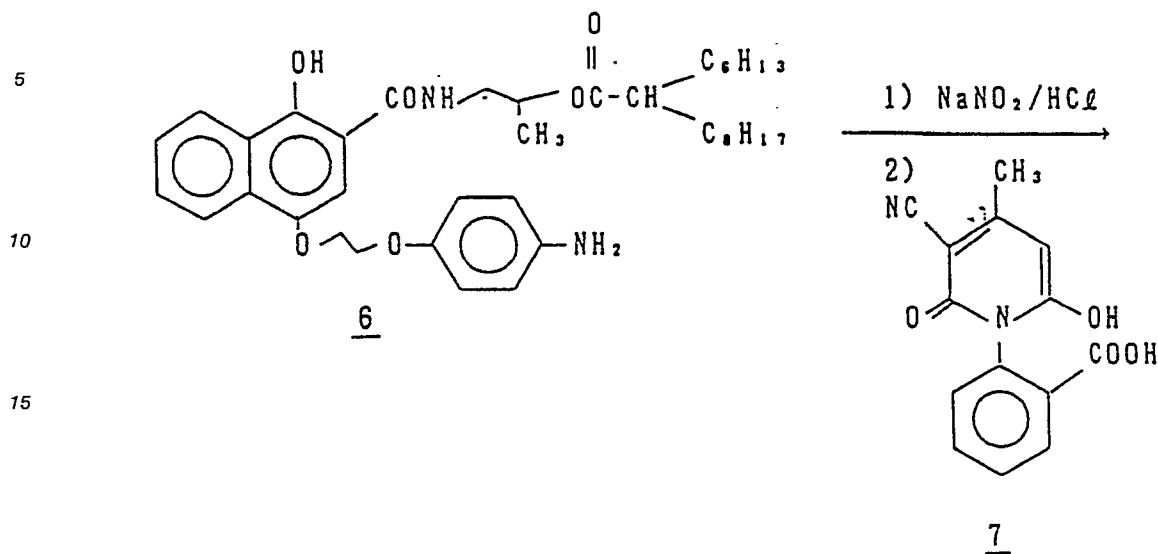
13.0 g of compound g synthesized according to the method described in U.S. Patent 4,138,258 was dissolved in 40 ml of N,N-dimethylformamide. While cooling the resulting solution with ice, 4.5 ml of concentrated hydrochloric acid was added thereto and a solution of 1.48 g of sodium nitrite in 5 ml of water was added dropwise thereto to prepare a diazonium solution. 20 ml of N,N-dimethylformamide and 15 ml of water were added to 6.0 g of compound f and 8 g of sodium acetate. While stirring the mixture under ice cooling, the above diazonium solution was added dropwise thereto. After the addition, the mixture was stirred at room temperature for 30 minutes and acidified with hydrochloric acid. The product was extracted with ethyl acetate, washed with water and concentrated under reduced pressure. The concentrate was crystallized from a mixed solvent of ethyl acetate and methanol to give 13 g of the coupler (YC-30) as a yellow crystal.

The coupler (YC-30) had a melting point of 154-6 °C. The structure thereof was confirmed by ¹HNMR spectrum, mass spectrum and elemental analysis. The compound exhibited a maximum absorption wavelength in methanol at 458.2 nm and had a molecular extinction coefficient of 42800. The compound was found to have good spectral absorption characteristics as a yellow colored coupler.

Synthesis Example 4

Synthesis Coupler (YC-86)





Coupler (YC-86)

(1) Synthesis of Compound 3

445.5 g of phenyl ether compound 1 and 90.1 g of isopropanol amine 2 were added to 600 ml of acetonitrile and the mixture was heated to reflux for 2 hours. After allowing to cool with water, crystals precipitated were recovered by filtration. The crystals were dried to give 342 g of compound 3 having a melting point of 162-5° C.

(2) Synthesis of Compound 5

341 g of hydroxyl compound 3 and 231 g of 2-hexyldecanoyl chloride were added to 880 ml of acetonitrile. The mixture was heated to reflux for 2 hours. After allowing to cool with ice, crystals precipitated were recovered by filtration. The crystals were dried to give 437 g of compound 5 having a melting point of 97-100° C.

(3) Synthesis of Compound 6

370 g of nitro compound 5, 6 g of a 10% Pb-C catalyst and 1 l of ethylacetate were placed in an autoclave and hydrogenation was conducted at 50 °C for 3 hours. After completion of reduction reaction, the catalyst was removed by filtration and the filtrate was concentrated under reduced pressure. The residue obtained was crystallized with n-hexane. The precipitated crystals were recovered by filtration and were dried to give 327 g of amine compound 7 having a melting point of 95-7 °C.

(4) Synthesis of coupler (YC-86)

20 g of amine compound 7 was dissolved in 60 l of dimethylformamide. While cooling the solution obtained with ice 7.6 ml of concentrated hydrochloric acid was added thereto. Furthermore, a solution of 2.7 g of sodium nitrite in 10 ml of water was added dropwise thereto over a period of 20 minutes and the solution was further stirred for 30 minutes to give a diazo solution.

9.7 g of pyridone 7 and 13 g of sodium acetate were added to a mixture of 30 ml of water and 30 ml of dimethylformamide and dissolved. After cooling the solution obtained with water, the diazo solution was added thereto gradually with stirring at a temperature of not higher than 10 °C. After further stirring for 15 minutes, the product was extracted with ethylacetate, washed with water 3 times and the organic layer was concentrated under reduced pressure. The residue was crystallized with a methanol-ethylacetate mixture, precipitated crystals were recovered by filtration and dried to give 21.2 g of coupler (YC-86) having a melting point of 117 to 119 °C.

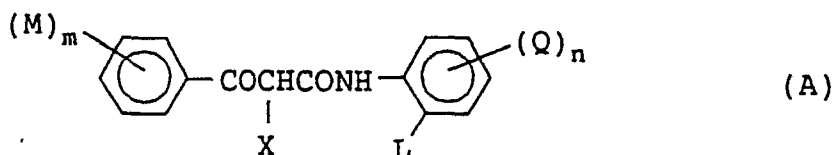
The yellow colored cyan couplers represented by formulas (CII) to (CIV) can be synthesized by methods described in JP-B-58-6939 (the term "JP-B" as used herein means an "examined published Japanese patent publication") and JP-A-1-197563. The couplers represented by general formula (CI) can be synthesized by the methods described in patent specifications cited above.

Among the yellow colored cyan couplers of the present invention, the couplers represented by formulas (CI) and (CII) are more preferred, and the couplers of formula (CI) are particularly preferred.

It is preferred that the yellow colored cyan couplers of the present invention be added to sensitive silver halide emulsion layers or adjoining layers in the photographic materials. It is particularly preferred that the yellow colored cyan couplers be added to the red-sensitive emulsion layer. The total amount of the couplers to be added to the photographic material is 0.005 to 0.30 g/m², preferably 0.02 to 0.20 g/m², more preferably 0.03 to 0.15 g/m².

The yellow colored couplers of the present invention can be added in the same manner as in the addition of conventional couplers described hereinafter.

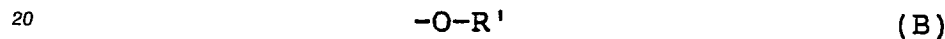
It is particularly preferred that benzoylacetyl type yellow couplers represented by the following general formula (A) be used in the silver halide color photographic materials of the present invention. The yellow couplers represented by formula (A) have high ϵ (molecular extinction coefficient) values so that the thickness of the photographic layers can be reduced. As a result, not only sharpness is improved, but also color reproducibility is improved, because the interlaminar effect is enhanced. Further, the yellow colored cyan couplers represented by formulas (CI) to (CIV) according to the present invention and the developed dyes of these yellow couplers are similar in terms of the spectral absorption wave forms. Accordingly, printability in various auto-printers using color filters having various spectral characteristics, various light sources and various density sensors manufactured by various companies is good (because stability can be kept even when photographing conditions and exposure amount are varied).



In formula (A), M and Q each represents a group or an atom which can be attached to the benzene ring; L represents a hydrogen atom, a halogen atom or an aliphatic oxy group; m represents an integer of 0 to 5; n represents an integer of 0 to 4; X represents a group which can be eliminated by a coupling reaction with an oxidation product of an aromatic primary amine developing agent; when m is 2 or greater, the two or more M groups may be the same or different groups; when n is 2 or greater, the two or more Q groups may be the same or different groups; and M, Q, L or X may be a single bond, or a bivalent to tetravalent

bonding group forming a bis-, tris- or tetrakis compound having 2 to 4 moieties of the yellow coupler represented by formula (A).

Examples of M and Q include a halogen atom (e.g., fluorine, chlorine, bromine), an aliphatic group having 1 to 20 carbon atoms, an aromatic group having 6 to 20 carbon atoms, an aliphatic oxy group having 1 to 20 carbon atoms, an aromatic oxy group having 6 to 20 carbon atoms, a carbonamide group having 2 to 24 carbon atoms, a sulfonamide group having 0 to 20 carbon atoms, a carbamoyl group having 1 to 24 carbon atoms, a sulfamoyl group having 0 to 20 carbon atoms, an acyloxy group having 2 to 20 carbon atoms, an aliphatic oxycarbonyl group having 2 to 20 carbon atoms, a substituted amino group having 2 to 24 carbon atoms, an aliphatic thio group having 1 to 24 carbon atoms, a ureido group having 0 to 20 carbon atoms, a sulfamoylamino group having 0 to 20 carbon atoms, a cyano group, an aliphatic oxycarbonylamino group having 2 to 20 carbon atoms, an imido group having 4 to 20 carbon atoms, an aliphatic sulfonyl group having 1 to 20 carbon atoms, an aromatic sulfonyl group having 6 to 20 carbon atoms and a heterocyclic group having 1 to 20 carbon atoms. These groups may be further substituted. L is a hydrogen atom, a halogen atom (fluorine, chlorine, bromine) or an aliphatic oxy group having 1 to 24 carbon atoms, which may be substituted. X is a group which is eliminated by a coupling reaction with an oxidation product of an aromatic primary amine developing agent. More specifically, X is a group represented by the following general formula (B), (C) or (D).

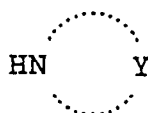


In formula (B), R' is an aromatic group having 2 to 30 carbon atoms, a heterocyclic group having 1 to 28 carbon atoms, an acyl group having 2 to 28 carbon atoms, an aliphatic sulfonyl group having 1 to 24 carbon atoms or an aromatic sulfonyl group having 6 to 24 carbon atoms.

In formula (C), R'' is an aliphatic group having 1 to 30 carbon atoms, an aromatic group having 6 to 30 carbon atoms or a heterocyclic group having 1 to 28 carbon atoms.

In formula (D), Y is a non-metallic atomic group required for forming a monocyclic or condensed ring 5-membered to 7-membered heterocyclic ring together with N. Examples of the heterocyclic ring formed by Y together with N include pyrrole, pyrazole, imidazole, 1,2,4-triazole, tetrazole, indole, indazole, benzimidazole, benztriazole, tetraazaindene, succinimide, phthalimide, saccharin, oxazolidine-2,4-dione, imidazolidine-2,4-dione, thiazolidine-2,4-dione, urazol, parabanic acid, maleinimide, 2-pyridone, 4-pyridone, 6-pyridazone, 6-pyrimidone, 2-pyrazolone, 1,3,5-triazine-2-one, 1,2,4-triazine-6-one, 1,3,4-triazine-6-one, 2-oxazolone, 2-thiazolone, 2-imidazolone, 3-isoxazolone, 5-tetrazolone and 1,2,4-triazo-5-one. These heterocyclic rings may be substituted. Examples of substituent groups include a halogen atom, a hydroxy group, a nitro group, a cyano group, a carboxyl group, an aliphatic group, an aromatic group, a heterocyclic group, an aliphatic oxy group, an aromatic oxy group, an aliphatic thio group, an aromatic thio group, an aliphatic oxycarbonyl group, a carbonamido group, a sulfonamido group, a carbamoyl group, a sulfamoyl group, a ureido group, a sulfamoylamino group, an aliphatic oxycarbonylamino group and a substituted amino group.

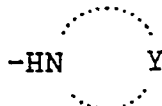
In formula (A) the aliphatic group includes straight chain, branched and cyclic alkyl, alkenyl and alkynyl groups. These groups may be substituted with, for example, an aryl group, a halogen atom, an alkoxy carbonyl group, an alkoxy group or an aryloxy group. Examples of the aliphatic group include methyl, ethyl, isopropyl, n-butyl, t-butyl, t-amyl, n-hexyl, cyclohexyl, n-octyl, 2-ethylhexyl, n-decyl, n-dodecyl, n-tetradecyl, n-hexadecyl, 2-hexyldecyl, n-octadecyl, allyl, benzyl, phenethyl, undecenyl, octadecenyl, trifluoromethyl, chloromethyl, cyanoethyl, 1-(ethoxycarbonyl)ethyl, methoxyethyl, butoxyethyl, 3-dodecyloxypropyl and phenoxyethyl. The heterocyclic group includes substituted or unsubstituted monocyclic or condensed ring heterocyclic rings. Examples of the heterocyclic group include 2-furyl, 2-thienyl, 2-pyridyl, 3-pyridyl, 4-pyridyl, 2-quinolyl, oxazole-2-yl, thiazole-2-yl, benzoxazole-2-yl, benzthiazole-2-yl, 1,3,4-thiadiazole-2-yl, 1,3,4-oxadiazole-2-yl and groups derived from the compounds of formula



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(wherein

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15 is the same as that in formula (D)).

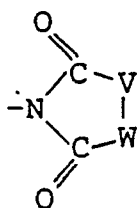
The aromatic group includes substituted or unsubstituted monocyclic or condensed ring aryl groups. Examples of substituents include an alkyl group, a halogen atom, and an alkoxy group. Examples of the aromatic group include phenyl, tolyl, 4-chlorophenyl, 4-methoxyphenyl, 1-naphthyl, 2-naphthyl and 4-t-butylphenoxyphenyl.

20 Preferred examples of the groups of the couplers of formula (A) which can be preferably used in the present invention will be illustrated below.

Preferably, M is an aliphatic group (e.g., methyl, ethyl, n-propyl, t-butyl), an aliphatic oxy group (e.g., methoxy, ethoxy, n-butoxy, n-dodecyloxy), a halogen atom (e.g., fluorine, chlorine, bromine), a carbonamido group (e.g., acetamido, n-butaneamido, n-tetradecaneamido, benzamido) or a sulfonamido group (e.g., methylsulfonamido, n-butylsulfonamido, n-octylsulfonamido, n-dodecylsulfonamido, toluenesulfonamido). 25 Preferably, L is a chlorine atom or an aliphatic oxy group (methoxy, ethoxy, methoxyethoxy, n-octyloxy, 2-ethylhexyloxy, n-tetradecyloxy).

Preferably, Q is, in addition to those groups described above as preferred examples for M, an aliphatic oxycarbonyl group (e.g., methoxycarbonyl, ethoxycarbonyl, n-butoxycarbonyl, n-hexyloxycarbonyl, 2-ethylhexyloxycarbonyl, 1-(ethoxycarbonyl)ethyloxycarbonyl, 3-dodecyloxypropyloxycarbonyl, n-decyloxycarbonyl, n-dodecyloxycarbonyl, phenethyloxycarbonyl) or a carbamoyl group (e.g., dimethylcarbamoyl, dibutylcarbamoyl, dihexylcarbamoyl, di-2-ethylhexylcarbamoyl, n-dodecylcarbamoyl). Preferably, m is an integer of 0 to 2 and n is an integer of 0 to 2. Preferably, X is the group of formula (B) where R' is an aromatic group (e.g., 4-methoxycarbonylphenoxy, 4-methylsulfonylphenoxy, 4-cyanophenoxy, 4-dimethylsulfamoylphenoxy, 2-acetamido-4-ethoxycarbonylphenoxy, 4-ethoxycarbonyl-2-methylsulfonamidophenoxy) or a group of formula (D). Among the groups represented by formula (D), a group represented by the following general formula (E) is more preferred:

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(E)

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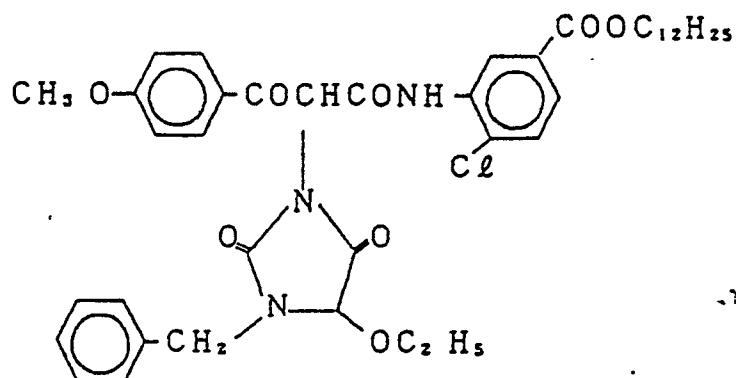
In formula (E), V is a substituted or unsubstituted methylene group or a substituted or unsubstituted imino group; W is an oxygen atom, a sulfur atom, a substituted or unsubstituted methylene group or an unsubstituted imino group; and when V is an imino group, W is neither an oxygen atom nor a sulfur atom. 50 Examples of the group represented by formula (E) include succinimido, phthalimido, 1-methyl-imidazolidine-2,4-dione-3-yl, 1-benzyl-imidazolidine-2,4-dione-3-yl, 5-ethoxy-1-methylimidazolidine-2,4-dione-3-yl, 5-methoxy-1-methylimidazolidine-2,4-dione-3-yl, 5,5-dimethylloxazolidine-2,4-dione-3-yl, thiazolidine-2,4-dione-3-yl, 1-benzyl-2-phenyltriazolidine-3,5-dione-4-yl, 1-n-propyl-2-phenyltriazolidine-3,5-dione-4-yl and 5-ethoxy-1-benzylimidazolidine-2,4-dione-3-yl.

55 Any one of the groups M, Q, L and X of the yellow coupler represented by formula (A) may be a single bond or a bivalent to tetravalent bonding group forming bi-, tris-, tetrakis-compound of the yellow coupler. However, compound having one or two yellow coupler moieties are preferable. When the yellow coupler of formula (A) is in the form of a bis- to tetrakis compound, the number of carbon atoms of M, Q, L or X may

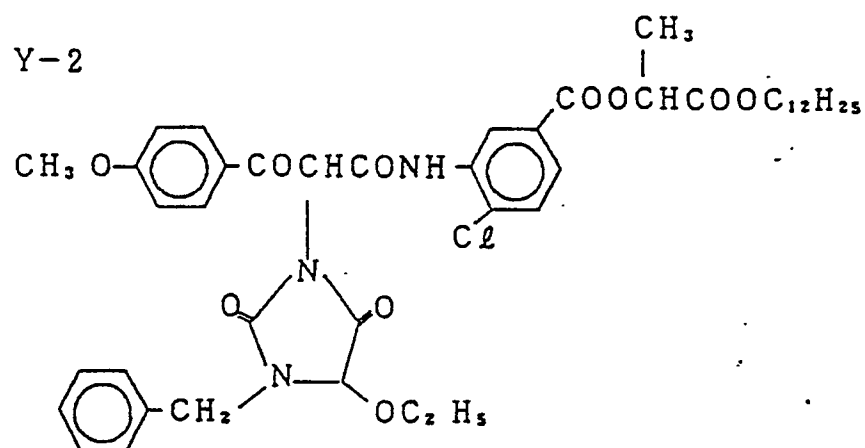
be beyond the extent described above.

Examples of the yellow couplers of formula (A) which can be used in the present invention include, but are not limited to, the following compounds.

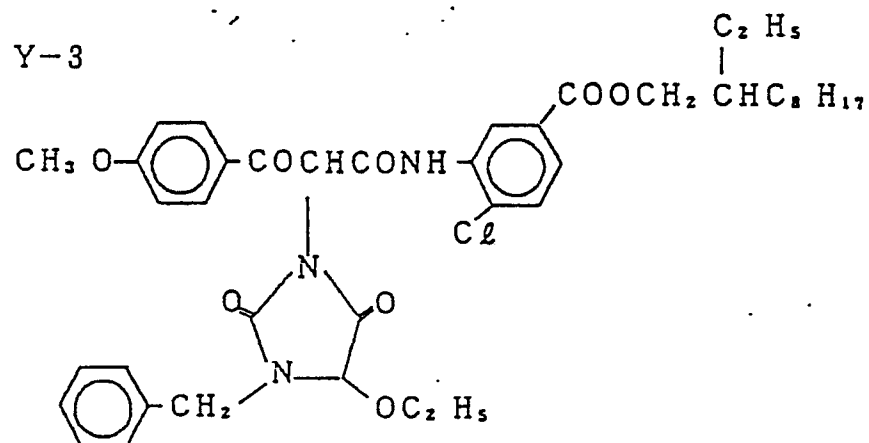
Y-1



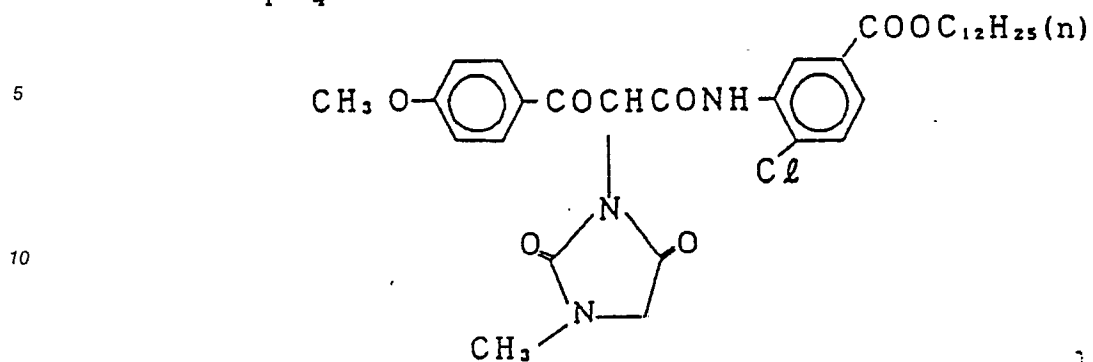
Y-2



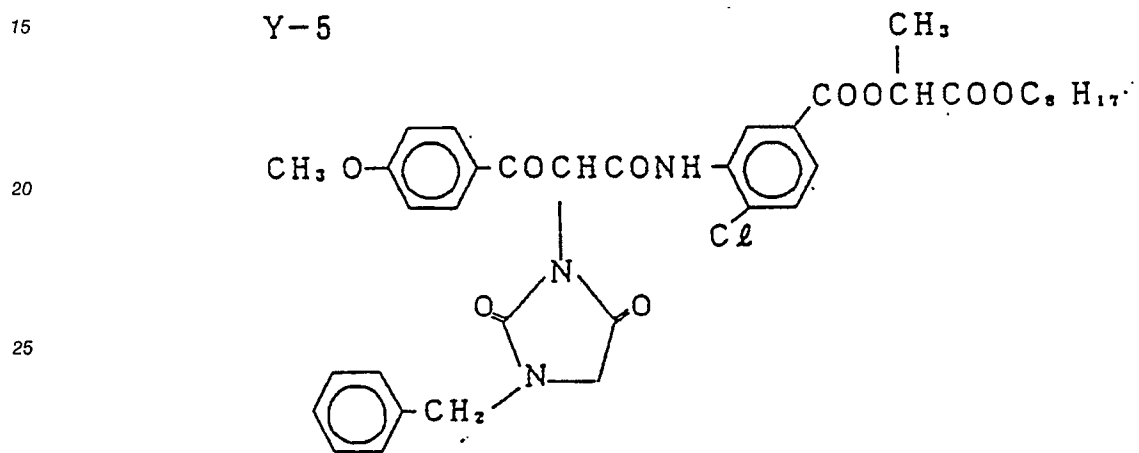
Y-3



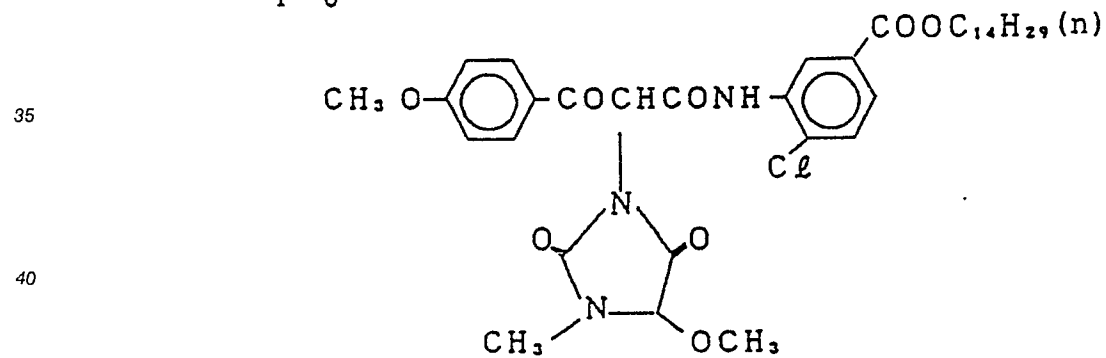
Y-4



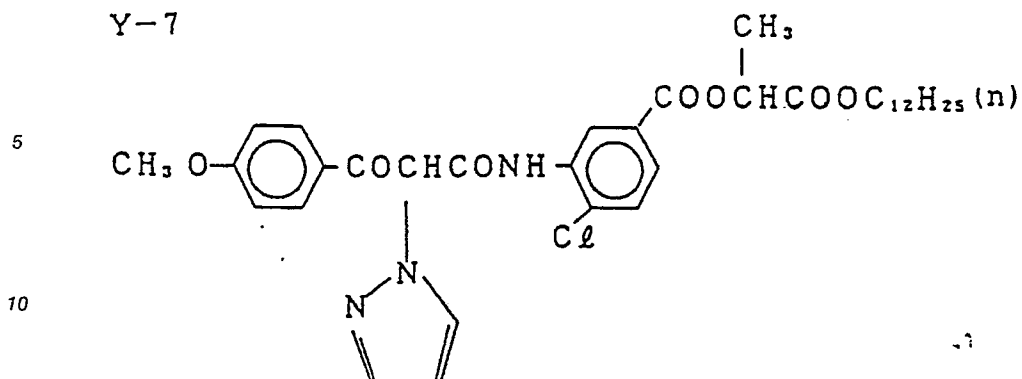
Y-5



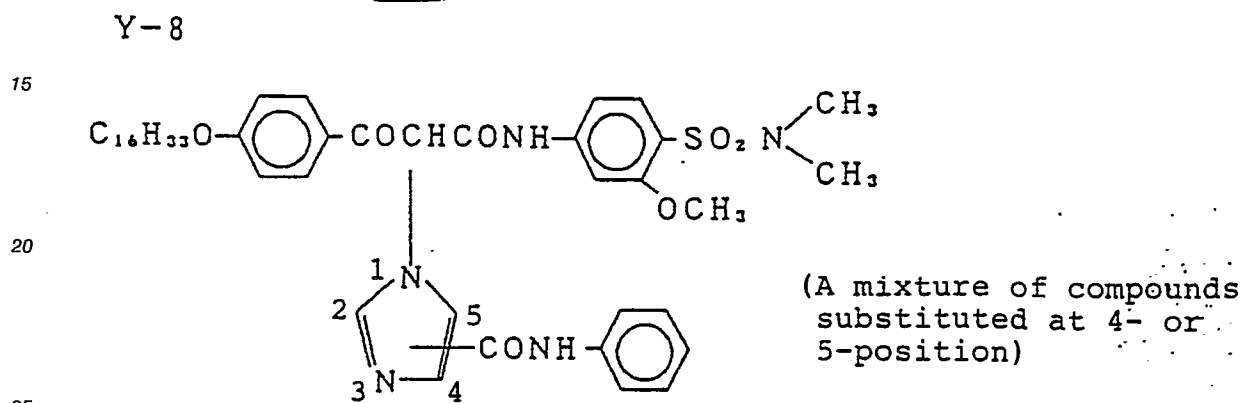
Y-6



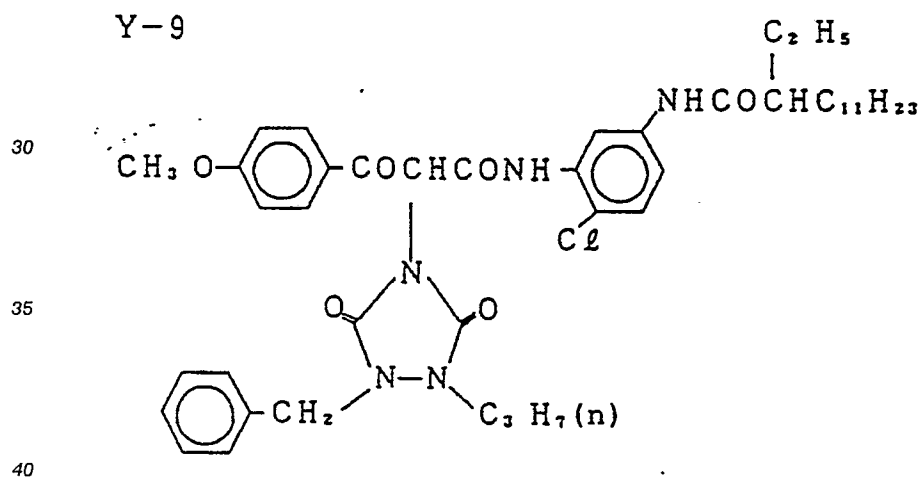
Y-7



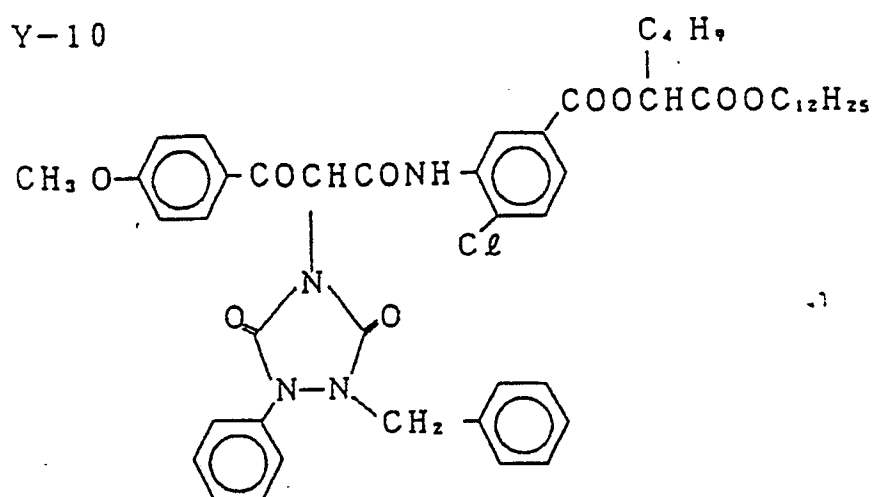
Y-8



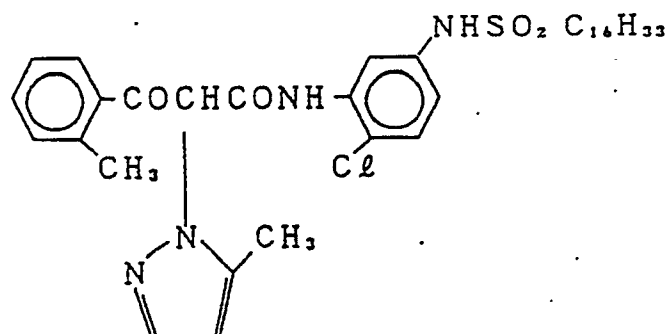
Y-9



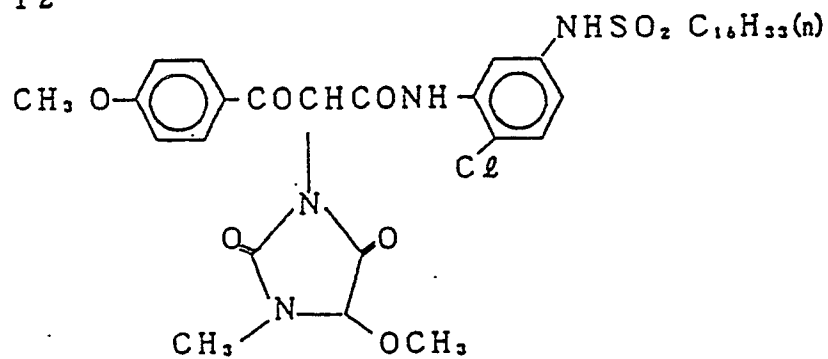
Y-10



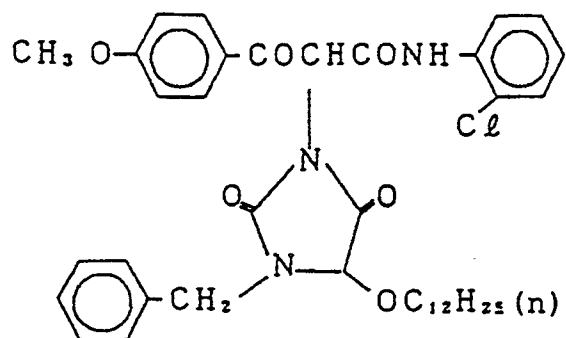
Y-11



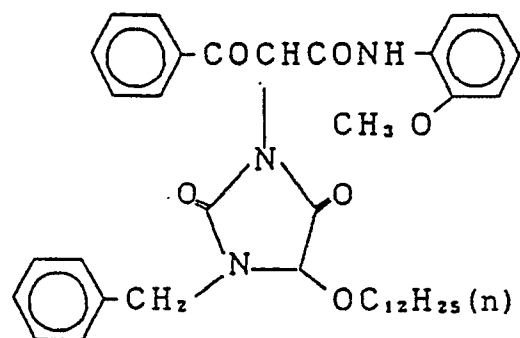
Y-12



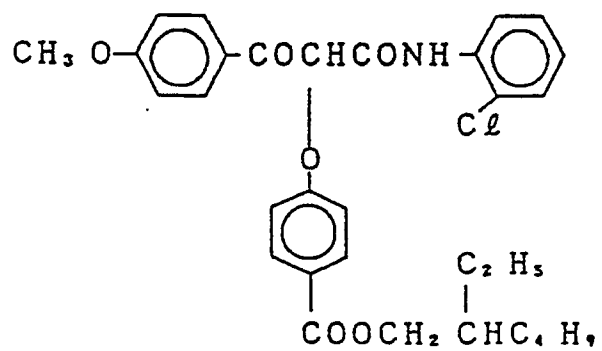
Y-13



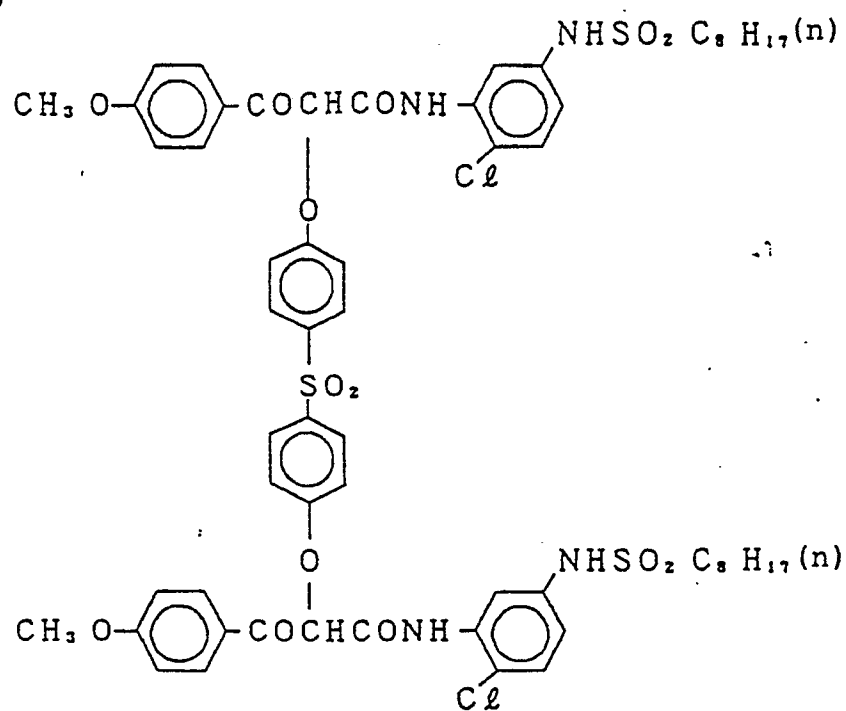
Y-14



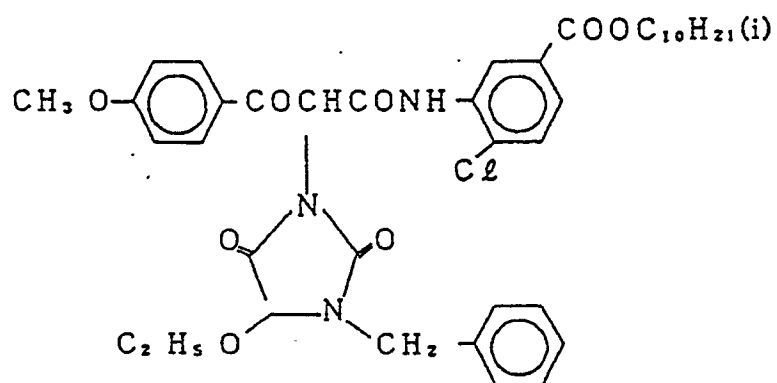
Y-15



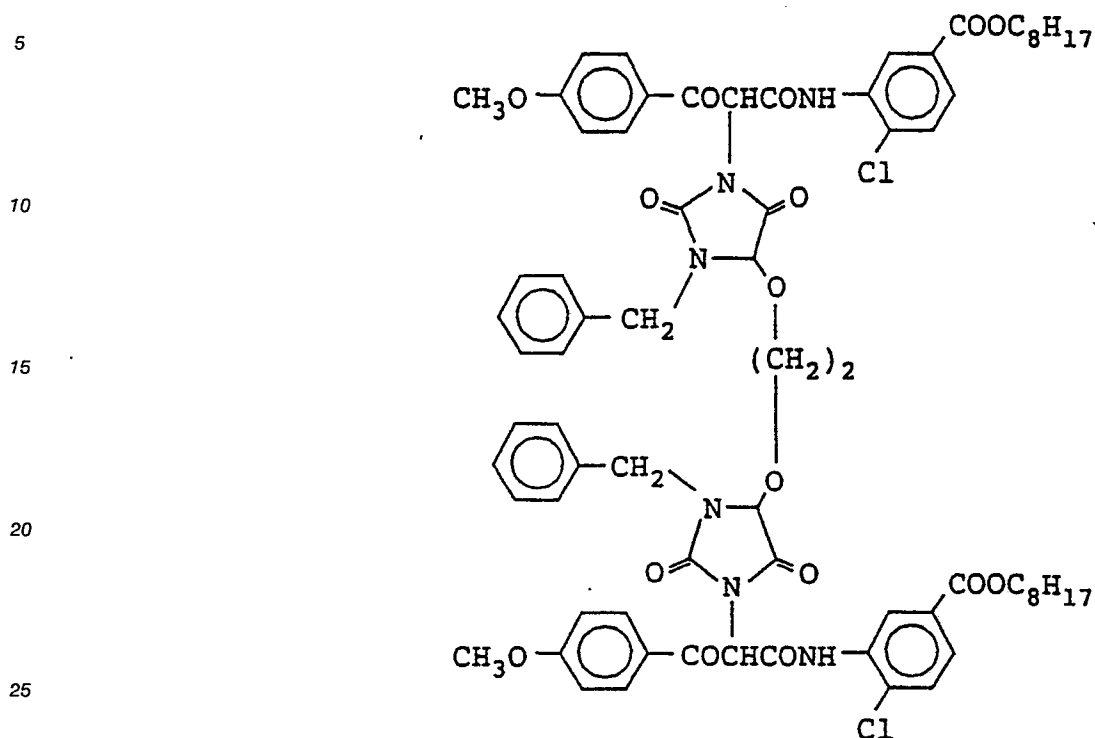
Y-16



Y-17



Y-18



The above-described yellow couplers which can be preferably used can be synthesized by conventional methods such as synthesis methods described in U.S. Patents 3,227,554, 3,408,194, 3,415,652, 3,447,928 and 4,401,752, U.K. Patent 1,040,710, JP-A-47-26133, JP-A-47-37736, JP-A-48-733147, JP-A-48-94432, JP-A-48-68834, JP-A-48-68835, JP-A-48-68836, JP-A-50-34232, JP-A-51-50734, JP-A-51-102636, JP-A-55-598, JP-A-55-161239, JP-A-56-95237, JP-A-56-161543, JP-A-56-153343, JP-A-59-174839 and JP-A-60-35730.

The photographic material of the present invention has a support having thereon at least one blue-sensitive silver halide emulsion layer, green-sensitive silver halide emulsion layer and red-sensitive silver halide emulsion layer. There is no particular limitation with regard to the number of layers of silver halide emulsion layers and non-sensitive layers and the order of the layers. A typical example is a silver halide photographic material having at least one sensitive layer composed of a plurality of silver halide emulsion layers having substantially the same color sensitivity, but different light sensitivity, the sensitive layer being a unit sensitive layer having color sensitivity to any one of blue light, green light and red light. In a multi-layer silver halide color photographic material, the unit sensitive layers are generally arranged in the order of a red-sensitive layer, a green-sensitive layer and a blue-sensitive layer from the support. However, the arrangement may be in the reverse order to that described above according to purpose. Further, the arrangement may be such that a different light-sensitive layer is inserted into the same color sensitive layers.

Non-sensitive layers such as various interlayers may be provided between silver halide sensitive layers, or on the uppermost layer or lowermost layer thereof.

The interlayers may contain couplers, or DIR compounds described in JP-A-61-43748, JP-A-59-113438, JP-A-59-113440, JP-A-61-20037 and JP-A-61-20038. The interlayers may also contain color mixing inhibitors as used conventionally.

A plurality of silver halide emulsion layers which constitute each unit sensitive layer preferably include a two-layer structure consisting of a high-sensitivity emulsion layer and a low-sensitivity emulsion layer as described in West German Patent 1,121,470 and U.K. Patent 923,045. It is preferred that the layers are disposed such that light sensitivity is lower toward the support. A non-sensitive layer may be provided between silver halide emulsion layers. The low-sensitivity emulsion layer may be provided on the farther side from the support and the high-sensitivity emulsion layer may be provided on the side nearer to the support as described in JP-A-57-112751, JP-A-62-200350, JP-A-62-206541 and JP-A-62-206543.

In specific embodiments, the layer may be arranged in order of low-sensitivity blue-sensitive layer (BL)-

/high-sensitivity blue-sensitive layer (BH)/ high-sensitivity green-sensitive layer (GH)/low-sensitivity green-sensitive layer (GL)/high-sensitivity red-sensitive layer (RH)/low-sensitivity red-sensitive layer (RL) from the outermost layer, or in order of BH/BL/GL/GH/RH/RL, or in order of BH/BL/GH/GL/RL/RH.

The arrangement may be made in order of blue-sensitive layer/GH/RH/GL/RL from the outermost layer as described in JP-B-55-34932. Further, the arrangement may be made in order of blue-sensitive layer/GL/RL/GH/RH from the outermost layer as described in JP-A-56-25738 and JP-A-62-63936.

In another embodiment, the layer structure contains three layers having different light sensitivity in such an arrangement that the upper layer is a silver halide emulsion layer having the highest light sensitivity, the medium layer is a silver halide emulsion layer having a light sensitivity lower than that of the upper layer and the lower layer is a silver halide emulsion layer having a light sensitivity lower than that of the medium layer so that light sensitivity becomes lower toward the support in order as described in JP-B-49-15495. Even when the layer structure is composed of three layers having different light sensitivity, the arrangement may be made in order of medium-sensitive emulsion layer/high-sensitivity emulsion layer/low-sensitivity emulsion layer from the outermost layer as described in JP-A-59-202464.

In still another embodiment, the arrangement may be made in order of high-sensitivity emulsion layer/low sensitivity emulsion layer/medium-sensitivity emulsion layer or in order of low sensitivity emulsion layer/medium-sensitivity emulsion layer/high-sensitivity emulsion layer.

When the layer structure is composed of four or more layers, the above-described various arrangements can be made.

It is preferred that a donor layer (CL) having a multilayer effect and different in spectral sensitivity distribution from the principal sensitive layers such as BL, GL and RL are provided adjacent to or near the principal sensitive layers to improve color reproducibility, said donor layer being described in U.S. Patents 4,663,271, 4,705,744 and 4,707,436, JP-A-62-160448 and JP-A-63-89850.

As stated above various layer structures and arrangement can be selected according on the purpose of use.

The preferred silver halide contained in the photographic emulsions of the photographic materials of the present invention is silver iodobromide, silver iodochloride or silver iodochlorobromide, each having a silver iodide content of not higher than about 30 mol%. Particularly preferred is silver iodobromide or silver iodochlorobromide, each having a silver iodide content of about 2 mol% to about 25 mol%.

Silver halide grains in the photographic emulsions may have a regular crystal form such as cube, octahedron or tetradecahedron, an irregular crystal form such as a sphere or tabular form, a crystal having a defect such as a twinning plane or a composite form thereof.

The size of silver halide grains may be in the range of from fine grains having a grain size of not larger than about 0.2 μm to large-size grains having a grain size of about 10 μm in terms of the diameter of projected area. Any of a polydisperse emulsion and monodisperse emulsion may be used.

The silver halide photographic emulsions of the present invention can be prepared according to the methods described in Research Disclosure (RD) No. 17643 (December 1978) pp 22-23 I. Emulsion Preparation and Types; ibid. No. 18716 (November 1979), p. 648; ibid. No. 307105 (November 1989), pp 863-865; P. Glafkides, Chimie et Physique Photographique (Paul Montel 1967), G.F. Duffin, Photographic Emulsion Chemistry (Focal Press 1966) and V.L. Zelikman et al, Making and Coating Photographic Emulsion (Focal Press 1964).

Monodisperse emulsions described in U.S. Patents 3,574,628 and 3,655,394 and U.K. Patent 1,413,748 are also preferred.

Tabular grains having an aspect ratio of not lower than about 5 can be used in the present invention. The tabular grains can be easily prepared by the methods described in Gutoff, Photographic Science and Engineering, Vol. 14, pp 248-257 (1970), U.S. Patents 4,434,226, 4,414,310, 4,433,048 and 4,439,520 and U.K. Patent 2,112,157.

Grains having a uniform crystal structure or a crystal structure different in halogen composition between the interior thereof and the surface thereof can be used. Grains having a laminar crystal structure may be used. Silver halide having a different composition may be joined to the grains by epitaxial growth. A compound such as silver rhodanide or lead oxide other than silver halide may be joined to the grains. A mixture of grains having various crystal forms may be used.

Silver halide emulsions are usually subjected to physical ripening, chemical ripening and spectral sensitization and then used. Additives used for these stages are described in Research Disclosure No. 17643, ibid. No. 18716 and ibid. No. 30716 and listed in a Table below.

It is preferred that non-light-sensitive finely divided silver halide grains are used in the present invention. The term "non-sensitive finely divided silver halide grains" as used herein refers to finely divided silver halide grains which are not light-sensitive during imagewise exposure for obtaining a dye image and are

substantially not developed in the processing stage. Grains which are previously not fogged are preferable.

Finely divided silver halide grains have a silver bromide content of 0 to 100 mol% and may optionally contain silver chloride and/or silver iodide. Grains containing 0.5 to 10 mol% of silver iodide are preferred.

Finely divided silver halide grains have a mean grain size (the mean value of diameters of the circles having areas corresponding to projected areas) of preferably 0.01 to 0.5 μm , more preferably 0.02 to 0.2 μm .

Finely divided silver halide grains can be prepared in the same manner as in the preparation of usual light-sensitive silver halides. In the preparation of finely divided silver halide grains, it is not necessary that the surfaces of silver halide grains be optically sensitized or spectrally-sensitized. However, it is preferred that a conventional stabilizer such as triazole, azaindene, benzthiazolium, a mercapto compound or a zinc compound be added before the finely divided silver halide grains are added to coating solutions. Colloidal silver is preferably incorporated in layers containing the finely divided silver halide grains.

Conventional photographic additives which can be used in the present invention are described in the three Research Disclosures are listed in the following Table.

15

	<u>Additives</u>	<u>RD 17643</u> (Dec. 1978)	<u>RD 18716</u> (Nov. 1979)	<u>RD307105</u> (Nov. 1989)
20	1. Chemical Sensitizing Agent	Page 23	Page 648 (right column)	Page 866
	2. Sensitivity Increaser		- ditto -	
25	3. Spectral Sensitizing Agent Supersensitizing Agent	Pages 23 to 24	Page 648 (right column) to page 649 (right column)	Pages 866 to 868
30	4. Brightening Agent	Page 24	Page 647 (right column)	Page 868
35	5. Anti-fogging Agent, Stabilizer	Pages 24 to 25	Page 649 (right column)	Pages 868 to 870
40	6. Light Absorber, Filter Dye and U.V. Light Absorber	Pages 25 to 26	Page 649 (right column) to page 650 (left column)	Page 873
45	7. Stain Inhibitor	Page 25 (right column)	Page 650 (left column) to right column)	Page 872
	8. Dye Image Stabilizer	Page 25	Page 650 (left column)	Page 872
50	9. Hardening Agent	Page 26	Page 651 (left column)	Pages 874 to 875
	10. Binder	Page 26	- ditto -	Pages 873 to 874
55	11. Plasticizer, Lubricant	Page 27	Page 650 (right column)	Page 876

	<u>Kind of Additives</u>	<u>RD 17643</u> (Dec. 1978)	<u>RD 18716</u> (Nov. 1979)	<u>RD307105</u> (Nov. 1989)
5	12. Coating Aid, Surfactant	Pages 26 to 27	- ditto -	Pages 875 to 876
	13. Antistatic Agent	Page 27	- ditto -	Pages 876 to 877
10	14. Matting Agent			Pages 878 to 879

15 It is preferred that compounds capable of reacting with formaldehyde to fix it as described in U.S. Patents 4,411,987 and 4,435,503 are added to photographic materials to prevent photographic performance from being deteriorated by formaldehyde gas.

Various color couplers can be used in the present invention. Examples thereof are described in patent specifications cited in the above-described Research Disclosure No. 17643, VII-C to G and ibid. No. 20 307105, VII-C to G.

Preferred examples of yellow couplers include those described in U.S. Patents 3,933,501, 4,022,620, 4,326,024, 4,401,752 and 4,248,961, JP-B-58-10739, U.K. Patents 1,425,020 and 1,476,760, U.S. Patents 3,973,968, 4,314,023 and 4,511,649 and European Patent 249,473A.

5-Pyrazolone compounds and pyrazoloazole compounds are preferred as magenta couplers. Particularly preferred are magenta couplers described in U.S. Patents 4,310,619 and 4,351,897, European Patent 25 73,636, U.S. Patents 3,061,432 and 3,725,067, Research Disclosure No. 24220 (June 1984), JP-A-60-33552, Research Disclosure No. 24230 (June 1984), JP-A-60-43659, JP-A-61-72238, JP-A-60-35730, JP-A-55-118034, JP-A-60-185951, U.S. Patents 4,500,630, 4,540,654 and 4,556,630 and WO88/04795.

As cyan couplers phenol couplers and naphthol couplers may be used. Preferred cyan couplers include 30 those described in U.S. Patents 4,052,212, 4,146,396, 4,228,233, 4,296,200, 2,369,929, 2,801,171, 2,772,162, 2,895,826, 3,772,002, 3,758,308, 4,334,011 and 4,327,173, West German Patent Application (Laid-Open) No. 3,329,729, European Patents 121,365A and 249,453A, U.S. Patents 3,446,622, 4,333,999, 4,775,616, 4,451,559, 4,427,767, 4,690,889, 4,254,212 and 4,296,199 and JP-A-61-42658.

Typical examples of dye-forming polymerized couplers are described in U.S. Patents 3,451,820, 35 4,080,211, 4,367,282, 4,409,320 and 4,576,910, U.K. Patent 2,102,137 and European Patent 341,188A.

As couplers forming developed dyes with controlled diffusion, there are preferred those described in U.S. Patent 4,366,237, U.K. Patent 2,125,570, European Patent 96,570 and West German Patent Application (Laid-Open) No. 3,234,533.

In addition to the colored couplers of the present invention, there are preferred compounds described in 40 Research Disclosure No. 17643, item VII-G, ibid. No. 307105, item VII-G, U.S. Patent 4,163,670, JP-B-57-39413, U.S. Patents 4,004,929 and 4,138,258 and U.K. Patent 1,146,368, as colored couplers for correcting the unnecessary absorption of developed dyes. It is also preferred to use couplers for correcting the unnecessary absorption of developed dyes by fluorescent dyes released during coupling as described in U.S. Patent 4,774,181 or couplers having, as an elimination group, a dye precursor group capable of 45 reacting with developing agents to form a dye as described in U.S. Patent 4,777,120.

Compounds which release a photographically useful residue with coupling can be preferably used in the present invention. Preferred DIR couplers which release development inhibitors other than those of the present invention, are described in patent specifications cited in the above-described RD No. 17643, item VII-F, ibid. No. 307105, item VII-F and in JP-A-60-184248.

50 As couplers which release imagewise nucleating agents or development accelerators during development, there are preferred those described in U.K. Patents 2,097,140 and 2,131,188, JP-A-59-157638 and JP-A-59-170840.

Other examples of compounds which can be used in the present invention include competitive couplers described in U.S. Patent 4,130,427, polyequivalent type couplers described in U.S. Patents 4,283,472, 55 4,338,393 and 4,310,618, couplers releasing DIR redox compounds, couplers releasing DIR couplers, redox compounds releasing DIR couplers and redox compounds releasing DIR redox compounds described in JP-A-60-185950 and JP-A-62-24252, couplers which release dyes capable of again forming color after elimination described in European Patents 173,302A and 313,308A, couplers releasing bleaching accelera-

tors described in RD No. 11449, RD No. 24241 and JP-A-61-201247, couplers releasing ligands described in U.S. Patent 4,555,477, couplers releasing leuco dyes described in JP-A-63-75747, and couplers releasing fluorescent dyes described in U.S. Patent 4,774,181.

Couplers used in the present invention can be introduced into photographic materials by various known dispersion methods.

Examples of high-boiling solvents used for the oil-in-water dispersion method are described in U.S. Patent 2,322,027.

Examples of the high-boiling organic solvents which have a boiling point of not lower than 175 °C at normal pressure used in the oil-in-water dispersion method include phthalic esters (e.g., dibutyl phthalate, dicyclohexyl phthalate, di-2-ethylhexyl phthalate, decyl phthalate, bis(2,4-di-*t*-amylphenyl) phthalate, bis(2,4-di-*t*-amylphenyl) isophthalate, bis(1,1-diethylpropyl) phthalate), phosphoric or phosphonic esters (e.g., triphenyl phosphate, tricresyl phosphate, 2-ethylhexyl diphenyl phosphate, tricyclohexyl phosphate, tri-2-ethylhexyl phosphate, tridodecyl phosphate, tributoxyethyl phosphate, trichloropropyl phosphate, di-2-ethylhexyl phenyl phosphate), benzoic esters (e.g., 2-ethylhexyl benzoate, dodecyl benzoate, 2-ethylhexyl *p*-hydroxybenzoate), amides (e.g., *N,N*-diethyldodecaneamide, *N,N*-diethylaurylamide, *N*-tetradecylpyrrolidone), alcohols or phenols (e.g., isostearyl alcohol, 2,4-di-*tert*-amylphenol), aliphatic carboxylic acid esters (e.g., bis(2-ethylhexyl) sebacate, dioctyl azelate, glycerol tributyrates, isostearyl lactate, trioctyl citrate), aniline derivatives (e.g., *N,N*-dibutyl-2-butoxy-5-*t*-octylaniline) and hydrocarbons (e.g., paraffin, dodecylbenzene, diisopropylnaphthalene). Organic solvents having a boiling point of not lower than about 30 °C, preferably not lower than about 50 °C, but not higher than about 160 °C can be used as co-solvents. Examples of the co-solvents include ethyl acetate, butyl acetate, ethyl propionate, methyl ethylketone, cyclohexanone, 2-ethoxyethyl acetate and dimethylformamide.

Examples of steps for latex dispersion methods, effects thereof and the impregnating latex are described in U.S. Patent 4,199,363, West German Patent Application (OLS) Nos. 2,541,274 and 2,541,230.

It is preferred that antiseptic and antifungal agents such as 1,2-benzisothiazoline-3-one, *n*-butyl *p*-hydroxybenzoate, phenol, 4-chloro-3,5-dimethylphenol, 2-phenoxyethanol and 2-(4-thiazolyl)benzimidazole described in JP-A-63-257747, JP-A-62-272248 and JP-A-1-80941 and phenethyl alcohol are added to the color photographic materials of the present invention.

The present invention can be applied to various color photographic materials. Typical examples of the color photographic materials according to the present invention include general-purpose and movie color negative films, reversal color films for slide or TV, color paper, color positive films and reversal color paper.

Examples of supports which can be used in the present invention include those described in the above-described RD No. 17643 (page 28), RD No. 18716 (right column of page 647 to left column of page 648) and RD No. 307105 (page 879).

In the photographic material of the present invention, the total of the layer thicknesses of the entire hydrophilic colloid layers on the emulsion layer side thereof is preferably not more than 28 μm, more preferably not more than 23 μm, still more preferably not more than 18 μm, particularly preferably not more than 16 μm. The layer-swelling rate $T_{1/2}$ is preferably not longer than 30 seconds, more preferably not longer than 20 seconds. The layer thickness refers to a layer thickness obtained by measuring the thickness of a layer at 25 °C and 55% RH under air conditioning (2 days). The layer-swelling rate $T_{1/2}$ can be measured by known method in the field of photography, for example, by using a swellometer described in A. Green et al., *Photogr. Sci. Eng.*, Vol. 19, No. 2, pp. 124-129. $T_{1/2}$ is defined as the time taken until layer thickness reaches 1/2 of saturated layer thickness when processing is conducted with a color developing solution at 30 °C for 3 min 15 sec and 90% of the attainable maximum swollen layer thickness is referred to as saturated layer thickness.

The layer-swelling rate $T_{1/2}$ can be controlled by adding a hardening agent to gelatin as a binder or by changing conditions with time after coating. A swelling ratio of 150 to 400% is preferred. The swelling ratio can be calculated from the maximum swollen layer thickness under the above conditions by using the formula (maximum swollen layer thickness - layer thickness)/layer thickness.

The color photographic materials of the present invention can be developed according to conventional methods described in RD No. 17643 (pp 28-29), RD No. 18716 (left column to right column of page 651) and RD No. 307105 (pp 880-881).

Color developing solutions which can be used in the processing of the photographic materials of the present invention are preferably aqueous alkaline solutions mainly composed of aromatic primary amine color developing agents. Aminophenol compounds are useful as the color developing agents and *p*-phenylenediamine compounds are preferred as the color developing agents. Typical examples thereof include 3-methyl-4-amino-*N,N*-diethylaniline, 3-methyl-4-amino-*N*-ethyl-*N*-β-hydroxyethylaniline, 3-methyl-4-amino-*N*-ethyl-*N*-β-methanesulfonamidoethylaniline, 3-methyl-4-amino-*N*-ethyl-*N*-β-methoxyethylaniline and

salts thereof such as sulfate, hydrochloride and p-toluenesulfonate. Among them, 3-methyl-4-amino-N-ethyl-N- β -hydroxyethylaniline sulfate is particularly preferred. These compounds may be used either alone or in combination of two or more of them according to purpose.

Generally, the color developing solutions contain pH buffering agents such as alkali metal carbonates, borates and phosphates, developed restrainers such as chlorides, bromides, iodides, benzimidazoles, benzothiazoles and mercapto compounds and anti-fogging agents. If desired, the color developing solutions may optionally contain preservatives such as hydroxylamine, diethylhydroxylamine, sulfites, hydrazine such as N,N-bis(carboxymethyl)hydrazine, phenylsemicarbazides, triethanolamine, catecholsulfonic acids; organic solvents such as ethylene glycol and diethylene glycol; development accelerators such as benzyl alcohol, polyethylene glycol, quaternary ammonium salts and amines; color forming couplers, competitive couplers; auxiliary developing agents such as 1-phenyl-3-pyrazolidone; tackifiers; and chelating agents such as aminopolycarboxylic acids, aminopolyphosphonic acids, alkylphosphonic acids and phosphonocarboxylic acids, for example, ethylenediaminetetraacetic acid, nitrilotriacetic acid, diethylenetriaminepentaacetic acid, cyclohexanediaminetetraacetic acid, hydroxyethyliminodiacetic acid, 1-hydroxyethylidene-1,1-diphosphonic acid, nitrilo-N,N,N-trimethylenephosphonic acid, ethylenediamine-N,N,N',N'-tetramethylenephosphonic acid and ethylenediamine-di(o-hydroxyphenylacetic acid) and salts thereof.

Generally, when reversal processing is to be conducted, black-and-white development is first carried out and color development is then carried out. Black-and-white developing solutions may contain conventional developing agents such as dihydroxybenzenes (e.g., hydroquinone), 3-pyrazolidones (e.g., 1-phenyl-3-pyrazolidone) and aminophenols (e.g., N-methyl-p-aminophenol). These developing agents may be used either alone or in combination of two or more of them.

The pH of the color developing solutions and the black-and-white developing solutions is generally in the range of 9 to 12. The replenishment rate of these developing solutions varies depending on the types of the color photographic materials, but is usually not more than 3 l per m² of the photographic material. The replenishment rate can be reduced to 500 ml or less when the concentration of bromide ion in the replenisher is reduced. When the replenishment is to be reduced, it is desirable that the contact area of the processing solution with air be reduced to prevent the solution from being evaporated or oxidized by air. The contact area of the photographic processing solution with air in the processing tank is represented by opening ratio defined below.

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$$\text{Opening ratio} = \frac{\text{Contact area (cm}^2\text{) of processing solution with air}}{\text{Capacity (cm}^3\text{) of processing solution}}$$

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The opening ratio is preferably not higher than 0.1, more preferably 0.001 to 0.05. Methods for reducing the opening ratio include a method wherein a cover such as a floating lid is provided on the surface of the photographic processing solution in the processing tank; a method wherein a movable lid is used as described in JP-A-1-82033; and a slit development method described in JP-A-63-216050. It is preferred the opening ratio be reduced not only for color development and black and white development stages, but also all of the subsequent stages such as bleaching, bleaching-fixing, fixing, rinsing and stabilization stages. The replenishment rate can be reduced by inhibiting the accumulation of bromide ion in the developing solution.

Color development is usually 2 to 5 minutes. However, when a higher temperature and a higher pH are used and the color developing agents are used at a higher concentration, processing time can be shortened.

After color development, the photographic emulsion layer is generally bleached. Bleaching may be carried out simultaneously with fixing (bleaching-fixing treatment) or separately carried out. After bleaching, a bleaching-fixing treatment may be conducted to expedite processing. Processing may be conducted with a bleaching-fixing bath composed of two consecutive baths. Fixing may be conducted before the bleaching-fixing treatment. After the bleaching-fixing treatment, bleaching may be conducted according to purpose. Examples of bleaching agents include compounds of polyvalent metals such as iron(III), peracids, quinones and nitro compounds. Typical examples of the bleaching agents include organic complex salts of iron(III) such as complex salts of aminopolycarboxylic acids (e.g., ethylenediaminetetraacetic acid, diethylenetriaminepentaacetic acid, cyclohexanediaminetetraacetic acid, methyliminodiacetic acid, 1,3-diaminopropanetetraacetic acid, glycol ether diaminetetraacetic acid), citric acid, tartaric acid, and malic acid. Among them, iron(III) complex salts of aminopolycarboxylic acids such as (ethylenediaminetetraacetato)-

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iron(III) complex and (1,3-diaminopropanetetraacetato)iron(III) complex are preferred for rapid processing and prevention of environmental pollution. Further, iron(III) complex salts of aminopolycarboxylic acids are useful for bleaching solutions and bleaching-fixing solutions. The pH of the bleaching solutions containing the iron(III) complex salts of aminopolycarboxylic acids and the bleaching-fixing solutions containing the iron(III) complex salts is generally in the range of 4.0 to 8. A lower pH may be used to expedite processing.

If desired, the bleaching solution, the bleaching-fixing solution and the pre-bath thereof may contain bleaching accelerators. Examples of the bleaching accelerators include compounds having a mercapto group or disulfide group described in U.S. Patent 3,893,858, West German Patents 1,290,812 and 2,059,988, JP-A-53-32736, JP-A-53-57831, JP-A-53-37418, JP-A-53-72623, JP-A-53-95630, JP-A-53-95631, JP-A-53-104232, JP-A-53-124424, JP-A-53-141623, JP-A-53-28426 and Research Disclosure No. 17129 (July 1978); thiazolidine derivatives described in JP-A-50-140219; thiourea derivatives described in JP-B-45-8506, JP-A-52-20832, JP-A-53-32735 and U.S. Patent 3,706,561; iodides described in West German Patent 1,127,715 and JP-A-58-16235; polyoxyethylene compounds described in West German Patents 996,410 and 2,748,430; polyamine compounds described in JP-B-45-8836; compounds described in JP-A-49-40943, JP-A-49-59644, JP-A-53-94927, JP-A-54-35727, JP-A-55-26506 and JP-A-58-163940; and bromide ions. Among them, the compounds having a mercapto group or disulfide group are preferred for their high accelerating effect. Particularly, the compounds described in U.S. Patent 3,893,858, West German Patent 1,290,812 and JP-A-53-95630 are preferred. Further, the compounds described in U.S. Patent 4,552,834 are preferred. These bleaching accelerators may be incorporated in the photographic materials. These bleaching accelerators are particularly effective in conducting bleaching-fixing of the color photographic materials for photographing.

It is preferred that in addition to the above-described compounds, the bleaching solution and the bleaching-fixing solution contain organic acids to prevent stain from being caused by bleaching. Particularly preferred organic acids are compounds having an acid dissociation constant (pKa) of 2 to 5. Examples of the organic acids include acetic acid and propionic acid.

Examples of fixing agents used in the fixing solution and the bleaching-fixing solution include thiosulfates, thiocyanates, thioether compounds, thioureas and a large amount of an iodide. The thiosulfates are widely used as the fixing agents. Particularly, ammonium thiosulfate is most widely used. A combination of a thiosulfate with a thiocyanate, a thioether compound or a thiourea is also preferred. Sulfites, bisulfites, carbonyl bisulfite adducts and sulfinic acid compounds described in European Patent 294769A are preferred as preservatives for the fixing solution and the bleaching-fixing solution. It is also preferred that aminopolycarboxylic acids or organic phosphonic acids are added to the fixing solution or the bleaching-fixing solution to stabilize the solution.

It is preferred that compounds having a pKa of 6.0 to 9.0, preferably imidazoles such as imidazole, 1-methylimidazole, 1-ethylimidazole and 2-methylimidazole, in an amount of 0.1 to 10 mol/l are added to the fixing solution or the bleaching-fixing solution to adjust the pH.

Shorter desilvering time (in total) is preferred, so long desilvering failure is not caused. Desilvering time is preferably 1 to 3 min, more preferably 1 to 2 min. Processing temperature is 25 to 50°C, preferably 35 to 45°C. When desilvering is carried out at a temperature within the preferred range, the desilvering rate is increased and stain is effectively prevented from being formed after processing.

It is preferred that agitation in the desilvering stage be intensified as much as possible. Methods for intensifying agitation include a method wherein a jet of the processing solution collides with the surfaces of the emulsions of photographic materials as described in JP-A-62-183460; a method wherein stirring is improved by a rotating means as described in JP-A-62-183461; a method wherein a wiper blade provided in the solution is brought into contact with the surfaces of the emulsions, the photographic material is transferred to thereby form a turbulent flow, whereby a stirring effect is improved; and a method wherein the whole amount of the processing solution circulated is increased. Such means for improving agitation are effectively applicable to any of the bleaching solution, the bleaching-fixing solution and the fixing solution. It is believed that an improvement agitation accelerates the feed of the bleaching solution and the fixing solution into the emulsion layers and as a result, the desilvering rate is enhanced. The above-described means for improving agitation is more effective when the bleaching accelerators are used. The accelerating effect can be greatly increased and the problem of inhibiting fixation caused by the bleaching accelerators can be solved.

It is preferred that automatic processors for use in the processing of the photographic materials of the present invention be provided with photographic material conveying means described in JP-A-60-191257, JP-A-60-191258 and JP-A-60-191259. As stated in JP-A-60-191257 the conveying means can greatly reduce the amount of the processing solution brought over from the previous bath to the subsequent bath so that preservation of the performance of the processing solution is very high. This is particularly effective

in shortening the processing time in each stage or reducing the replenishment rate of the processing solution.

Usually, the silver halide color photographic materials of the present invention are subjected to washing and/or stabilization after desilvering. The amount of rinsing water in the washing stage varies widely depending on the characteristics (e.g., depending on materials used such as couplers) of the photographic materials, their use, the temperature of rinsing water, the number of rinsing tanks (the number of stages), replenishing system (countercurrent, direct flow) and other conditions. The relationship between the amount of water and the number of rinsing tanks in the multi-stage countercurrent system can be determined by the method described in Journal of the Society of Motion Picture and Television Engineers, Vol. 64, p. 248-253 (May 1955).

According to the multi-stage countercurrent system described in the above article, the amount of rinsing water can be greatly reduced. However, the residence time of water in the tanks is prolonged and as a result, bacteria are grown and the resulting suspended matter is deposited on the photographic material. A method for reducing calcium ion and magnesium ion concentrations described in JP-A-62-288838 can be effectively used for the color photographic materials of the present invention to solve this problem. Further, isothiazolone compounds, thiabendazole compounds, chlorine-containing germicides such as sodium chlorinated isocyanurate and benzotriazole described in JP-A-57-8542 and germicides described in Chemistry of Germicidal Antifungal Agent, (1986) written by Hiroshi Horiguchi (Sankyo Shuppan), Sterilization, Disinfection, Antifungal Technique, edited by Sanitary Technique Society and Antibacterial and Antifungal Cyclopedie, (19-86) edited by Nippon Antibacterial Antifungal Society, can be used.

The pH of rinsing water in the treatment of the photographic materials of the present invention is in the range of 4 to 9, preferably 5 to 8. The temperature of rinsing water and washing time vary depending on the characteristics of the photographic materials and use, but the temperature and time of washing are generally 15 to 45°C for 20 seconds to 10 minutes, preferably 25 to 40°C for 30 seconds to 5 minutes. The photographic materials of the present invention may be processed directly with stabilizing solutions in place of rinsing water. Such stabilizing treatment can be carried out by conventional methods described in JP-A-57-8543, JP-A-58-14834 and JP-A-60-220345.

A stabilizing treatment subsequent to rinsing may be conducted. The stabilizing treatment may be used as the final bath for the color photographic materials for photographing. An example thereof include a stabilizing bath containing a dye stabilizer and a surfactant. Examples of the dye stabilizer include aldehydes such as formalin and glutaraldehyde, N-methylol compounds, hexamethylenetetramine and aldehydesulfite adducts.

The stabilizing bath may contain various chelating agents and antifungal agents.

Overflow solution from the replenishment of rinsing water and/or stabilizing can be reused in other stages such as desilvering stage.

When the processing solutions are concentrated by evaporation in processing with automatic processors, it is preferred that water is added thereto to make up the amount of water evaporated.

The color developing agents may be incorporated in the silver halide color photographic materials of the present invention for the purpose of simplifying and expediting processing. It is preferred that precursors for the color developing agents are used for the incorporation thereof in the photographic materials. Examples of the precursors include indoaniline compounds described in U.S. Patent 3,342,597; Schiff base compounds described in U.S. Patent 3,342,599 Research Disclosure No. 14850 and ibid., No. 15159; aldol compounds described in Research Disclosure No. 13924; metal complex salts described in U.S. Patent 3,719,492; and urethane compounds described in JP-A-53-135628.

If desired, 1-phenyl-3-pyrazolidones may be incorporated in the silver halide color photographic materials of the present invention for the purpose of accelerating color development. Typical examples of the compounds include those described in JP-A-56-64339, JP-A-57-144547 and JP-A-58-115438.

In the present invention, various processing solutions are used at a temperature of 10 to 50°C. Generally, a temperature of 33 to 38°C is used. However, a higher temperature can be used to accelerate processing and to shorten processing time, while a lower temperature is used to improve image quality and to improve the stability of the processing solutions.

The silver halide photographic materials of the present invention include heat developable photo sensitive materials described in U.S. Patent 4,500,626, JP-A-60-133449, JP-A-59-218443, JP-A-61-238056 and European Patent 210,660A2.

The present invention is now illustrated in greater detail with reference to the following examples which, however, are not to be construed as limiting the invention in any way. Unless otherwise indicated, all parts, percents and ratios are by weight.

EXAMPLE 1

The surface of a cellulose triacetate film support having an undercoat applied thereto was coated with the following layers having the following compositions to prepare a multi-layer color photographic material as Sample 101.

Compositions of Photographic Layers

The coating weights of silver halide and colloidal silver are represented by g/m² in terms of silver. The coating weights of couplers, additives and gelatin are represented by g/m². The amounts of sensitizing dyes are represented by moles per mole of silver halide in the same layer.

<u>First Layer:</u> Antihalation Layer	<u>Amount</u>
Black colloidal silver	0.15
Gelatin	1.5
ExM-8	0.02
<u>Second Layer:</u> Interlayer	
Gelatin	1.5
UV-1	0.03

	UV-2	0.06
5	UV-3	0.07
	ExF-1	0.004
10	Solv-2	0.07

Third Layer: Low-sensitivity Red-sensitive Emulsion Layer

15	Silver iodobromide emulsion [AgI: 2 mol%, interior high AgI type, diameter (in terms of sphere): 0.3 μ m, coefficient of variation in diameter (in terms of sphere): 29%, normal crystal- twin mixed grains, diameter/ thickness ratio: 2.5]; coated silver	0.5
	Gelatin	1.00
25	ExS-1	1.0×10^{-4}
	ExS-2	3.0×10^{-4}
	ExS-3	1.0×10^{-5}
30	ExC-3	0.22
	ExC-4	0.02
35	ExC-13	0.01
	Solv-1	0.007

Fourth Layer: Medium-sensitivity Red-sensitive Emulsion Layer

45	Silver iodobromide emulsion [AgI: 4 mol%, interior high AgI type, diameter (in terms of sphere): 0.55 μ m, coefficient of variation in diameter (in terms of sphere): 20%, normal crystal- twin mixed grains, diameter/ thickness ratio: 1]; coated silver	0.85
50	Gelatin	1.26

	ExS-1	1.0×10^{-4}
5	ExS-2	3.0×10^{-4}
	ExS-3	1.0×10^{-5}
	ExC-3	0.33
10	ExC-4	0.01
	ExC-13	0.03
15	ExC-2	0.08
	Cpd-10	1.0×10^{-4}
	Solv-1	0.10
20	<u>Fifth Layer:</u> High-sensitivity Red-sensitive Emulsion	
	Layer	
25	Silver iodobromide emulsion [AgI: 10 mol%, interior high AgI type, diameter (in terms of sphere): 0.7 μ m, coefficient of variation in diameter (in terms 30 of sphere): 30%, twin mixed grains, diameter/thickness ratio: 2]; coated silver amount	0.7
35	Gelatin	1.0
	ExS-1	1.0×10^{-4}
	ExS-2	3.0×10^{-4}
40	ExS-3	1.0×10^{-5}
	ExC-5	0.07
	ExC-6	0.08
45	ExY-13	0.03
	Solv-1	0.15
50	Solv-2	0.08

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Sixth Layer: Interlayer

5	Gelatin	1.0
	P-2	0.17
	Cpd-1	0.10
10	Cpd-4	0.17
	Solv-1	0.05

Seventh Layer: Low-sensitivity Green-sensitive Emulsion Layer

15	Silver iodobromide emulsion [AgI: 2 mol%, interior high AgI type, diameter (in terms of 20 sphere): 0.3 μ m, coefficient of variation in diameter (in terms of sphere): 28%, normal crystal- twin mixed grains, diameter/ 25 thickness ratio: 2.5]; coated silver amount	0.30
	Gelatin	0.4
30	ExS-4	5.0×10^{-4}
	ExS-6	0.3×10^{-4}
	ExS-5	2.0×10^{-4}
35	ExM-9	0.2
	ExM-14	0.03
40	Solv-1	0.2

Eighth Layer: Medium-sensitivity Green-sensitive Emulsion Layer

45	Silver iodobromide emulsion [AgI: 4 mol%, interior high AgI type, diameter (in terms of sphere): 0.55 μ m, coefficient of 50 variation in diameter (in terms of sphere): 20%, normal crystal- twin mixed grains, diameter/	0.7
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thickness ratio: 4]; coated
silver amount

5	Gelatin	1.0
	ExS-4	5.0×10^{-4}
	ExS-5	2.0×10^{-4}
10	ExS-6	0.3×10^{-4}
	ExM-9	0.25
15	ExM-8	0.03
	ExM-10	0.015
	ExY-14	0.04
20	Solv-1	0.20

Ninth Layer: High-sensitivity Green-sensitive Emulsion Layer

25	Silver iodobromide emulsion [AgI: 10 mol%, interior high AgI type, diameter (in terms of sphere): 0.7 μm , coefficient of variation in diameter (in terms of sphere): 30%, normal crystal- twin mixed grains, diameter/ thickness ratio: 2.0]; coated silver amount	0.50
35	Gelatin	0.80
	ExS-4	2.0×10^{-4}
40	ExS-5	2.0×10^{-4}
	ExS-6	0.2×10^{-4}
45	ExS-7	3.0×10^{-4}
	ExM-11	0.06
	ExM-12	0.02
50	ExM-8	0.02

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	Cpd-2	0.01
5	Cpd-9	2.0×10^{-4}
	Cpd-10	2.0×10^{-4}
	Solv-1	0.20
10	Solv-2	0.05

Tenth Layer: Yellow Filter Layer

15	Gelatin	0.6
	Yellow colloidal silver	0.05
	Cpd-1	0.2
20	Solv-1	0.15

Eleventh Layer: Low-sensitivity Blue-sensitive Emulsion Layer

25	Silver iodobromide emulsion [AgI: 4 mol%, interior high AgI type, diameter (in terms of sphere): 0.5 μ m, coefficient of variation in diameter (in terms of sphere): 15%, octahedral grains]; coated silver amount	0.4
35	Gelatin	1.0
	ExS-8	2.0×10^{-4}
	(Y-1) (preferable coupler of the present invention)	0.9
40	ExC-13	0.03
	Cpd-2	0.01
45	Solv-1	0.3

Twelfth Layer: High-sensitivity Blue-sensitive Emulsion Layer

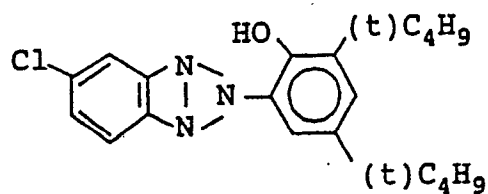
50	Silver iodobromide emulsion [AgI: 10 mol%, interior high	0.5
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5	AgI type, diameter (in terms of sphere): 1.3 μm , coefficient of variation in diameter (in terms of sphere): 25%, normal crystal-twin mixed grains, diameter/thickness ratio: 4.5]; coated silver amount	
10	Gelatin	0.6
	ExS-8	1.0×10^{-4}
15	(Y-1) (preferable coupler of the present invention)	0.12
	ExC-13	0.01
20	Cpd-2	0.001
	Cpd-5	2.0×10^{-4}
	Solv-1	0.04
25	<u>Thirteenth Layer:</u> First Protective Layer	
	Finely divided silver iodobromide (mean grain size: 0.07 μm , AgI: 1 mol%)	0.2
30	Gelatin	0.8
	UV-2	0.10
35	UV-3	0.10
	UV-4	0.2
40	Solv-3	0.04
	<u>Fourteenth Layer:</u> Second Protective Layer	
	Gelatin	0.9
45	Polymethyl methacrylate particles (diameter: 1.5 μm)	0.2
	H-1	0.4

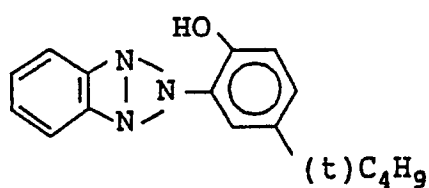
Further, the following Cpd-3, Cpd-5, Cpd-6, Cpd-7, Cpd-8, P-1, P-2, W-1, W-2, W-3 were added to improve preservability, processability, pressure resistance, mildewproofing and antifungal properties, antistatic properties, and coatability.

The chemical structural formulas and chemical names of compounds used in the present invention are as follows.

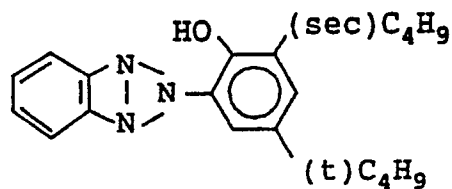
UV-1



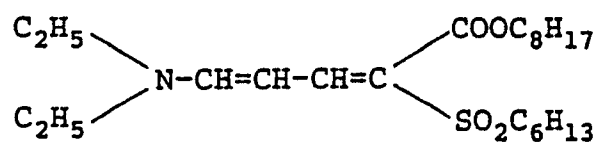
UV-2



UV-3



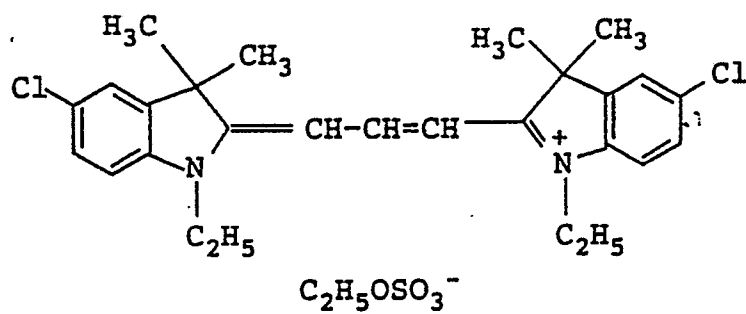
UV-4



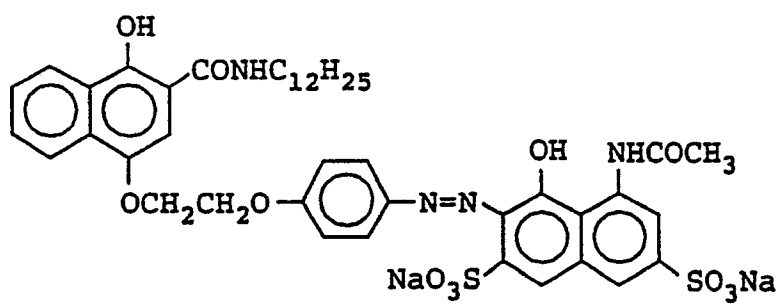
- 45
- 50
- Solv-1: Tricresyl phosphate
- Solv-2: Dibutyl phthalate
- Solv-3: Tri(2-ethylhexyl) phosphate

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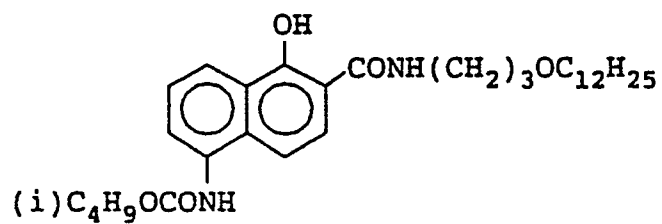
ExF-1



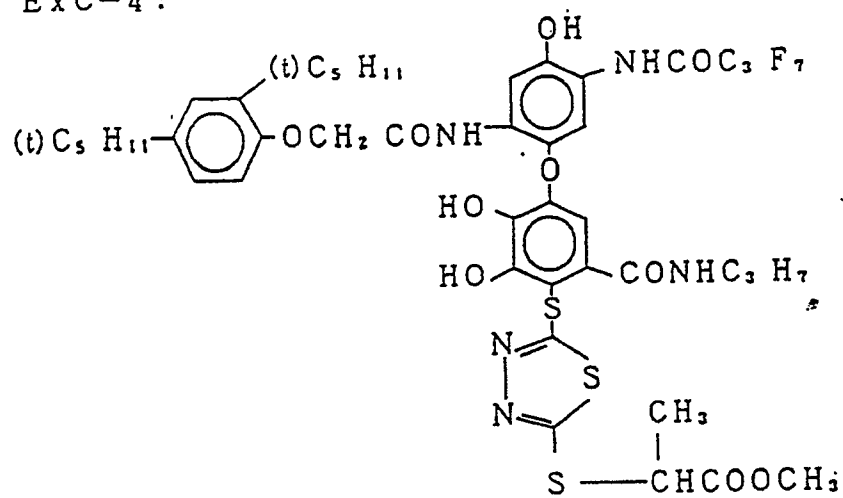
ExC-2



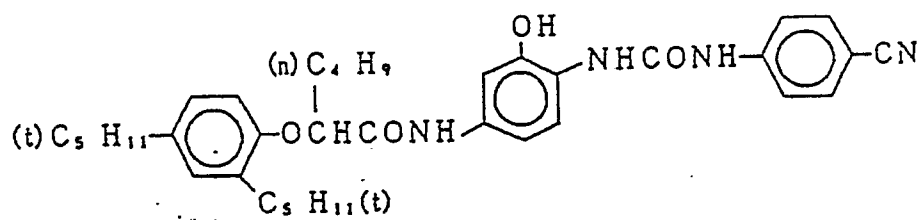
ExC-3



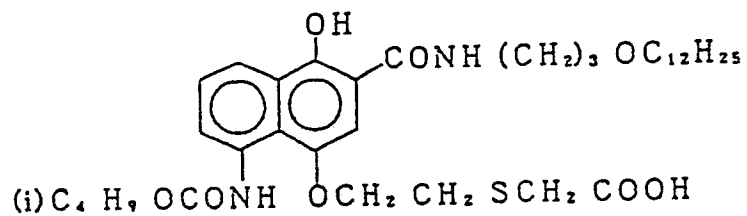
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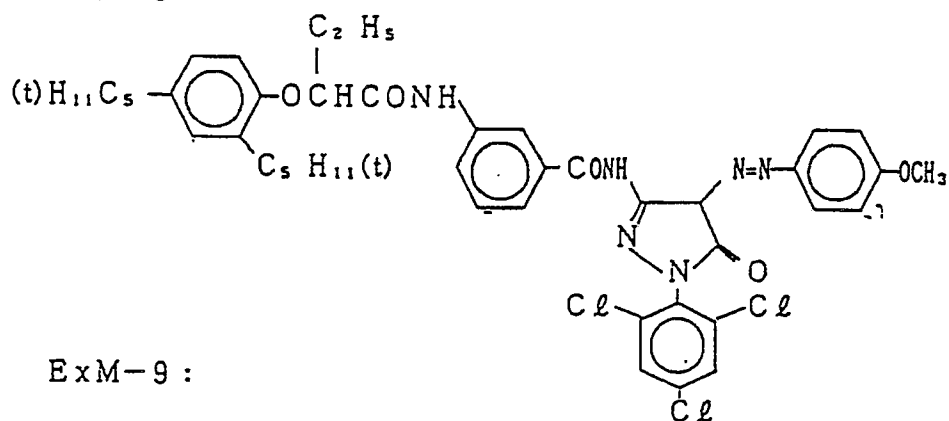
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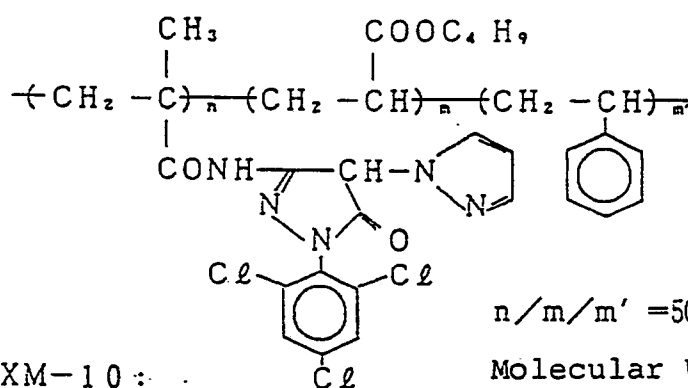
Ex C-6 :



ExM-8 :



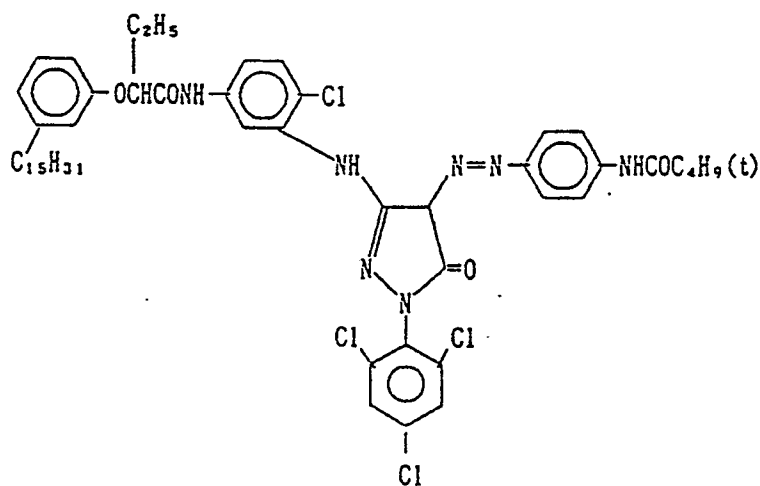
ExM-9 :



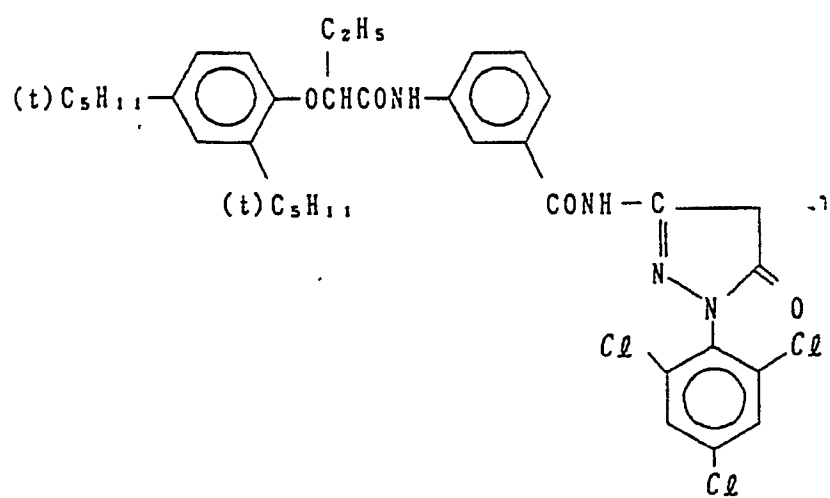
n/m/m' = 50/25/25 (weight ratio)

Molecular Weight: about 20,000

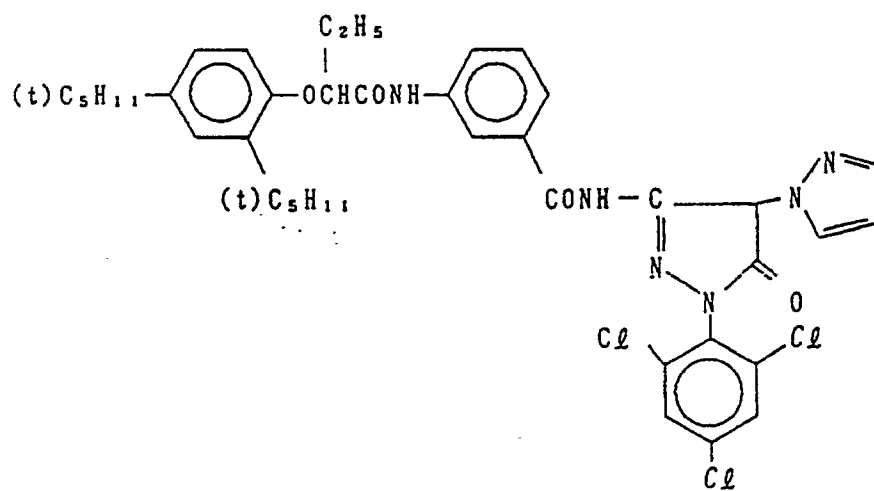
EXM-10 :



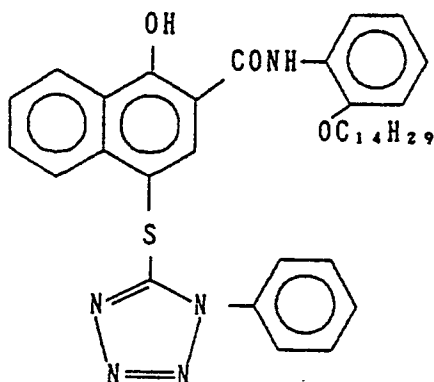
Ex M - 11 :



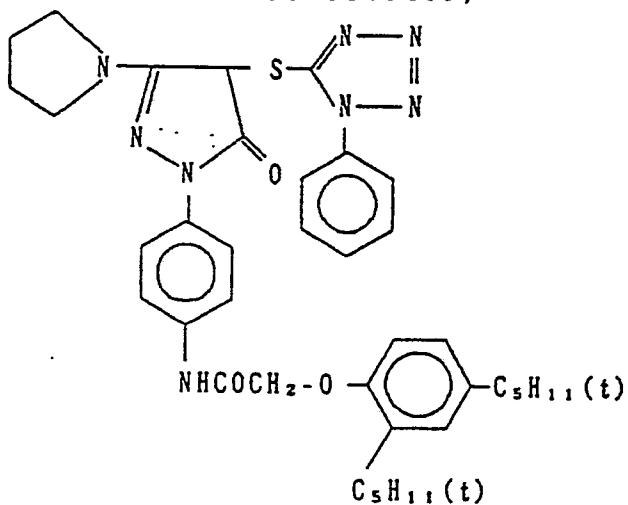
Ex M - 12 :



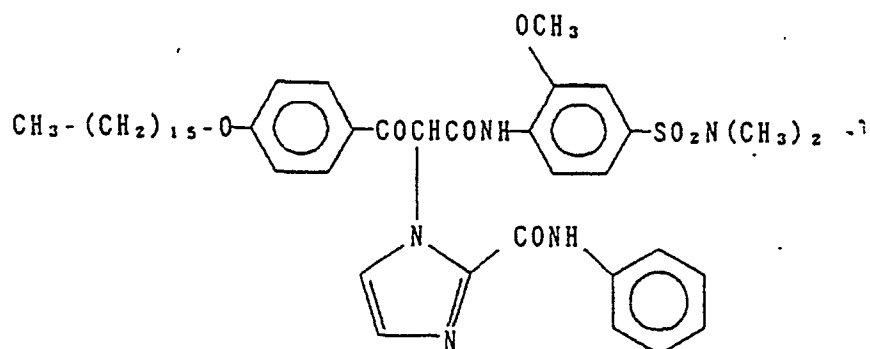
E x C - 1 3 : (DC-1 of West German Patent
Laid-Open No. 3815469)



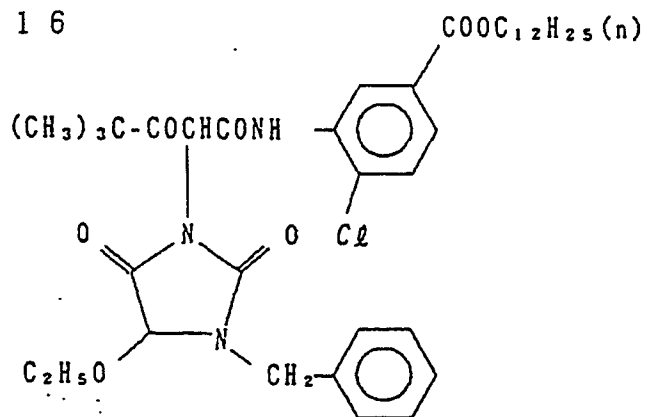
E x M - 1 4 : (DIR coupler similar to DC-3 of
West German Patent Laid Open
No. 3815469)



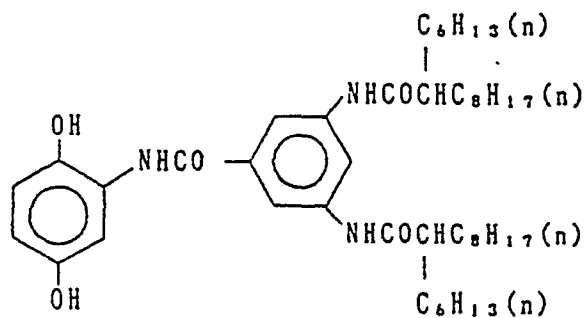
Ex Y - 15 : (Y-1 of West German Patent
Laid-Open No. 3815469)



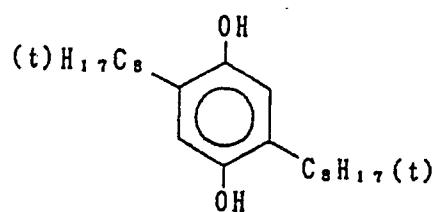
Ex Y - 16



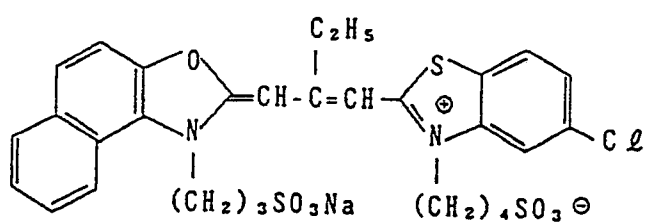
Cpd - 1 :



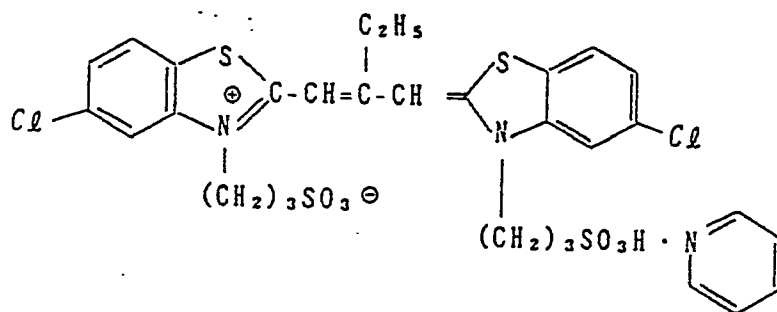
C p d - 2 :



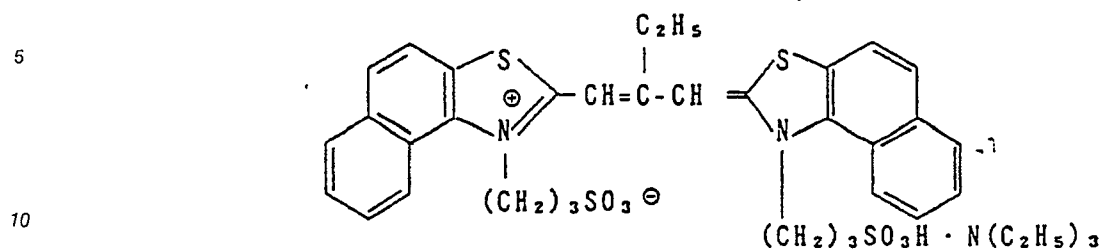
E x S - 1 :



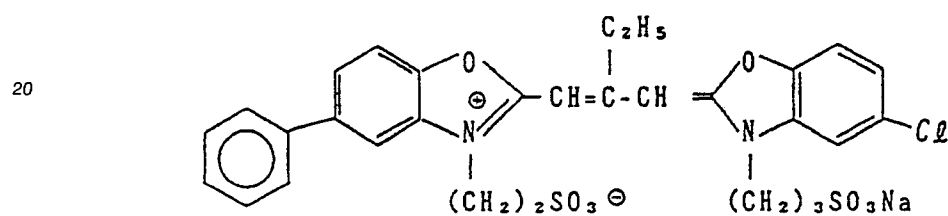
E x S - 2 :



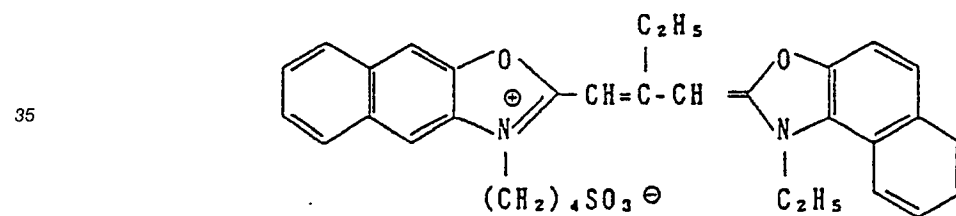
E x S - 3 :



E x S - 4 :



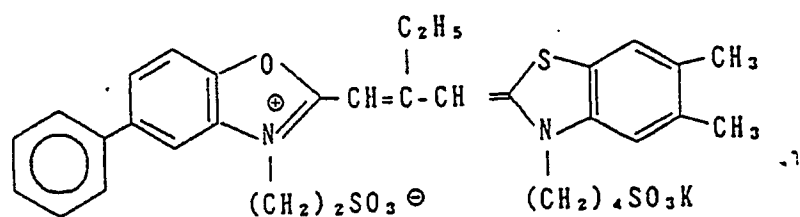
E x S - 5 :



Ex S - 6 :

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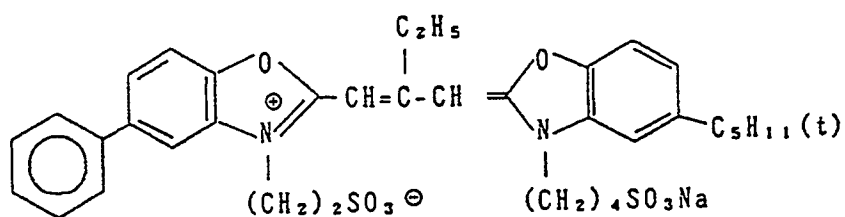
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Ex C - 7 :

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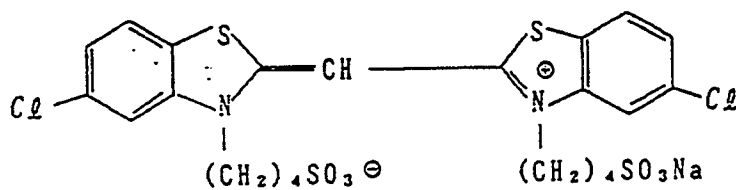


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Ex S - 8 :

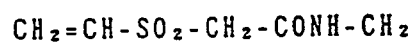
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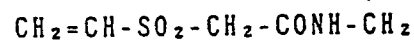


H - 1 :

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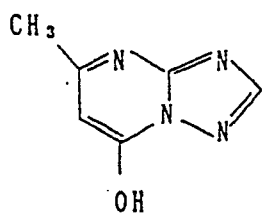
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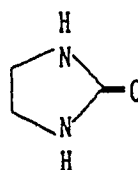
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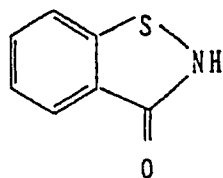
C p d - 3 :



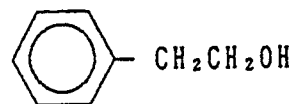
C p d - 4 :



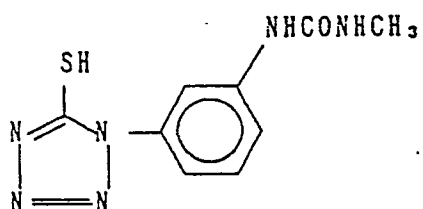
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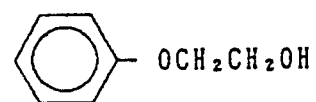
C p d - 6



C p d - 7

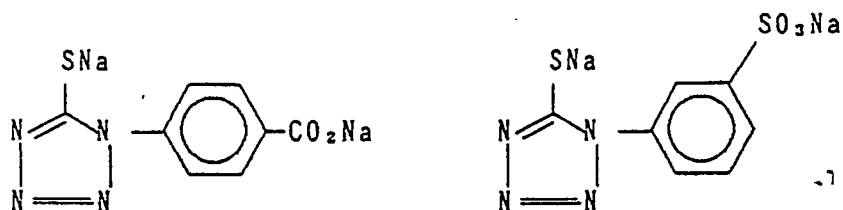


C p d - 8

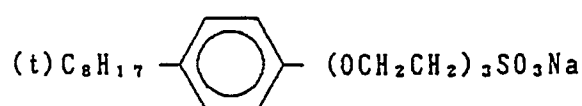


C p d - 9

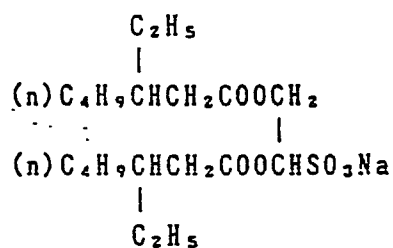
C p d - 1 0



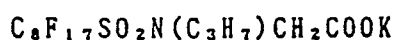
W - 1



W - 2



W - 3



- 45
- P-1 Copolymer of vinyl-pyrrolidone and vinyl alcohol (copolymerization ratio = 70:30 by weight)
- P-2 Polyethyl acrylate

Samples 102 to 104

50 Each of Samples 102, 103 and 104 was prepared in the same way as in the preparation of Sample 101 except that a twice molar amount of Compound (D-14) or (D-29) of the present invention or an equimolar amount of (D-7) of the present invention was used in place of ExC-13 in each of the third layer, the fourth layer, the eleventh layer and the twelfth layer of Sample 101.

Samples 105 to 116

55 Each of Samples 105 to 108 was prepared in the same way as in the preparation of each of Samples 101 to 104 except that the yellow colored cyan coupler (YC-28) of the present invention in an amount of

0.02 g/m² and 0.01 g/m² was added to the third layer and the fourth layer of each of Samples 101 to 104, respectively. Similarly, (YC-32) and (YC-47) were added to prepare Samples 109 to 116.

Samples 117 to 120

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Each of Samples 117 to 120 was prepared in the same way as in the preparation of Sample 107 except that (YC-24), (YC-26), (YC-30) or (YC-3) was used in place of (YC-28).

Samples 121 to 122

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Each of Samples 121 and 122 was prepared in the same way as in the preparation of Sample 107 except that ExY-15 in an amount of 1.10 g/m² or 1.20 g/m² was used in place of (Y-1) in the eleventh layer of Sample 107; the amount of gelatin was changed to 1.50 g/m²; the amount of Solv-1 was changed to 0.40 g/m²; and further ExY-15 or ExY-16 in an amount of 0.18 g/m² was used in place of (Y-1) in the twelfth layer of Sample 107.

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The samples prepared above were subjected to imagewise red exposure and then to the following color development (Condition A). Separately, the samples were subjected to uniform blue exposure so that the yellow density of the red unexposed area of Sample 101 in the following color development became 1.2 after imagewise red exposure, and the samples were then subjected to imagewise red exposure and developed (condition B).

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Relative sensitivity was determined from the logarithm of the reciprocal of exposure amount giving a density of (Fog + 0.2) under the Condition A. Color turbidity was determined from a value obtained by subtracting the yellow density in the red unexposed area from the yellow density in an exposure amount giving a cyan density of (Fog + 0.5) and (Fog + 1.0) under the Conditions A and B.

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The sharpness of these samples was determined by the conventional MTF method.

The development was carried out at 38 °C under the following conditions.

30

1. Color development	2 min 45 sec
2. Bleaching	6 min 30 sec
3. Rinse with water	3 min 15 sec
4. Fixing	6 min 30 sec
5. Rinse with water	3 min 15 sec
6. Stabilization	3 min 15 sec

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Each processing solution used in each stage had the following composition.

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Color Developing Solution

5	Sodium nitrilotriacetate	1.0 g
	Sodium sulfite	4.0 g
	Sodium carbonate	30.0 g
10	Potassium bromide	1.4 g
	Hydroxylamine sulfate	2.4 g
15	4-(N-Ethyl-N-β-hydroxyethylamino)- 2-methylaniline sulfate	4.5 g
	Add water to make	1 liter

Bleaching Solution

20	Ammonium bromide	160.0 g
	Ammonia water (28%)	25.0 ml
25	Sodium iron salt of ethylenediaminetetraacetic acid	130 g
30	Glacial acetic acid	14 ml
	Add water to make	1 liter

Fixing Solution

35	Sodium tetrapolyphosphate	2.0 g
	Sodium sulfite	4.0 g
40	Ammonium thiosulfate (70% aqueous solution)	175.0 ml
	Sodium bisulfite	4.6 g
45	Add water to make	1 liter

Stabilizing Solution

50	Formalin	2.0 ml
	Add water to make	1 liter

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Table 1

Sample	DIR Com- pound in 3rd, 4th, 11th, and 12th Layers	Yellow Colored Coupler in 3rd and 11th, 12th Layers	Rela- tive Sensi- tivity	Color Turbidity				MTF Value (20 cycle/mm) Yellow Cyan Image Image		
				Condition A		Condition B				
				Fog+0.5	Fog+1.0	Fog+0.5	Fog+1.0			
101 (Comparison)	ExC-13	-	Y-1	0.00	+0.05	+0.19	+0.04	+0.17	0.85	0.62
102 (")	D-14	-	"	0.04	+0.07	+0.14	+0.05	+0.08	0.86	0.64
103 (")	D-29	-	"	0.05	+0.05	+0.12	+0.04	+0.06	0.87	0.64
104 (")	D-7	-	"	0.05	+0.05	+0.12	+0.04	+0.06	0.87	0.64
105 (")	ExC-13	YC-28	"	0.00	+0.01	+0.11	0.00	+0.09	0.88	0.63
106 (Invention)	D-14	"	"	0.04	+0.02	+0.06	+0.01	0.00	0.89	0.65
107 (")	D-29	"	"	0.05	+0.01	+0.04	0.00	-0.02	0.90	0.65
108 (")	D-7	"	"	0.05	+0.01	+0.04	0.00	-0.02	0.90	0.65
109 (Comparison)	ExC-13	YC-32	"	-0.01	+0.02	+0.12	+0.01	+0.10	0.88	0.63
110 (Invention)	D-14	"	"	0.03	+0.03	+0.07	+0.02	-0.01	0.89	0.65
111 (")	D-29	"	"	0.03	+0.02	+0.05	+0.01	-0.01	0.90	0.65

Table 1 (cont'd)

Sample	DIR Com- pound in 3rd, 4th, 11th, and 12th Layers	Yellow Colored Coupler in 3rd and 11th Layers	Yellow Coupler in 11th, 12th Layers	Rela- tive Sensi- tivity	Color Turbidity		MTF Value (20 cycle/mm) Yellow Cyan Image Image
					Condition A Fog+0.5	Condition B Fog+1.0	
112 (Invention)	D-7	YC-32	Y-1	0.03	+0.02	+0.01	0.90 0.65
113 (Comparison)	ExC-13	YC-47	"	-0.02	+0.04	+0.13	0.87 0.64
114 (Invention)	D-14	"	"	0.02	+0.05	+0.04	0.89 0.65
115 (")	D-29	"	"	0.02	+0.04	+0.03	0.89 0.65
116 (")	D-7	"	"	0.02	+0.04	+0.03	0.89 0.65
117 (")	D-29	YC-24	"	0.04	+0.01	-0.02	0.90 0.65
118 (")	"	YC-26	"	0.05	0.00	-0.01	0.90 0.65
119 (")	"	YC-30	"	0.05	+0.01	-0.02	0.90 0.65
120 (")	"	YC-3	"	0.06	-0.01	-0.03	0.90 0.65
121 (")	"	YC-28	*	0.04	+0.03	0.00	0.87 0.63
122 (")	"	"	**	0.04	+0.03	0.00	0.87 0.63

*: 11th: ExY-15 (1.10 g/m²)

12th: ExY-15

**: 11th: ExY-15 (1.10 g/m²)

12th: ExY-16

It is clear from Table 1 that the samples of the present invention are highly sensitive in comparison with the samples which are outside the scope of the present invention. For example, all of the samples of the present invention are high in sensitivity in comparison with Sample 113 which is suggested as a photographic material in West German Patent 3815469. The samples of the present invention exhibit low color turbidity in any exposure amount under both the conditions A and B in comparison with Samples 102 to 104 using only a DIR compound of the present invention and Samples 105, 109 and 113 using only a yellow colored coupler. The effect of the present invention on color turbidity is remarkable under the Condition B under which there is color turbidity during exposure and an improvement in chromaticity is desired, rather than under the Condition A under which exposure is only pure red exposure. Further, it is clear that the effect of the present invention is high in the high density region where exposure amount is increased. Namely, Table 1 shows that an improvement in color reproducibility under various exposure conditions has been achieved by the present invention.

Further, it is clear that the MTF values of both the yellow dye image and the cyan dye image of the samples of the present invention are raised.

It is also clear that Sample 107 using yellow coupler (Y-1) is high-sensitivity, exhibits low turbidity and is excellent in sharpness in comparison with Samples 121 and 122 using ExY-15 and ExY-16.

EXAMPLE 2

Each of Samples 107, 121 and 122 was slit into films of 35 mm in width and processed into 135 size patron (24 exposures) to prepare each of photographic materials 201, 202 and 203. A half-length of a person was photographed through a color checker (manufactured by Macbeth) with a Canon EOS-630 camera using these photographic materials under each setting condition of ISO speed 400, 100 and 12. The same subject was photographed using commercially available super HG-400 under each setting condition of ISO speed 1600, 400 and 50.

Color development was carried out at 38°C using an automatic processor under the following conditions:

30	Color development	3 min 15 sec
	Bleaching	1 min
35	Bleaching-fixing	3 min 15 sec
	Rinse with water (1)	40 sec
	Rinse with water (2)	1 min
40		
	Stabilization	40 sec
45	Drying (50°C)	1 min 15 sec

In the above processing stage, rinses (1) and (2) were conducted by a system running countercurrent from (2) to (1). Each processing solution had the composition shown below.

The replenishment rate of each processing solution was such that the replenishment rate in the color development stage was 1200 ml per m² of color photographic material and that in each of the other stages including the rinses was 800 ml. The amount of the processing solution carried over from the previous bath to the rinse stage was 50 ml per m² of color photographic material.

Color Developing Solution

		<u>Mother Solution</u>	<u>Replenisher</u>
5			
	Diethylenetriaminepentaacetic acid	1.0 g	1.1 g
10			
	1-Hydroxyethylidene-1,1- diphosphonic acid	2.0 g	2.2 g
	Sodium sulfite	4.0 g	4.4 g
15			
	Potassium carbonate	30.0 g	32.0 g
	Potassium bromide	1.4 g	0.7 g
20			
	Potassium iodide	1.3 mg	-
	Hydroxylamine sulfate	2.4 g	2.6 g

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4-(N-Ethyl-N-β-hydroxyethyl- amino)-2-methylaniline sulfate	4.5 g	5.0 g
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Add water to make	1 liter	1 liter
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pH	10.0	10.05
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Bleaching Solution

Mother solution and replenisher being the same¹.

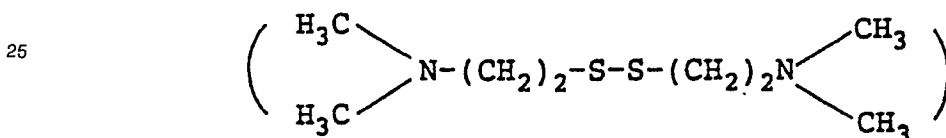
Ethylenediaminetetraacetic acid iron(III) ammonium salt	120.0 g
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Disodium ethylenediaminetetraacetate	10.0 g
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Ammonium nitrate	10.0 g
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Ammonium bromide	100.0 g
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Bleaching accelerator	5×10^{-3} mol
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Add ammonia water to make	pH 6.3
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Add water to make	1 liter
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Bleaching-fixing Solution

Mother solution and replenisher being the same.

Ethylenediaminetetraacetic acid iron(III) ammonium salt	50.0 g
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Disodium ethylenediaminetetraacetate	5.0 g
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Sodium sulfite	12.0 g
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Aqueous solution of ammonium thiosulfate (70%)	240 ml
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Add ammonia water to make	pH 7.3
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Add water to make	1 liter
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Rinsing Water

Tap water containing calcium ions (32 mg/l) and magnesium ions # (7.3 mg/l) was passed through a column packed with an H-type strongly acidic cation exchange resin and an OH-type strongly basic anion exchange resin to reduce calcium ion concentration to 1.2 mg/l and magnesium ion concentration to 0.4 mg/l. Sodium isocyanurate dichloride in an amount of 20 mg/l was then added to the treated water.

Stabilizing Solution

Mother solution and replenisher being the same.

Formalin (37% w/v)	2.0 ml
Polyoxyethylene p-monononylphenyl ether (average degree of polymerization: 10)	0.3 g
Disodium ethylenediaminetetraacetate	0.05 g
Add water to make	1 liter
pH	5.8

Drying

Drying temperature was 50° C.

An auto-printer FAP-3500 manufactured by Fuji Photo Film Co., Ltd. was set so that each density of B, G and R of neutral 5 of the Macbeth color checker became 0.75 ± 0.02 in printing under three conditions of super HG400. The printing of the photosensitive materials 201 to 203 was done under the above conditions. Fuji color paper HG was used for printing. The Macbeth color checker density of these samples was measured on paper. The results are shown in Table 2.

Table 2

Sample	Setting of 12		Setting of 100		Setting of 400		
	Density	Difference in Density*	Density	Difference in Density*	Density	Difference in Density*	
201	B	0.71	0	0.72	-0.01	0.73	-0.01
	G	0.71	-	0.73	-	0.74	-
	R	0.72	+0.01	0.73	0.00	0.74	0.00
202	B	0.67	-0.04	0.71	-0.02	0.72	-0.01
	G	0.71	-	0.73	-	0.73	-
	R	0.72	+0.01	0.73	0.00	0.73	0.00
203	B	0.66	-0.04	0.71	-0.02	0.72	-0.01
	G	0.70	-	0.73	-	0.73	-
	R	0.71	+0.01	0.73	0.00	0.73	0.00

* Difference in density: Difference in density between B or R and G (on a G basis);

It is clear from Table 2 that Sample 201 containing yellow coupler (Y-1) showed less change in color density (under each exposure condition, particularly under the setting of ISO speed 12 which is an over-exposure setting) in comparison with Samples 202 and 203 obtained by using ExY-15 and ExY-16.

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EXAMPLE 3

A yellow colored cyan coupler (YC-1) of the present invention in an amount of 0.015 g/m² and 0.005 g/m² was added to the fourth layer and the fifth layer, respectively, of Sample 105 (the coupler Ex-10 being the same as D-29 of the present invention) of JP-A-1-214849 to prepare Sample 301. Similarly, (YC-25),
10 (YC-27), (YC-52), (YC-85), (YC-86), (YC-88) and (YC-89) were added to prepare Samples 302 to 308.

These samples were exposed under Conditions A and B in the same way as in Example 1 and color-developed. The MTF value was measured in the same way as in Example 1.

Development was carried out using the following processing stages and processing solutions in a cine
15 system automatic processor.

The samples for use in the evaluation of performance were processed after imagewise exposed samples were processed until the amount of replenisher added to the color developing solution was three times the tank capacity of mother solution.

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Stage	<u>Processing Stage</u>		Replenish- ment Rate*	Capacity of Tank
	<u>Processing Time</u>	<u>Processing Temp.</u>		
Color development	3 min 15 sec	38.0°C	23 ml	15 ℓ
Bleaching	50 sec	38.0°C	5ml	5 ℓ
Bleaching-fixing	50 sec	38.0°C	-	5 ℓ
Fixing	50 sec	38.0°C	16 ml	5 ℓ
Rinse with water (1)	30 sec	38.0°C	-	3 ℓ
Rinse with water (2)	20 sec	38.0°C	34 ml	3 ℓ
Stabilization	20 sec	38.0°C	20 ml	3 ℓ
Drying	1 min	55°C		

* Replenishment rate being amount per 35 mm wide x 1 m long.

Rinsing water was supplied by a system running countercurrent from (2) to (1). All of the overflow solution of rinsing water was introduced into the fixing bath. The replenishment to the bleaching-fixing bath was conducted in such a manner that the upper part of the bleaching bath in the automatic processor was connected with the bottom of the bleaching-fixing bath through a pipe, the upper part of the fixing bath was connected with the bottom of the bleaching-fixing bath through a pipe and all of the overflow solution resulting from the feeding of the replenisher to the bleaching bath and the fixing bath was allowed to flow into the bleaching-fixing bath. The amount of the developing solution brought into the bleaching stage, that of the bleaching solution brought into the bleaching-fixing stage, that of the bleaching-fixing solution brought into the fixing stage and that of the fixing solution brought into the rinse stage were 2.5 ml, 2.0 ml, 2.0 ml and 2.0 ml, respectively, each amount being per 35 mm wide x 1 m long of the photographic material. Cross-over time was 5 seconds in each of these stages. The cross-over time was included within the processing time of the previous stage. Each process bath was provided with a means for allowing the jet stream of each processing solution to collide with the surfaces of the emulsion layers as described in JP-A-62-183460.

Each processing solution had the following composition.

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Developing Solution

	<u>Mother Solution (g)</u>	<u>Replenisher (g)</u>
Diethylenetriaminepentaacetic acid	2.0	2.2
1-Hydroxyethylidene-1,1-diphosphonic acid	3.3	3.3
Sodium sulfite	3.9	5.2
Potassium carbonate	37.5	39.0
Potassium bromide	1.4	0.4
Potassium iodide	1.3 mg	-
Hydroxylamine sulfate	2.4	3.3
2-Methyl-4-[N-ethyl-N-(β -hydroxyethyl)amino]aniline sulfate	4.5	6.1
Add water	1.0 ℓ	1.0 ℓ
pH	10.05	10.15

Bleaching Solution

	<u>Mother Solution (g)</u>	<u>Replenisher (g)</u>
1,3-Propylenediaminetetraacetic acid iron(III) ammonium monohydrate	144.0	206.0
Ammonium bromide	84.0	120.0
Ammonium nitrate	17.5	25.0
Hydroxyacetic acid	63.0	90.0
Acetic acid	33.2	47.4
Add water	1.0 ℓ	1.0 ℓ
pH (adjusted with ammonia water)	3.20	2.80

Mother Solution of Bleaching-fixing Solution

A mixed solution of the mother solution of the above bleaching solution and the mother solution of the following fixing solution (15:85 by volume).

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Fixing Solution

	<u>Mother Solution (g)</u>	<u>Replenisher (g)</u>
Ammonium sulfite	19.0	57.0
Aqueous solution of ammonium thiosulfate (700 g/l)	280 ml	840 ml
Imidazole	28.5	85.8
Ethylenediaminetetraacetic acid	12.5	37.5
Add water	1.0 l	1.0 l
pH (adjusted with ammonia water and acetic acid)	7.40	7.45

30 Rinsing Water

Tap water was passed through a mixed-bed column packed with an H-type strongly acidic cation exchange resin (Amberlite IR-120B, manufactured by Rhom & Haas Co.) and an OH-type strongly basic anion exchange resin (Amberlite IRA-400) to reduce the concentrations of calcium and magnesium ions to 3 mg/l or lower. Sodium isocyanurate dichloride in an amount of 20 mg/l and sodium sulfate in an amount of 150 mg/l were then added thereto. The pH of the resulting solution was in the range of 6.5 to 7.5.

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Stabilizing Solution

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Mother solution and replenisher being the same.

Formalin (37%)	2.0 ml
Polyoxyethylene p-monononylphenyl ether (average degree of polymerization: 10)	0.3 g
Disodium ethylenediaminetetraacetate	0.05 g
Add water to make	1.0 l
pH	5.0 to 8.0

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Table 3

Sample	DIR Compound in 4th Layer	Colored Coupler in 4th and 5th Layers	Relative Sensitivity	Color Turbidity		MTF Value (20 cycle/mm)			
				Condition A Fog+0.5	Condition B Fog+1.0	Yellow Image	Cyan Image		
105* (Comparison) D-29**		-	0.00	+0.03	+0.11	+0.02	+0.06	0.83	0.57
301 (Invention)	"	YC-1	0.02	-0.01	+0.04	-0.02	-0.01	0.85	0.58
302 (")	"	YC-25	0.03	-0.02	+0.04	-0.03	-0.01	0.85	0.58
303 (")	"	YC-27	0.02	-0.01	+0.04	-0.02	-0.01	0.85	0.58
304 (")	"	YC-52	0.01	0.00	+0.06	-0.01	+0.01	0.85	0.58
305 (")	"	YC-85	0.02	-0.01	+0.03	-0.02	-0.02	0.85	0.58
306 (")	"	YC-86	0.02	-0.01	+0.03	-0.02	-0.02	0.85	0.58
307 (")	"	YC-88	0.01	0.00	+0.04	-0.01	-0.01	0.85	0.58
308 (")	"	YC-89	0.01	0.00	+0.04	-0.01	-0.01	0.85	0.58

*: Sample 105 of JP-A-1-214849

**: Compound of the present invention which corresponds to Ex-10 of JP-A-1-214849

It is clear from Table 3 that Samples 301 to 308 of the present invention have higher sensitivity, cause less color turbidity irrespective of conditions A and B and more exposure amount and are excellent in sharpness in terms of MTF value than Sample 105 of JP-A-1-214849.

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

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1. A silver halide color photographic material comprising a support having thereon at least one red-sensitive silver halide emulsion layer containing a cyan coupler, at least one green-sensitive silver halide emulsion layer containing a magenta coupler and at least one blue-sensitive silver halide emulsion layer containing a yellow coupler, characterized in that the photographic material contains at least one compound represented by the following general formula (I) and at least one yellow colored cyan coupler:

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wherein A represents a coupler moiety which is released from (TIME)_n-B by a coupling reaction with an oxidation product of an aromatic primary amine developing agent; TIME represents a timing group which is bonded to the active coupling site of A and which releases B after release from A by the coupling reaction; B represents a group represented by the following general formulas (IIa), (IIb), (IIc), (IId), (IIe), (IIf), (IIg), (IIh), (Iii), (Iij), (IIk), (IIl), (IIm), (IIo) or (Iip); and n represents 0 or 1 and when n is 0, B is directly bonded to A:

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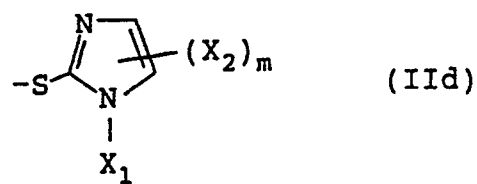
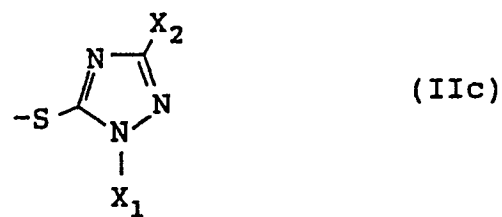
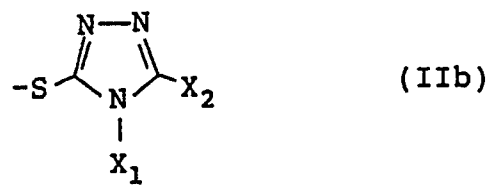
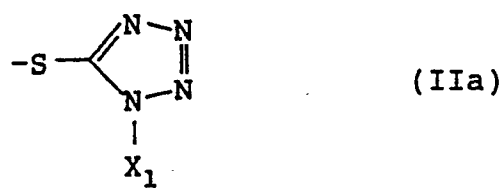
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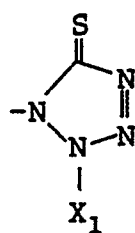
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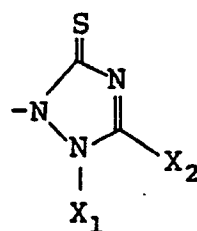
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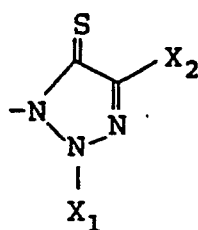




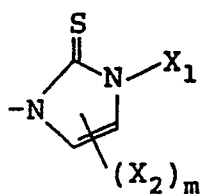
(IIe)



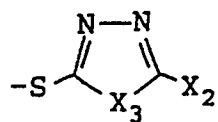
(IIf)



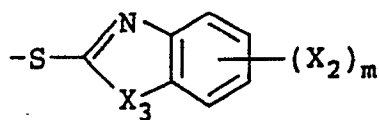
(IIg)



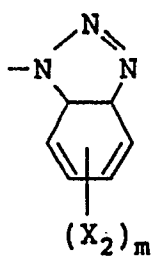
(IIh)



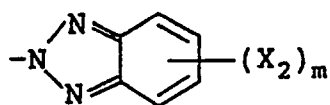
(IIIi)



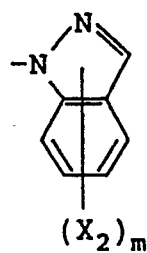
(IIj)



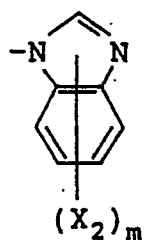
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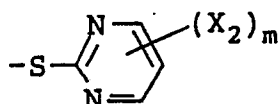
(IIl)



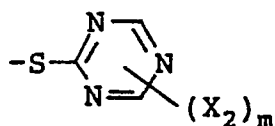
(IIIm)



(IIIn)



(IIIo)



(IIIp)

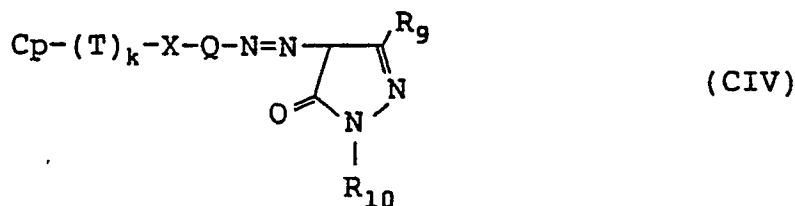
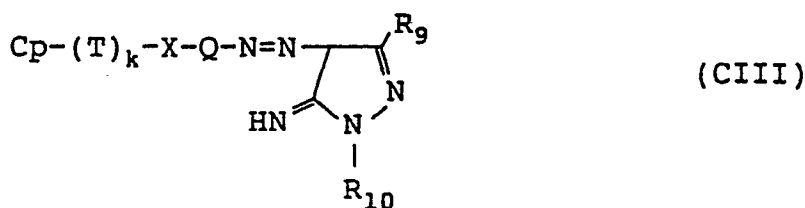
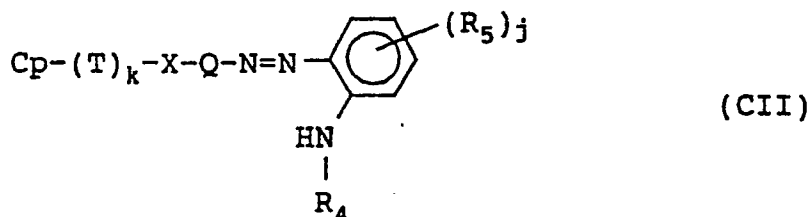
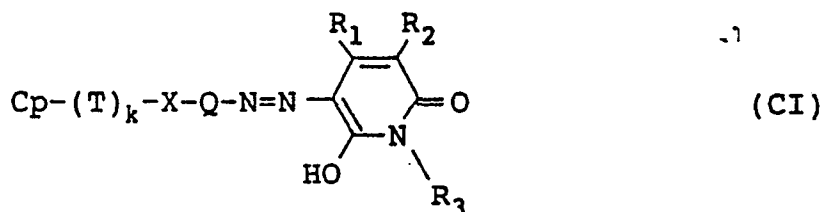
wherein X_1 represents a substituted or unsubstituted aliphatic group having 1 to 4 carbon atoms or a substituted phenyl group; X_2 represents a hydrogen atom, an aliphatic group, a halogen atom, a hydroxyl group, an alkoxy group, an alkylthio group, an alkoxy carbonyl group, an acylamino group, a carbamoyl group, a sulfonyl group, a sulfonamido group, a sulfamoyl group, an acyloxy group, a ureido group, a cyano group, a nitro group, an amino group, an alkoxy carbonylamino group, an aryloxy carbonyl group, or an acyl group; X_3 represents an oxygen atom, a sulfur atom or an imino group having not more than 4 carbon atoms; m represents an integer of 1 or 2; the total of carbon atoms in X_2 or $(X_2)_m$ groups is not more than 8; and when m is 2, the two X_2 groups may be the same or different groups.

2. The silver halide color photographic material as in claim 1, wherein A in formula (I) is a coupler moiety selected from the group consisting of a yellow coupler moiety, a magenta coupler moiety, a cyan coupler moiety and a coupler moiety which forms a coupling reaction product having substantially no absorption in the region of visible light.
3. The silver halide color photographic material as in claim 1, wherein the compound represented by formula (I) is incorporated in at least one of silver halide emulsion layers and a light-insensitive intermediate layer.
4. The silver halide color photographic material as in claim 1, wherein the ration of the compound represented by formula (I) to the principal coupler in the same layer when the compound is incorporated in a silver halide emulsion layer or in the adjacent silver halide emulsion layer containing a larger amount of silver halide when the compound is incorporated in a light-insensitive intermediate layer is 0.1 to 100 mol%.
5. The silver halide color photographic material as in claim 1, wherein the proportion of the compound represented by formula (I) to silver halide is 0.01 to 20 mol% per mol of silver halide in the same layer when the compound is incorporated in a silver halide emulsion layer or in the adjacent silver halide emulsion layer containing a larger amount of silver halide when the compound is incorporated in a light-insensitive intermediate layer.

6. The silver halide color photographic material as in claim 1, wherein the yellow colored cyan coupler has an absorption maximum at 400 nm to 500 nm and forms a cyan dye having an absorption maximum at 630 nm to 750 nm by coupling with the oxidation product of an aromatic primary amine developing agent.

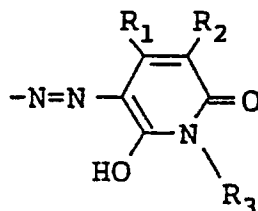
7. The silver halide color photographic material as in claim 1, wherein said yellow colored cyan coupler is capable of releasing a moiety of a water-soluble dye having a group selected from the group consisting of a 6-hydroxy-2-pyridone-5-ylazo group, a pyrazolone-4-ylazo group, a 2-acylamino-phenylazo group, a 2-sulfonamidophenylazo group, and 5-aminopyrazole-4-ylazo group by a coupling reaction with an oxidation product of an aromatic primary amine developing agent.

8. The silver halide color photographic material as in claim 1, wherein said yellow colored cyan coupler is selected from the group consisting of couplers represented by formulas (CI) to (CIV):



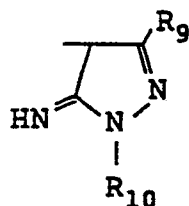
wherein Cp represents a cyan coupler moiety (T is bonded to the coupling site thereof); T represents a timing group; k represents 0 or 1; X represents an N-, O- or S-containing bivalent group which is bonded to (T)_k through the N, O or S atom and which also is bonded to Q; Q represents an arylene group or a bivalent heterocyclic group;

R₁ and R₂ each represents a hydrogen atom, a carboxyl group, a sulfo group, a cyano group, an alkyl group, a cycloalkyl group, an aryl group, a heterocyclic group, a carbamoyl group, a sulfamoyl group, a carbonamido group, a sulfonamido group or an alkylsulfonyl group; R₃ is a hydrogen atom, an alkyl group, a cycloalkyl group, an aryl group or a heterocyclic group;
 5 the group of



may be in the form of at least one of other tautomeric form thereof;

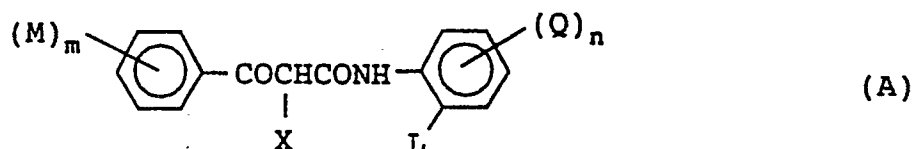
R₄ is an acyl group or a sulfonyl group; R₅ is a group which can be attached to the benzene ring; j is an integer of 0 to 4; when j is 2 or greater, the two or more R₅ groups may be the same or different; R₉ is a hydrogen atom, a carboxyl group, a sulfo group, a cyano group, an alkyl group, a cycloalkyl group, an aryl group, an alkoxy group, a cycloalkyloxy group, an aryloxy group, a heterocyclic group, a carbamoyl group, a sulfamoyl group, a carbonamido group, a sulfonamido group or an alkylsulfonyl group; R₁₀ is hydrogen atom, an alkyl group, a cycloalkyl group, an aryl group or a heterocyclic group;
 20 the group



may be in the tautomeric form thereof; and

said coupler has at least one water-solubilizing group at T, X, Q, R₁, R₂, R₃, R₄, R₅, R₉ and R₁₀.

9. The silver halide color photographic material as in claim 1, wherein said yellow colored cyan coupler is added to a silver halide emulsion layer or a light-insensitive intermediate layer adjacent thereto.
10. The silver halide color photographic material as in claim 1, wherein said yellow colored cyan coupler is added to a red sensitive silver halide emulsion layer.
11. The silver halide color photographic material as in claim 1, wherein said yellow colored cyan coupler is added in an amount of 0.005 to 0.30 g/m².
12. The silver halide color photographic material as in claim 1, wherein at least one yellow coupler contained in the blue-sensitive silver halide emulsion layer is a compound represented by the following general formula (A):



wherein M and Q each represents a group or an atom which can be attached to the benzene ring; L represents a hydrogen atom, a halogen atom or an aliphatic oxy group; m represents an integer of 0 to 5; n represents an integer of 0 to 4; X represents a group which can be eliminated by a coupling

reaction with an oxidation product of an aromatic primary amine developing agent; when m is 2 or greater, two or more M groups may be the same or different groups; when n is 2 or greater, two or more Q groups may be the same or different groups; and M, Q, L or X may be a single bond or a bivalent to tetravalent bonding group forming a compound having 2 to 4 of moieties of the yellow coupler represented by formula (A).

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13. The silver halide color photographic material as in claim 1, wherein the compound represented by formula (I) is incorporated in the layer having the same color sensitivity as that of the layer containing the yellow colored cyan coupler.

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14. The silver halide color photographic material as in claim 13, wherein the layer containing the compound represented by formula (I) is a red-sensitive layer.

15. The silver halide color photographic material as in claim 1, wherein the compound represented by formula (I) and the yellow colored cyan coupler are contained in the same red-sensitive layer.

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