⑲ Europäisches Patentamt
European Patent Office
Office européen des brevets

⑪ Publication number: **0 377 463**
A2

⑫ **EUROPEAN PATENT APPLICATION**

㉑ Application number: **90100163.6**

(51) Int. Cl.^{5}: **G03C 7/30**

㉒ Date of filing: **04.01.90**

㉚ Priority: **05.01.89 JP 746/89**

㊸ Date of publication of application:
11.07.90 Bulletin 90/28

(84) Designated Contracting States:
DE FR GB NL

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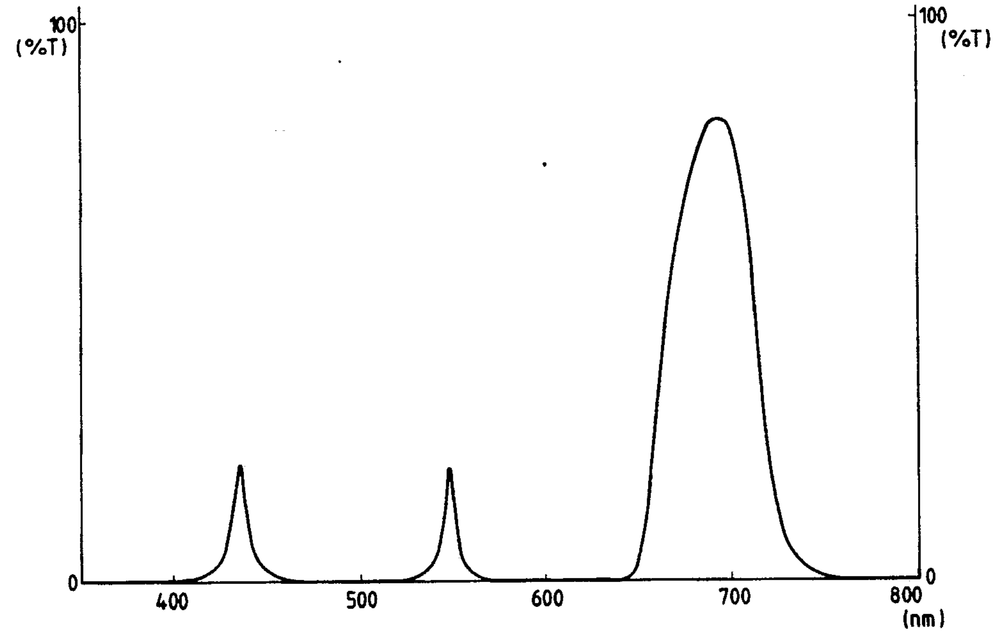
(54) **Silver halide color photographic material.**

(57) A silver halide color photographic material comprising at least one red-sensitive emulsion layer, at least one green-sensitive emulsion layer, at least one blue-sensitive emulsion layer and at least one yellow filter layer provided on a support. With the material, the relationship between the sensitivity (S_G^{480}) of the green-sensitive silver halide emulsion layer to monochromic light of 480 nm and the sensitivity (S_B^{480}) of the blue-sensitive silver halide emulsion layer to monochromic light of 480 nm is in the range of $-0.85 \leq S_G^{480} - S_B^{480} \leq 0.2$ when measured after the silver halide color photographic material having ISO sensitivity of S is uniformly exposed to white light of 2/S lux•sec and the optical density of the yellow filter layer at peak wavelength is 1.0 or above.

FIG. 1



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SILVER HALIDE COLOR PHOTOGRAPHIC MATERIAL

FIELD OF THE INVENTION

This invention relates to a silver halide color photographic material. More particularly the invention relates to a silver halide color photographic material which provides excellent high-fidelity color reproducibility of primary colors and neutral tints with high chroma.

BACKGROUND OF THE INVENTION

Multi-layer silver halide color photographic materials generally comprise a red-sensitive silver halide emulsion layer containing a nondiffusing cyan dye image forming coupler, a green-sensitive silver halide emulsion layer containing a nondiffusing magenta dye image forming coupler and a blue-sensitive silver halide emulsion layer containing a nondiffusing yellow dye image forming coupler. These layers are laminated onto a support such as a cellulose ester support or a polyester support.

There have been many efforts to improve the color reproducibility of the color photographic materials. For example, colored couplers have been developed in the field of color negative films which remove unnecessary absorption of the colored dyes of couplers. JP-A-50-2537 (the term "JP-A" as used herein means an "unexamined published Japanese patent application") corresponding to U.S. Patent 3,990,899 discloses that the interlaminar restraining effect is increased and chroma is improved by adding couplers which are reacted with the oxidation products of developing agents in p-phenylenediamine color developing solutions to release restrainers.

However, currently used color photographic materials have some disadvantages related to color reproducibility. One of them is that the colors of hue between blue and green (e.g., greenish blue, bluish green, etc) differ from the hue of the actual object. For example, blue is not always clearly distinguishable from green.

With the purposes of reproducing color with high fidelity and providing photographic materials for photography, in which color reproducibility does not vary significantly when used with various light sources, U.S. Patent 3,672,898 discloses a method wherein the spectral sensitivity distributions of the blue-sensitive, green-sensitive and red-sensitive silver halide emulsions are limited to certain ranges.

The present inventors have examined various combinations of the above-described techniques. However, it was determined that fully satisfactory photographic materials could not be obtained in terms of providing acceptable chroma as well as fidelity of hue. It is believed that (1) the color chroma is lowered when spectral sensitivity is set to the ranges described in U.S. Patent 3,672,898. Furthermore, (2) when the overlapping zones of spectral sensitivity distributions of blue-sensitive, green-sensitive and red-sensitive silver halide emulsion layers are restrained from one another, the spectral sensitivity distributions are distorted. As a result, there is a difference in hue when DIR compounds such as those described in JP-A-50-2537, are used to compensate for a lowering in chroma in the above item (1), or when masking is enhanced with colored couplers to improve color chroma.

SUMMARY OF THE INVENTION

It is therefore a general object of the present invention to provide a novel multi-layer silver halide color photographic material.

Another object of the present invention is to provide a silver halide color photographic material which provides excellent high-fidelity color reproducibility of primary colors and neutral tints, particularly those colors between blue and green with high color chroma.

The above-described objects of the present invention can be achieved by providing a silver halide color photographic material comprising at least one red-sensitive emulsion layer, at least one green-sensitive emulsion layer, at least one blue-sensitive emulsion layer, and at least one yellow filter layer provided on a support, wherein the relationship between the sensitivity (S_G^{480} of the green-sensitive silver halide emulsion layer to monochromatic light of 480 nm and the sensitivity (S_B^{480}) of the blue-sensitive silver halide emulsion layer to monochromatic light of 480 nm is in the range of 0.85 $\leqq S_G^{480} - S_B^{480} \leqq 0.2$, when measured after the silver halide color photographic material having ISO sensitivity of S is uniformly exposed to white light of 2/S lux•sec and the optical density of the yellow filter layer at peak wavelength is 1.0 or above.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a graph showing the spectral characteristics of blue, green and red filters for use in the measurement of density.

DETAILED DESCRIPTION OF THE INVENTION

The determination and definition of S_G^{480} and S_B^{480} will be described in detail below. The ISO sensitivity of color photographic materials is determined according to the method described in ISO 5800-1979 (E). In particular, a photographic material to be tested with an exposure amount of 2×1/S lux•sec for a period of the same exposure time as in the determination of ISO sensitivity, is uniformly exposed by using a light source of the same relative spectral energy as that used for the determination of ISO sensitivity of a color photographic material having ISO sensitivity of S. The test is carried out inside a room under such conditions that the temperature is 20±5°C and the relative humidity is 60±10%. The photographic material to be tested is left to stand under the above conditions for at least one hour and then used. The photographic material is exposed by changing the illuminance with monochromatic light of 500 nm within one hour after uniform exposure. As the exposure device, those of the non-intermittent exposure illuminance scale type, etc., are used as in the measurement of ISO sensitivity. The change of illuminance is made through a light modulator such as an optical wedge. The term "monochromatic light of 480 nm" as used herein refers to light in which the peak wavelength of relative spectral energy is 480 ±2 nm with a half width of not more than 20 nm. The monochromatic light can be obtained by combining a conventional light source for exposure such as a tungsten lamp with a commercially available interference filter.

After exposure to monochromatic light, the photographic material to be tested is kept at a temperature of 20±5°C and a relative humidity of 60±10% till development. Development is completed after 30 minutes or longer from the completion of exposure, but within 6 hours after the exposure. Processing is to be made by procedures recommended by film manufactures. Density is measured by each of blue, green and red filters having the spectral characteristics shown in Figure 1. Photographic sensitivities, S_G^{480} and S_B^{480}, can be calculated by the following formulae:

$$S_G^{480} = \log_{10} \frac{1}{H_G^{480}}$$

$$S_B^{480} = \log_{10} \frac{1}{H_B^{480}}$$

wherein H_G^{480} lux•sec and$_B^{480}$ lux•sec represent each exposure amount which give a density of minimum density (after uniform exposure) +0.6.

For accomplishing high-fidelity reproduction of bluish green, while maintaining high chroma, it was found, after many studies on the sensitivity, gradation and spectral sensitivity of the green-sensitive layer and blue-sensitive layer of color photographic materials, referring to U.S. Patent 3,672,898, JP-A-50-2537, etc., that $S_G^{480} - S_B^{480}$ should be set to give a particular range by sensitometry of monochromatic light of 480 nm after the above-described uniform exposure. That is, $S_G^{480} - S_B^{480}$ should be $-0.85 \leqq S_G^{480} - S_B^{480} \leqq 0.2$ preferably $-0.75 \leqq S_G^{480} - S_B^{480} \leqq 0$, and more preferably $-0.70 \leqq S_G^{480} - S_B^{480} \leqq -0.1$.

In order to achieve the appropriate value of $S_G^{480} - S_B^{480}$ for the present invention, there can be used various techniques. For example, there can be used emulsions containing sensitizing amounts of supersensitizing agents and cyanine dye forming J-associated material (see JP-A-1-223441), or suitable sensitizing dyes can be selected, or various filter layers can be introduced.

It is preferred that silver halide emulsions used for the blue-sensitive emulsion layer of the present invention are of a monodisperse system.

Monodisperse silver halide grains have good graininess and give an image having excellent sharpness when the size range causes little light scattering. Monodisperse silver halide grains are described, for example, in JP-A-54-48521, JP-A-54-99419, JP-A-56-16124, JP-A-56-78831, U.S. Patent No. 4,444,877, JP-A-57-182730, JP-A-58-49938, JP-A-58-37635, U.S. Patent No. 4,446,228, JP-A-58-106532, JP-A-58-107530, JP-A-58-126531, JP-A-58-149037, JP-A-59-10947, JP-A-59-29243, JP-A-59-72440, JP-A-59-140443, JP-A-59-148049, JP-A-59-177535, JP-A-59-152438, etc.

It is preferred to use an emulsions wherein the amount of ultra-tabular (ultra-plate form) silver halide grains having a diameter of at least 5 times the thickness of grain, accounts for at least 50% of the total projected area of the total grains.

Spectral sensitization is preferably carried out with methine dyes, etc. Among conventional sensitizing dyes, cyanine dyes forming a J-associated material are particularly preferred.

Silver halide emulsions used in the green-sensitive emulsion layer of the present invention can be spectral-sensitized by any conventional method. Examples of suitable dyes which can be used in the present invention include cyanine dyes, merocyanine dyes, complex cyanine dyes, complex merocyanine dyes, holopolar cyanine dyes, hemicyanine dyes, styryl dyes and hemioxonol dyes. Among these, particularly useful dyes are cyanine dyes, merocyanine dyes and complex merocyanine dyes. These dyes may have any nucleus which is conventionally applied to the cyanine dyes as a basic heterocyclic nucleus. Examples of such a nucleus include a pyrroline nucleus, oxazoline nucleus, thiazoline nucleus, pyrrole nucleus, oxazole nucleus, thiazole nucleus, selenazole nucleus, imidazole nucleus, tetrazole nucleus, pyridine nucleus; nucleui formed by fusing an alicyclic hydrocarbon ring with any of the above-described heterocyclic nucleui; and nuclei formed by fusing an aromatic hydrocarbon ring with the above-described heterocyclic nucleui such as an indolenine nucleus, benzindolenine nucleus, indole nucleus, benzoxazole nucleus, naphthoxazole nucleus, benzthiazole nucleus, naphothiazole nucleus, benzselenazole nucleus, benzimidazole nucleus and quinoline nucleus. These nuclei may be substituted on carbon atoms.

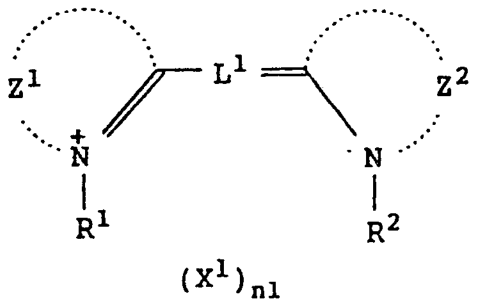
Merocyanine dyes or complex merocyanine dyes may have nuclei having a keto-methylene structure. Examples of such nuclei include five-membered to six-membered heterocyclic nuclei such as a pyrazoline-5-one nucleus, thiohydantoin nucleus, 2-thiooxazolidine-2,4-dione nucleus, thiazolidine-2,4-dione nucleus, rhodanine nucleus and thiobarbituric acid nucleus.

Specific examples of useful sensitizing dyes include those described in German Patent No. 929,080, U.S. Patent Nos. 2,231,658, 2,493,748, 2,503,776, 2,519,001, 2,912,323, 3,656,959, 3,672,897, 3,694,217, 4,025,349 and 4,046,572. U.K. Patent No. 1,242,588, JP-B-44-14030 (the term "JP-B" as used herein means an "examined Japanese patent publication") and JP-B-52-24844.

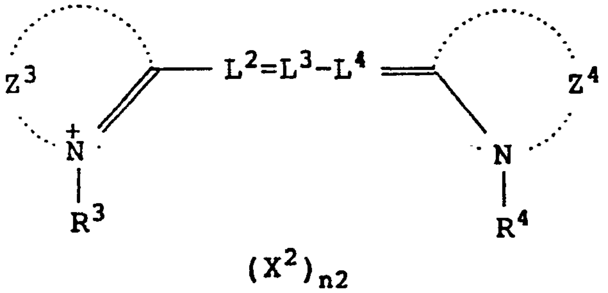
The sensitizing dyes may be used either alone or in combination. Combinations of sensitizing dyes are often used for the purpose of supersensitization. Typical examples of such combinations are described in U.S. Patent Nos. 2,688,545, 2,977,229, 3,397,060, 3,522,052, 3,527,641, 3,617,293, 3,628,964, 3,666,480, 3,672,898, 3,679,428, 3,703,377, 3,769,301, 3,814,609, 3,837,862 and 4,026,707, U.K. Patent Nos. 1,344,281 and 1,507,803, JP-B-43-4936, JP-B-53-12375, JP-A-52-110618 and JP-A-52-109925.

In addition to the sensitizing agent, emulsions may contain a dye which itself does not have a spectral sensitizing effect or a substance which does not substantially absorb visible light, but has a supersensitization activity. Examples of such dyes or substances include aminostyryl compounds substituted by a nitrogen containing heterocyclic group (see. e.g., those described in U.S. Patent Nos. 2,933,390 and 3,635,721), aromatic organic acid-formaldehyde condensates (see e.g., those described in U.S. Patent No. 3,743,510), cadmium salts and azaindene compounds. The combinations described in U.S. Patent Nos. 3,615,613, 3,615,641, 3,617,295 and 3,635,721 are particularly preferred.

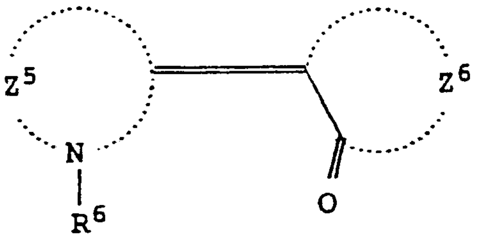
It is preferred that sensitizing dyes used in the green-sensitive emulsion layer of the present invention contain at least one sensitizing dye represented by the following general formulae (S-1) to (S-VI).


(S-I)

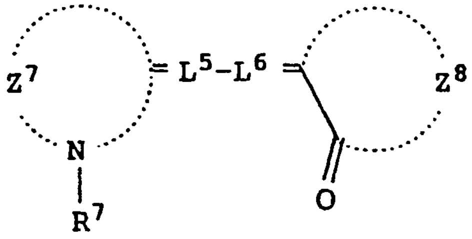
In formula (S-1), Z^1 and Z^2 each represent an appropriate atomic group for the formation of a nucleus originating from tellurazole nucleus, benztellurazole nucleus, naphthotellurazole nucleus, quinoline nucleus, benzoxazole nucleus, naphthoxazole nucleus, benzthiazole nucleus, naphthothiazole nucleus, benzselenazole nucleus or naphthoselenazole nucleus; R^1 and R^2 each represent an alkyl group, preferably at least one of R^1 and R^2 is an alkyl group substituted by sulfo group or carboxyl group; L^1 represents methine group; X^1 represents an anion; and n^1 represents 0 or 1 provided that when an inner salt is formed, n^1 is 0.


(S-II)

In formula (S-II), Z^3 and Z^4 each represent an appropriate atomic group for the formation of a nucleus originating from tellurazole nucleus, benztellurazole nucleus, naphthotellurazole nucleus, benzoxazole nucleus, naphthoxazole nucleus, benzimidazole nucleus, naphthoimidazole nucleus, oxazolidine nucleus, oxazole nucleus, thiazolidine nucleus or selenazolidine nucleus; R^3 and R^4 have the same definition as R^1 and R^2; L^2, L^3 and L^4 have the same defination as L^1; X^2 has the same meaning as in X^1; and n^2 has the same meaning as n^1.

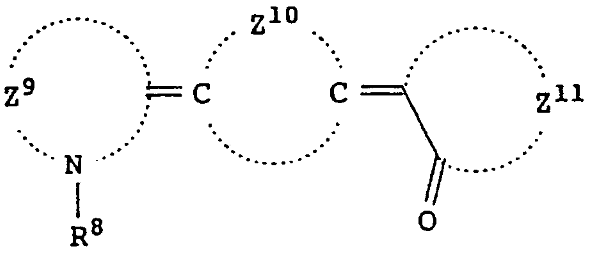

(S-III)

In formula (S-III), Z^5 represents an appropriate atomic group for the formation of a nucleus originating from tellurazole nucleus, benztellurazole nucleus, naphthotellurazole nucleus, benzthiazole nucleus, naphthothiazole nucleus, benzselenazole nucleus, naphthoselenazole nucleus, benzoxazole nucleus, naphthoxazole nucleus, quinoline nucleus, pyridine nucleus, thiazole nucleus or pyrrolidine nucleus; Z^6 represents an appropriate atomic group for the formation of a nucleus originating from rhodanine nucleus, 2-thioxooxazolidine nucleus or thiohydantoin nucleus; and R^6 represents an alkyl group.



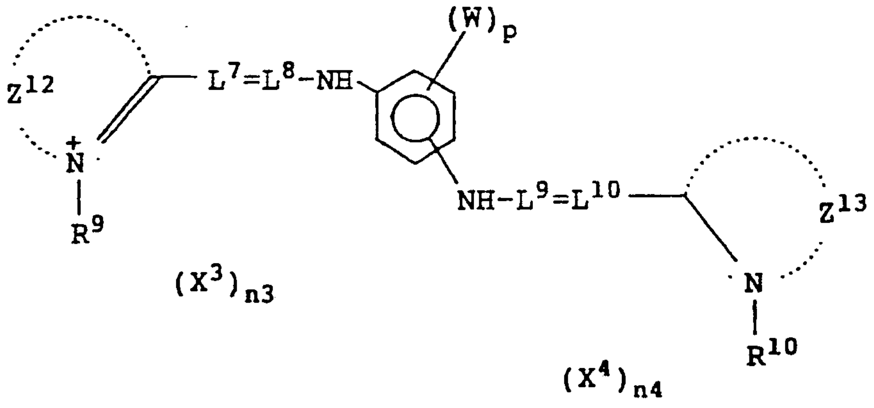
(S-IV)

In formula (S-IV), Z^7 represents an appropriate atomic group for the formation of a nucleus originating from tellurazole nucleus, benztellurazole nucleus, naphthotellurazole nucleus, oxazole nucleus, oxazolidine nucleus, isoxazole nucleus, benzoxazole nucleus, naphthoxazole nucleus, thiazolidine nucleus, selenazolidine nucleus, benzthiazole nucleus, naphthothiazole nucleus, benzimidazole nucleus, naphthoimidazole nucleus, pyrrolidine nucleus or tetrazole nucleus; Z^8 represents an appropriate atomic group for the formation of a nucleus originating from rhodanine nucleus, thiohydantoin nucleus, pyrazolone nucleus, thiobarbituric acid nucleus, pyrazolone nucleus, 2-thioxooxazolidinone nucleus or barbituric nucleus; L^5 and L^6 have the same meaning as L^1; and R^7 has the same definition as R^6.



(S-V)

In formula (S-V), Z^9 represents an appropriate atomic group for the formation of a nucleus originating from tellurazole nucleus, benztellurazole nucleus, naphthotellurazole nucleus, thiazolidine nucleus or selenazolidine nucleus; Z^{10} and Z^{11} each represent an appropriate atomic group for the formation of a nucleus originating from rhodanine nucleus; and R^8 has the same meaning as R^6.



(S-IV)

In formula (S-VI), Z^{12} and Z^{13} each represent an appropriate atomic group for the formation of a nucleus originating from oxazolidine nucleus, oxazole nucleus, benzoxazole nucleus, naphthooxazole nucleus, thiazolidine nucleus, thiazole nucleus, benzthiazole nucleus, naphthothiazole nucleus, selenazolidine nucleus, selenazole nucleus, benzselenazole nucleus, naphthoselenazole nucleus, tellurazole nucleus, benztellurazole nucleus or naphthotellurazole nucleus; R^9 and R^{10} have the same as R^1 and R^2; L^7, L^8, L^9 and L^{10} have the same meaning as L^1; X^3 and X^4 have the same meaning as X^1; n^3 and n^4 have the same meaning as n^1; W represents a hydrogen atom, carboxyl group or sulfo group; and p represents an integer of from 1 to 4.

The compounds represented by the formulae (S-I) to (S-VI) will be illustrated in more detail below.

R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8, R^9 and R^{10} are each preferably hydrogen atom, an unsubstituted alkyl group having not more than 18 carbon atoms (e.g., methyl, ethyl, propyl, butyl, pentyl, octyl, decyl, dodecyl, octadecyl), a substituted alkyl group having not more than 18 carbon atoms (examples of substituent groups include carboxyl group, sulfo group, cyano group, halogen (e.g., fluorine, chlorine, and bromine), hydroxyl group, and alkoxycarbonyl group having not more than 8 carbon atoms (e.g., methoxycarbonyl, ethoxycarbonyl, phenoxycarbonyl, and benzyloxycarbonyl), an alkoxy group having not more than 8 carbon atoms (e.g., methoxy, ethoxy, benzyloxy, and phenethyloxy), a monocyclic aryloxy group having not more than 10 carbon atoms (e.g., phenoxy, and p-tolyloxy), an acyloxy group having not more than 3 carbon atoms (e.g., acetyloxy, and propionyloxy), an acyl group having not more than 8 carbon atoms (e.g., acetyl, propionyl, benzoyl, and mesyl), a carbamoyl group (e.g., carbamoyl and N,N-dimethylcarbamoyl, morpholinocarbamoyl, and piperidinocarbamoyl), a sulfamoyl group (e.g., sulfamoyl, N,N-dimethylsulfamoyl, morpholinosulfonyl, and piperidinosulfonyl) and an aryl group having not more than 10 carbon atoms (e.g., phenyl, 4-chlorophenyl, 4-methylphenyl, and α-naphthyl), an aryl group (e.g., phenyl, and 2-naphthyl), a substituted aryl group (e.g., 4-carboxyphenyl, 4-sulfophenyl, 3-chlorophenyl, 3-chlorophenyl, and 3-methylphenyl) or a heterocyclic group (e.g., 2-pyridyl, and 2-thiazolyl).

Among the above, an unsubstituted alkyl group (e.g., methyl, and ethyl) and a sulfoalkyl group (e.g., 2-sulfoethyl, 3-sulfopropyl, and 4-sulfobutyl) are particularly preferred.

As metal atoms capable of forming a salt with R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8, R^9 or R^{10}, alkali metals are particularly preferred. As organic compounds, pyridines and amines are preferred.

Examples of nuclei formed by Z^1, Z^2, Z^3, Z^4, Z^5, Z^7, Z^9, Z^{12} and Z^{13} include thiazole nuclei such as thiazole, 4-methylthiazole, 4-phenylthiazole, 4,5-di-methylthiazole, and 4,5-diphenylthiazole; benzthiazole nuclei such as benzthiazole, 4-chlorobenzthiazole, 5- chlorobenzthiazole, 6-chlorobenzthiazole, 5-nitrobenzthiazole, 4-methylbenzthiazole, 5-methylbenzthiazole, 6-methylbenzthiazole, 5-bromobenzthiazole, 6-bromobenzthiazole, 5-iodobenzthiazole, 5-phenylbenzthiazole, 5-methoxybenzthiazole, 6-methoxybenzthiazole, 5-ethoxybenzthiazole, 5-ethoxycarbonylbenzthiazole, 5-carboxybenzthiazole, 5-phenethylbenzthiazole, 5-fluorobenzthiazole, 5-chloro-6-methylbenzthiazole, 5,5-dimethylbenzthiazole, 5,6-dimethoxybenzthiazole, 5-hydroxy-6-methylbenzthiazole, tetrahydrobenzthiazole, and 4-phenylbenzthiazole; naphthothiazole nuclei such as naphtho[2,1-d]thiazole, naphtho[1,2-d]thiazole, naphtho-[2,3-d]thiazole, 5-methoxynaphtho-[1,2-d]thiazole, 6-methoxynaphtho[1,2-d]thiazole, 7-ethoxynaphtho[2,1-d]thiazole, 8-methoxynaphtho[2,1-d]-thiazole and 5-methoxynaphtho[2,3-d]thiazole; thiazoline nuclei such as thiazoline, 4-methylthiazoline and 4-nitrothiazoline; oxazole nuclei such as oxazole nuclei (e.g., oxazole, 4-methyloxazole, 4-nitrooxazole, 5-methyloxazole, 4-phenyloxazole, 4,5-diphenyloxazole, and 4-ethyloxazole), benzoxazole nuclei (e.g., benzoxazole, 5-chlorobenzoxazole, 5-methylbenzoxazole, 5-bromobenzoxazole, 5-fluorobenzoxazole, 5-phenylbenzoxazole, 5-methoxybenzoxazole, 5-nitrobenzoxazole, 5-trifluoromethylbenzoxazole, 5-hydroxybenzoxazole, 5-carboxybenzoxazole, 6- methylbenzoxazole, 6-chlorobenzoxazole, 6-nitrobenzoxazole, 6-methoxybenzoxazole, 6-hydroxybenzoxazole, 5,6-dimethylbenzoxazole, 4,6-dimethylbenzoxazole, and 5-ethoxybenzoxazole) and naphthoxazole nuclei (e.g., naphtho[2,1-d]oxazole, naphtho[1,2-d]oxazole, naphtho[2,3-d]oxazole, and 5-nitronaphtho[2,1-d]oxazole); oxazoline nuclei such as 4,4-dimethyloxazoline; selenazole nuclei such as selenazole nuclei (e.g., 4-methylselenazole, 4-nitroselenazole, and 4-phenylselenazole), benzselenazole nuclei (e.g., benzselenazole, 5-chlorobenzselenazole, 5-nitrobenzselenazole, 5-methoxybenzselenazole, 5-hydroxybenzselenazole, 6-nitrobenzselenazole, 5-chloro-6-nitrobenzselenazole, and 5,6-dimethylbenzselenazole) and naphthoselenazole nuclei (e.g., naphtho[2,1-d]selenazole, and naphtho[1,2-d]selenazole); selenazoline nuclei such as selenazoline, 4-methylselenazoline; tellurazole nuclei such as tellurazole nuclei (e.g., tellurazole, 4-methyltellurazole, and 4-phenyltellurazole), benztellurazole nuclei (e.g., benztellurazole, 5-chlorobenztellurazole, 5-methylbenztellurazole, 5,6-dimethylbenztellurazole, and 6-methoxybenztellurazole) and naphthotellurazole nuclei (e.g., naphtho[2,1-d]tellurazole, and naphtho[1,2-d]tellurazole); tellurazoline nuclei such as tellurazoline; and 4-methyltellurazoline; 3,3- dialkylindolenine nuclei such as 3,3-dimethylindolenine, 3,3-diethylindolenine, 3,3-dimethyl-5-cyanoindolenine, 3,3-dimethyl-6-nitroindolenine, 3,3-dimethyl-5-nitroindolenine, 3,3-dimethyl-5-methoxyindolenine, 3,3,5-trimethylindolenine, and 3,3,5-dimethyl-5-chloroindolenine; imidazole nuclei such as imidazole nuclei (e.g., 1-alkylimidazole, and 1-alkyl-4-phenylimidazole) benzimidazole nuclei (e.g., 1-alkylbenzimidazole, 1-alkyl-5-chlorobenzimidazole, 1-alkyl-5,6-dichlorobenzimidazole, 1-alkyl-5-methoxybenzimidazole, 1-alkyl-5-cyanobenzimidazole, 1-alkyl-5-fluorobenzimidazole, 1-alkyl-5-trifluoromethylbenzimidazole, 1-alkyl-6-chloro-5-cyanobenzimidazole, 1-alkyl-6-chloro-5-trifluoromethylbenzimidazole, 1-allyl-5,6-dichlorobenzimidazole, 1-allyl-5-chlorobenzimidazole, 1-arylbenzimidazole, 1-aryl-5-chlorobenzimidazole, 1-aryl-5,6-dichlorobenzimidazole, 1-aryl-5-methoxybenzimidazole, and 1-aryl-5-cyanobenzimidazole) and naphthoimidazole nuclei (e.g., 2-alkylnaphtho[1,2-d]-imidazole, and 2-arylnaphtho[1,2-d]imidazole) with the above-described alkyl groups having from 1 to 8 carbon atoms (e.g., an unsubstituted alkyl group such as methyl, ethyl, propyl, isopropyl and butyl and a hydroxylalkyl group such as 2-hydroxyethyl and 3-hydroxypropyl with methyl and ethyl being particularly preferred, and examples of the above- described aryl groups including phenyl, a halogen (e.g., chlorine-substituted phenyl, an alkyl (e.g., methyl)-substituted phenyl and an alkoxy (e.g., methoxy)-substituted phenyl]; pyridine nuclei such as 2-pyridine, 4-pyridine, 5-methyl-2-pyridine, 3-methyl-4-pyridine; quinoline nuclei such as quinoline nuclei (e.g., 2-quinoline, 3-methyl-2-quinoline, 5-ethyl-2-quinoline, 6-methyl-2-quinoline, 6-nitro-2-quinoline, 8-fluoro-2-quinoline, 6-methoxy-2-quinoline, 6-hydroxy-2-quinoline, 8-chloro-2-quinoline, 4-quinoline, 6-ethoxy-4-quinoline, 6-nitro-4-quinoline, 8-chloro-4-quinoline, 8-fluoro-4-quinoline, 8-methyl-4-quinoline, 8-methoxy-4-quinoline, 6-methyl-4-quinoline, 6-methoxy-4-quinoline, 6-chloro-4-quinoline) and isoquinoline nuclei (e.g., 6-nitro-1-isoquinoline, 3,4-dihydro-1-isoquinoline, 6-nitro-3-isoquinoline); tetrazole nuclei; and pyrrolidine nuclei.

Examples of nuclei formed by Z^6, Z^8, Z^{10} and Z^{11} include 2-pyrazoline-5-one, pyrazolidine-3,5-dione, imidazoline-5-one, hydantoin, 2- or 4-thiohydantoin, 2-iminooxazolidine-4-one, 2-oxazoline-5-one, 2-thiooxazolidine-2,4-dione, isoxazoline-5-one, 2-thiazoline-4-one, thiazolidine-4-one, thiazolidine-2,4-dione, rhodanine, thiazolidine-2,4-dithione, isorhodanine, indane-1,3-dione, barbituric acid and 2-thiobarbituric acid.

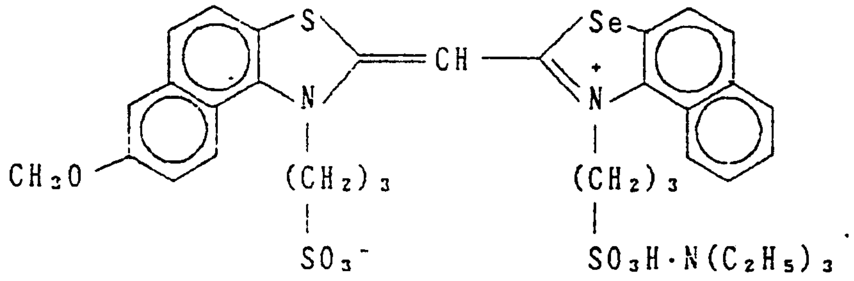
Preferred examples of substituent groups attached to the nitrogen atoms which constitute members of the nuclei include hydrogen atom, an alkyl group having from 1 to 18 carbon atoms, preferably 1 to 7 carbon atoms, more preferably 1 to 4 carbon atoms (e.g., methyl, ethyl, propyl, isopropyl, butyl, isobutyl, hexyl, octyl, dodecyl, and octadecyl), a substituted alkyl group (e.g., an aralkyl group such as benzyl, and 2-phenylethyl), a hydroxyalkyl group (e.g., 2-hydroxyethyl, and 3-hydroxypropyl), a carboxyalkyl group (e.g., 2-carboxyethyl, 3-carboxypropyl, and 4-carboxybutyl, carboxymethyl), an alkoxyalkyl group (e.g., 2-methoxyethyl, and 2-(2-methoxyethoxy)ethyl), a sulfoalkyl group (e.g., 2-sulfoethyl, 3-sulfopropyl, 3-sulfobutyl, 4-sulfobutyl, 2-(3-sulfopropoxy)ethyl, 2-hydroxy-3-sulfopropyl, and 3-sulfopropoxyethoxyethyl), a sulfatoalkyl group (e.g., 3-sulfatopropyl, and 4-sulfatobutyl) a heterocyclic ring-substituted alkyl group (e.g., 2-(pyrrolidine-2-one-1-yl)ethyl, tetrahydrofurfuryl, and 2-morpholinoethyl), 2-acetoxyethyl, carbomethoxymethyl, 2-methanesulfonylaminoethyl, allyl group, an aryl group (e.g., phenyl, and 2-naphthyl), a substituted aryl group (e.g., 4-carboxyphenyl, 4-sulfophenyl, 3-chlorophenyl, and 3-methylphenyl) and a heterocyclic group (e.g., 2-pyridyl, and 2-thiazolyl).

L^1, L^2, L^3, L^4, L^5, L^6, L^7, L^8, L^9 and L^{10} each represent a methine group which may be optionally substituted by a substituted or unsubstituted alkyl group (e.g., methyl, and ethyl), a substituted or unsubstituted aryl group (e.g., phenyl) or halogen (e.g., chlorine, and bromine). The methine groups may combine together to form a ring or may form a ring together with auxochrome.

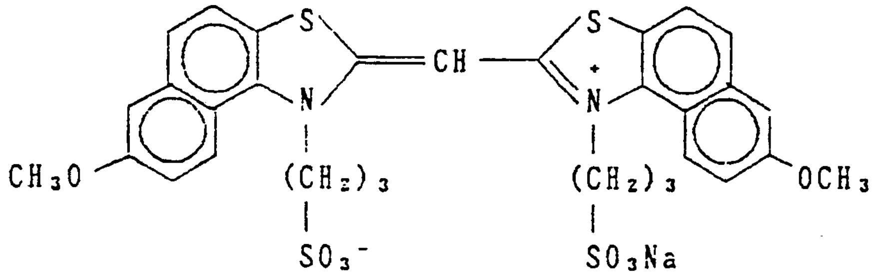
The anion represented by X^1, X^2, X^3 and X^4 may be any of an inorganic anion or an organic anion. Examples of anions include halogen anions (e.g., fluorine ion, chlorine ion, bromine ion, and iodine ion), substituted arylsulfonate ions (e.g., p-toluenesulfonate ion, and p-chlorobenzenesulfonate ion), aryldisulfonate ions (e.g., 1,3-benzenesulfonate ion, 1,5-naphthalenedisulfonate ion, and 2,6-naphthalenedisulfonate ion), alkylsulfate ions (e.g., methylsulfate ion), sulfate ions, thiocyanate ions, perchlorate ions, tetrafluoroborate ions, picrate ions, acetate ions and trifluoromethanesulfonate ions.

Particularly preferred examples of the dyes include the following compounds.

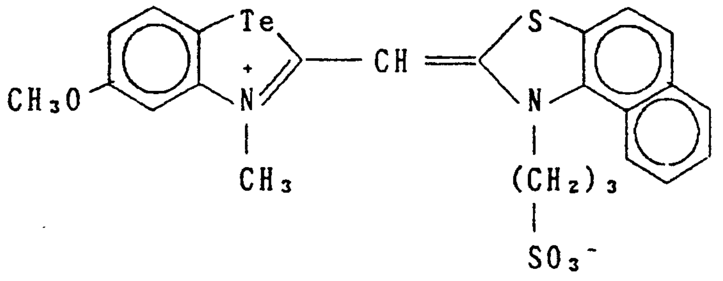
S - 1.



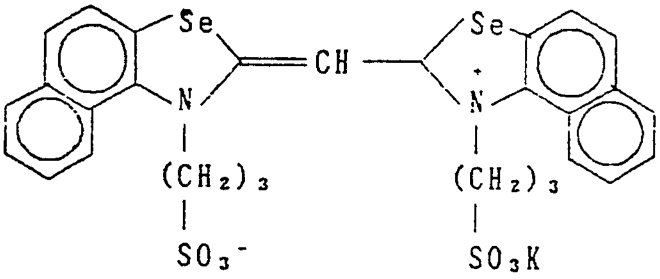
S - 2.



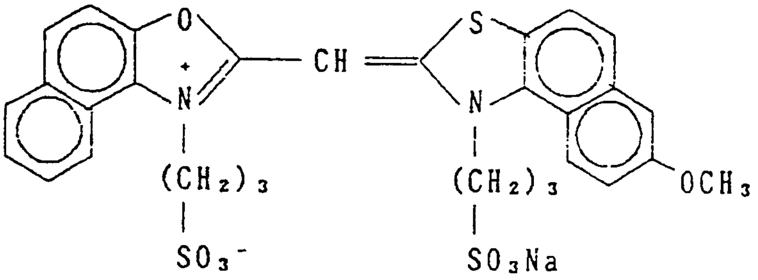
S - 3.



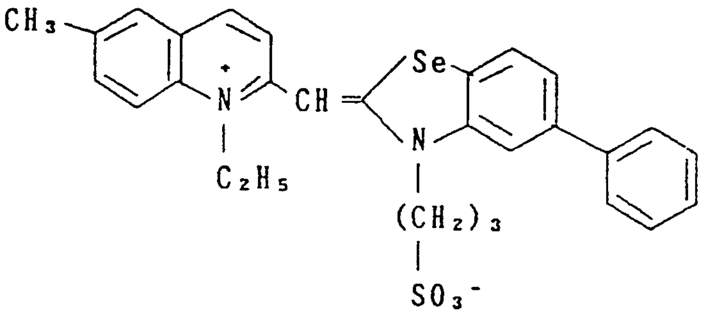
S－4.


Se
CH
Se
N
N
(CH2)3
(CH2)3
SO3-
SO3K

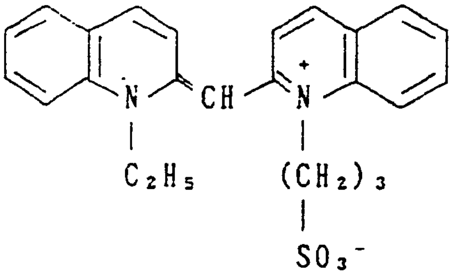
S－5.


O
CH
S
N
N
(CH2)3
(CH2)3
OCH3
SO3-
SO3Na

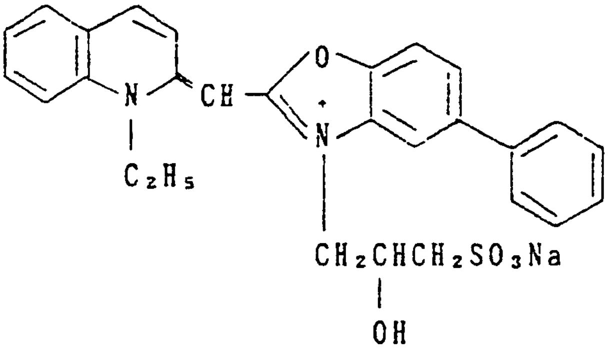
S－6.


CH3
N
CH
Se
N
C2H5
(CH2)3
SO3-

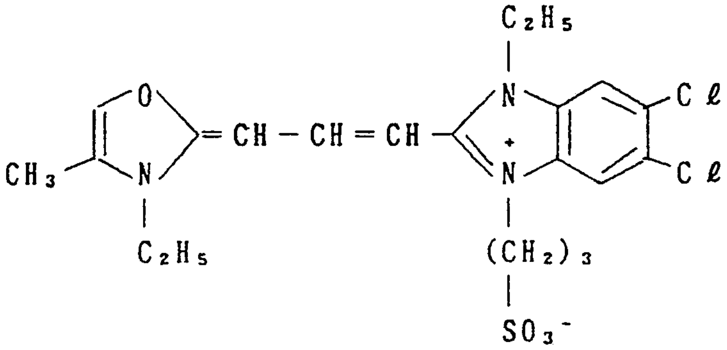
S - 7



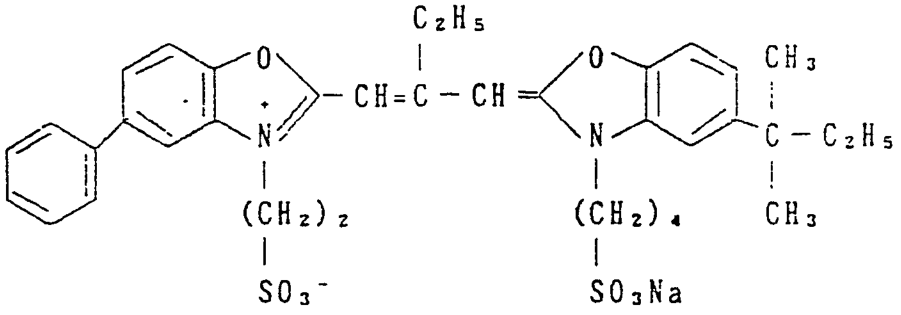
S - 8 .



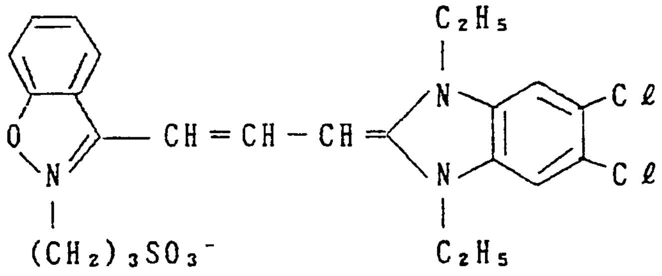
S - 9 .



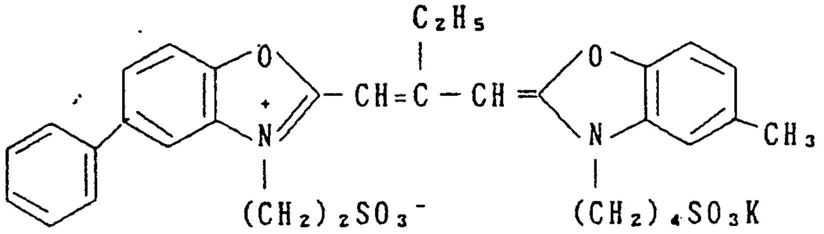
S-10.



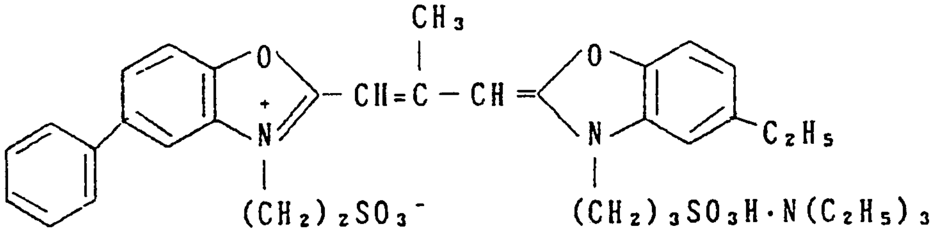
S-11.



S-12.



S-13.



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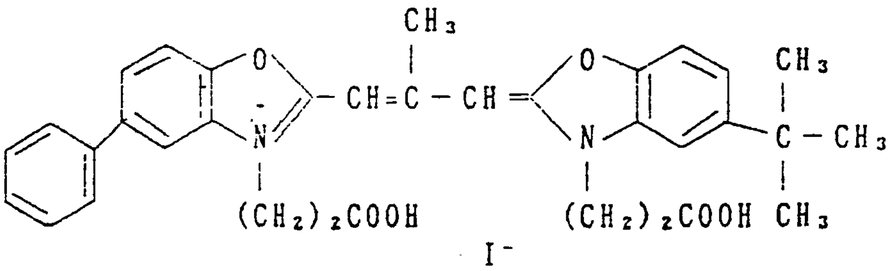
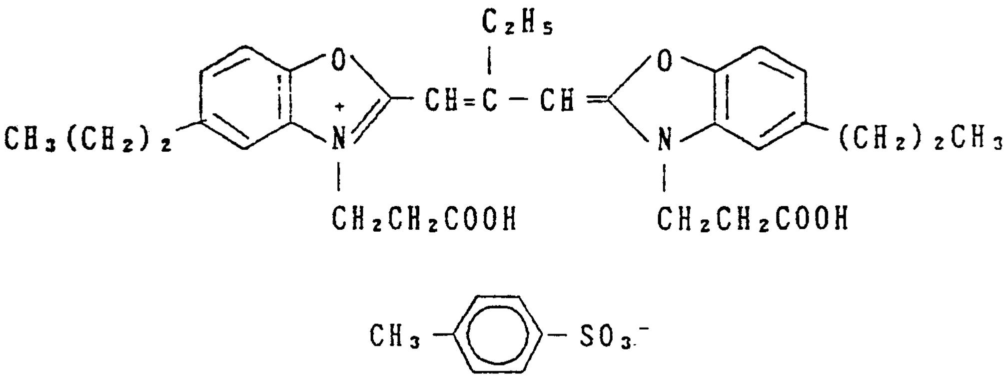
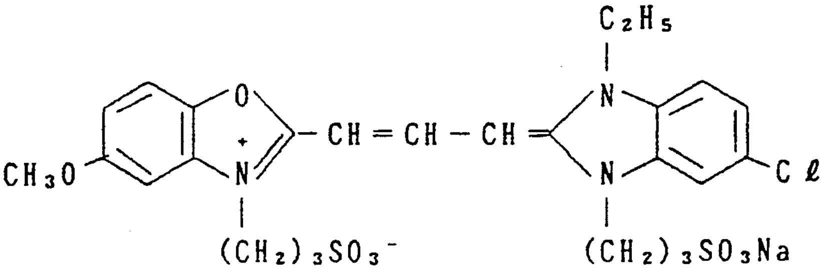


S-15.



S-16.



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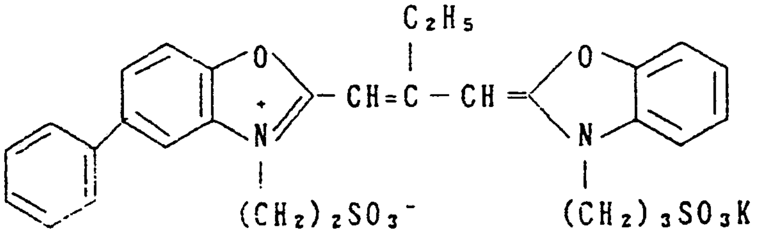

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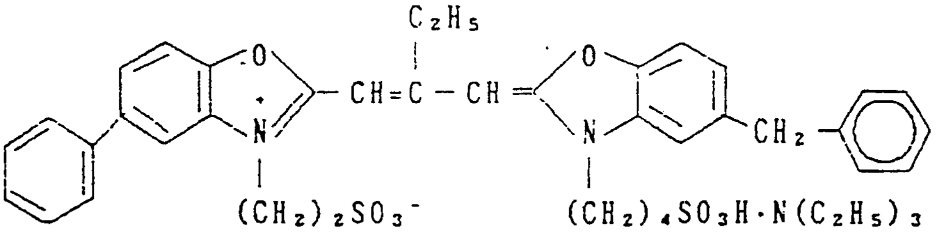
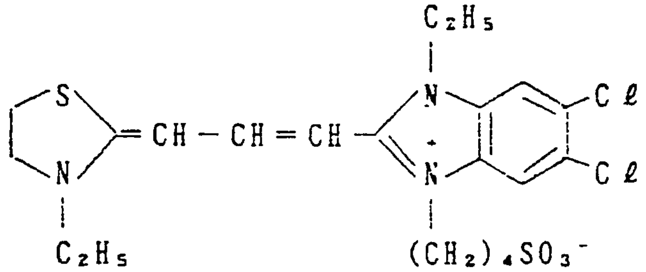
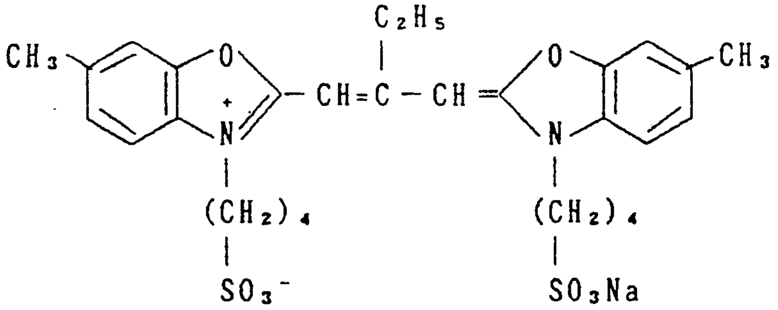


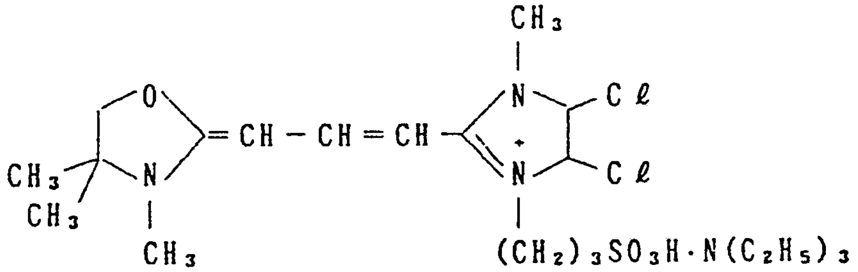
S-19.



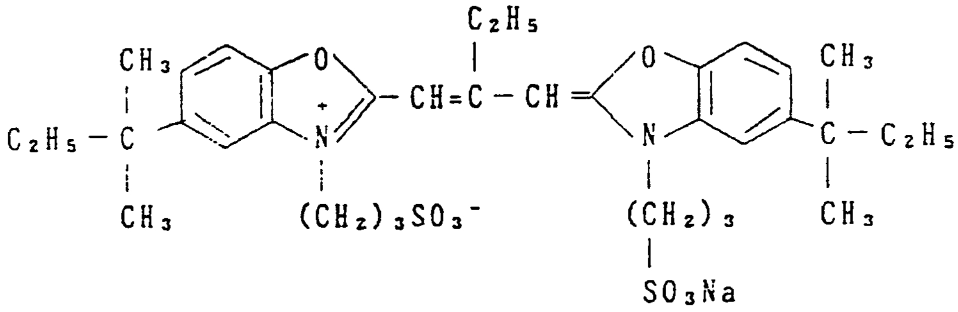
S-20.



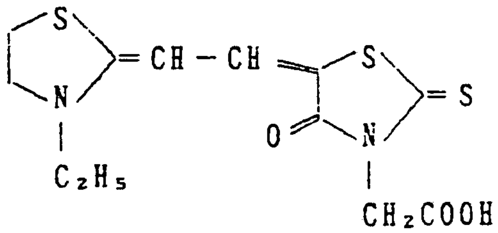
S-21.



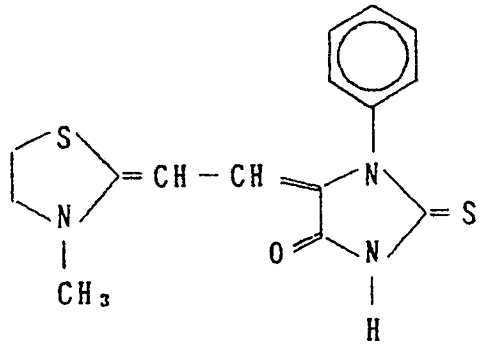
S - 22.



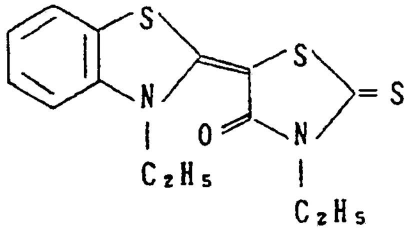
S - 23.



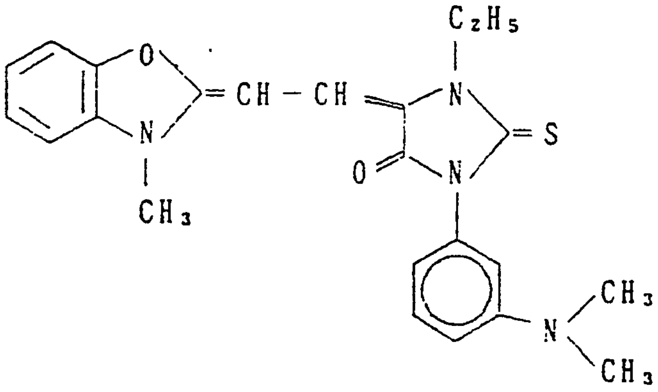
S - 24.



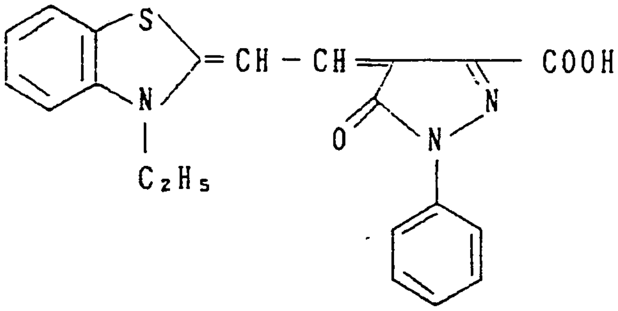
S - 25.



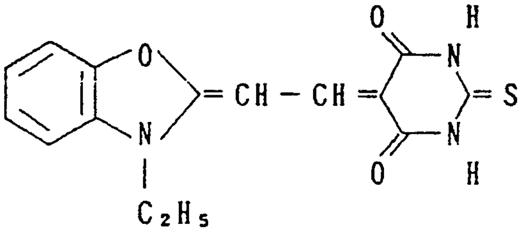
S－２６.


O
N
CH₃
CH － CH
C₂H₅
N
N
S
O
N
CH₃
CH₃

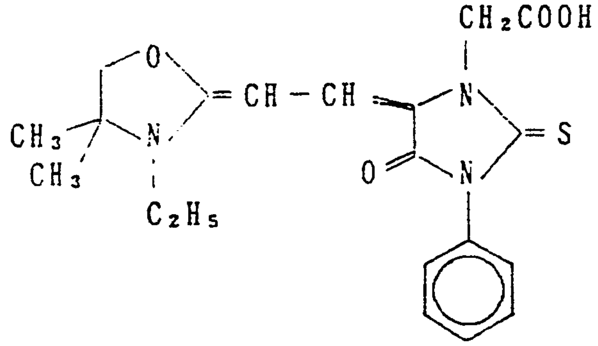
S－２７.


S
N
C₂H₅
CH － CH
COOH
N
N
O

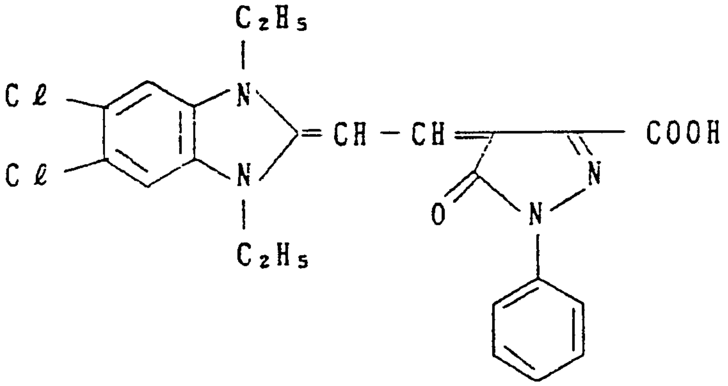
S－２８.


O
N
C₂H₅
CH － CH
O
H
N
S
N
O
H

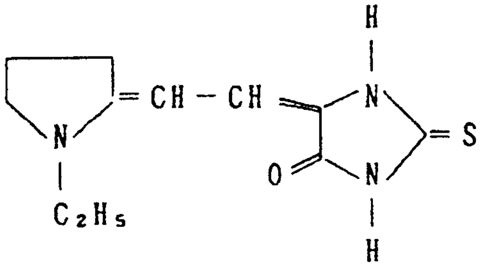
S－29.


CH₂COOH
O
= CH – CH
N
= S
CH₃
CH₃
N
O
N
C₂H₅

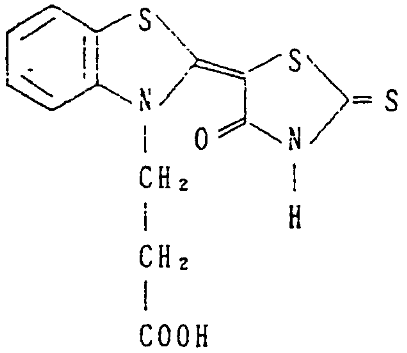
S－30.


C₂H₅
Cℓ
N
= CH – CH
COOH
Cℓ
N
N
O
N
C₂H₅

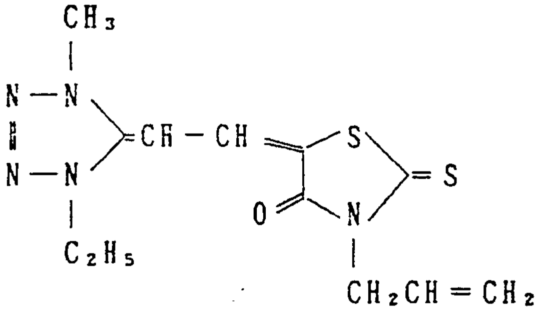
S－31.


H
= CH – CH
N
= S
N
O
N
C₂H₅
H

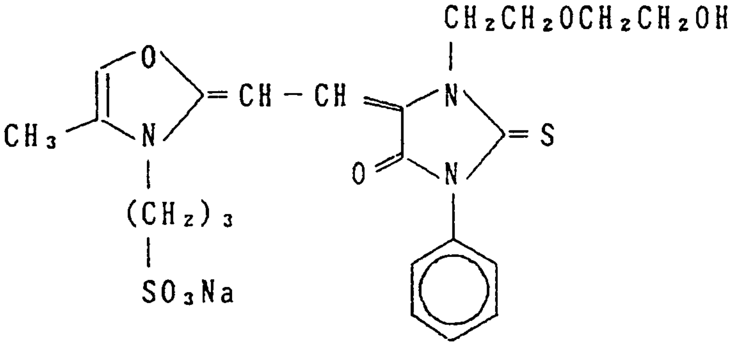
S-32.



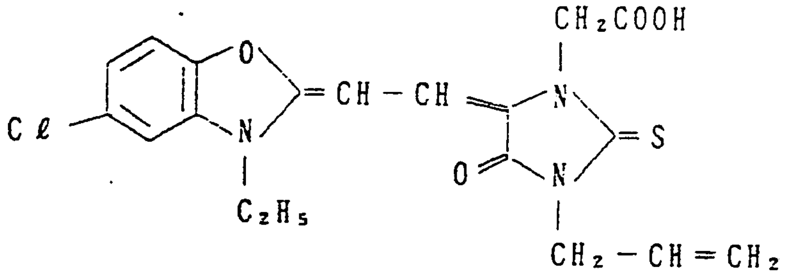
S-33.



S-34.

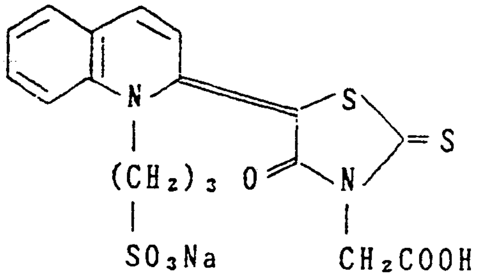


S－35.



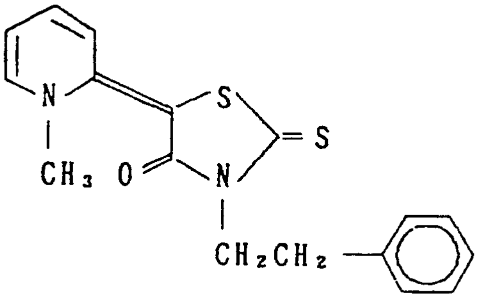
CH₂COOH
O
N
Cℓ
CH－CH
N
S
O
N
C₂H₅
CH₂－CH＝CH₂

S－36.



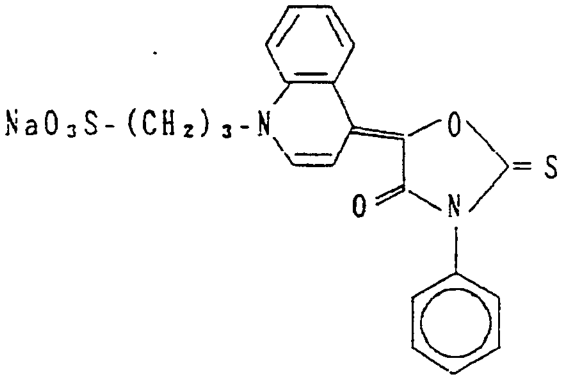
N
S
S
(CH₂)₃
O
N
SO₃Na
CH₂COOH

S－37.

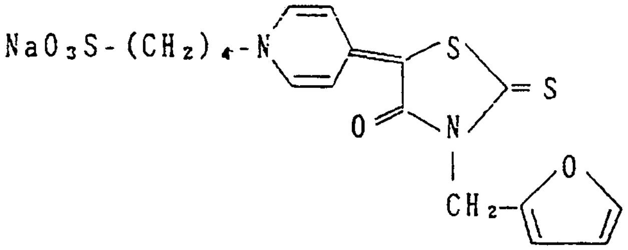


N
S
S
CH₃
O
N
CH₂CH₂

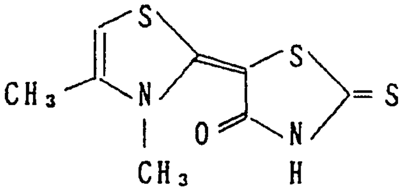
S－38．



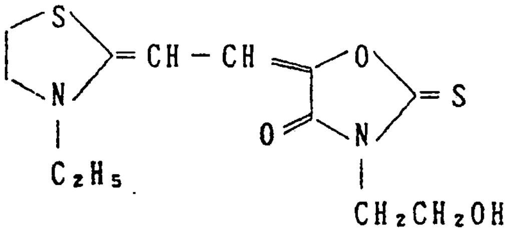
S－39．



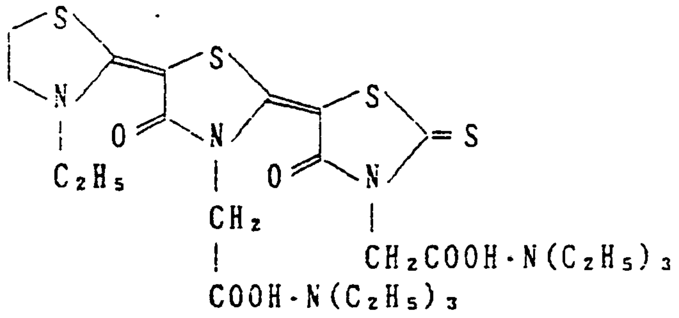
S－40．



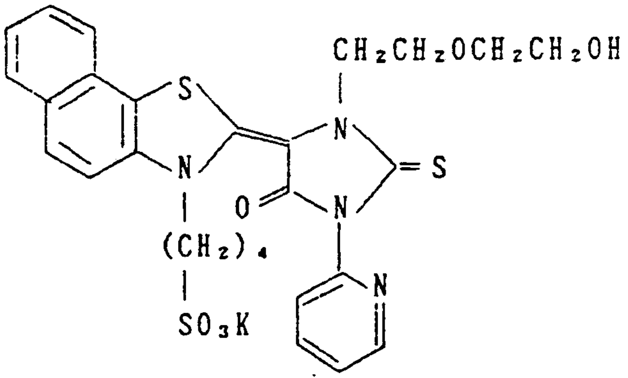
S－41．



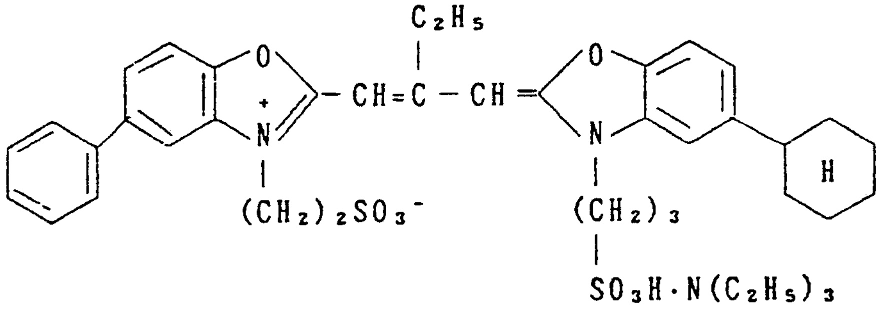
S-42.


S
N
C₂H₅
O
S
N
CH₂
COOH·N(C₂H₅)₃
O
S
N
= S
CH₂COOH·N(C₂H₅)₃

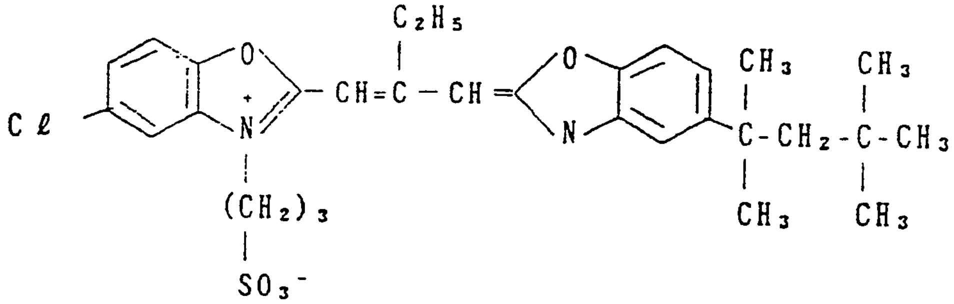
S-43.


S
N
(CH₂)₄
SO₃K
CH₂CH₂OCH₂CH₂OH
N
= S
O
N
N

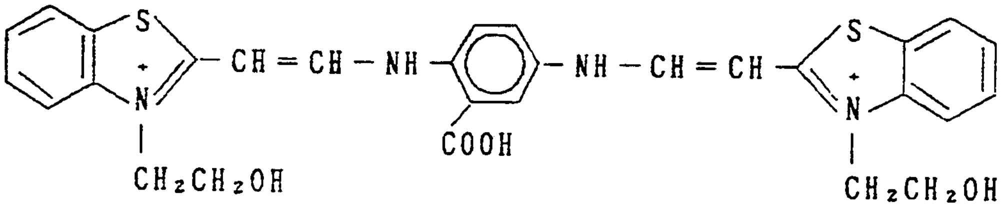
S-44.


C₂H₅
O
+
N
(CH₂)₂SO₃⁻
CH=C − CH =
O
N
(CH₂)₃
SO₃H·N(C₂H₅)₃
H

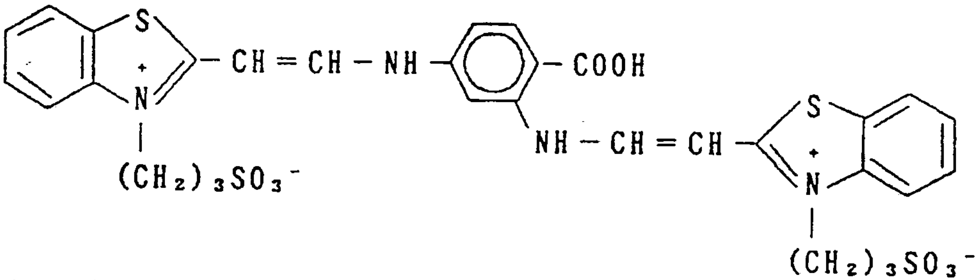
S - 4 5 .



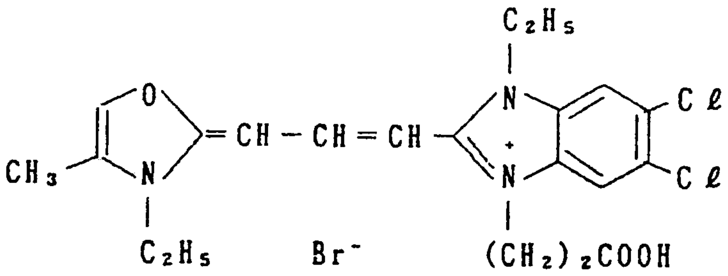
S - 4 6 .



S - 4 7 .



S - 4 8 .



The terms "red-sensitive emulsion layer" "green-sensitive emulsion layer" and "blue-sensitive emulsion layer" as used herein refer to silver halide emulsion layers which are reacted with red light, green light and blue light to form cyan dye image, magenta dye image and yellow dye image, respectively. They do not contain a donor layer exhibiting multi-layer effect as described in JP-A-54-118245 and JP-A-61-34541 which correspond to U.S. Patents 4,306,015 and 4,705,744, respectively.

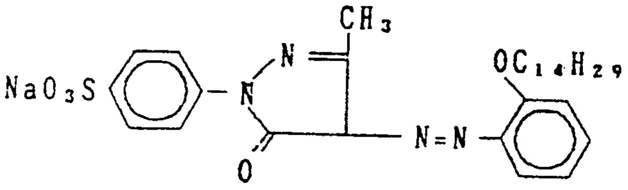
The red-sensitive emulsion layer and the green-sensitive emulsion layer are usually sensitive to blue light. Accordingly it is necessary to provide the yellow filter layer above these layers to prevent blue light from reaching the red-sensitive and green-sensitive emulsion layers. In order to maintain the fidelity of the primary blue color and the chroma thereof, the optical density of the yellow filter layer at peak wavelength should be at least 1.0, preferably 1.2 or above, more preferably 1.4 or above.

Colloidal silver grains, yellow colored magenta couplers and nondiffusing yellow organic dyes can be used as the yellow filter.

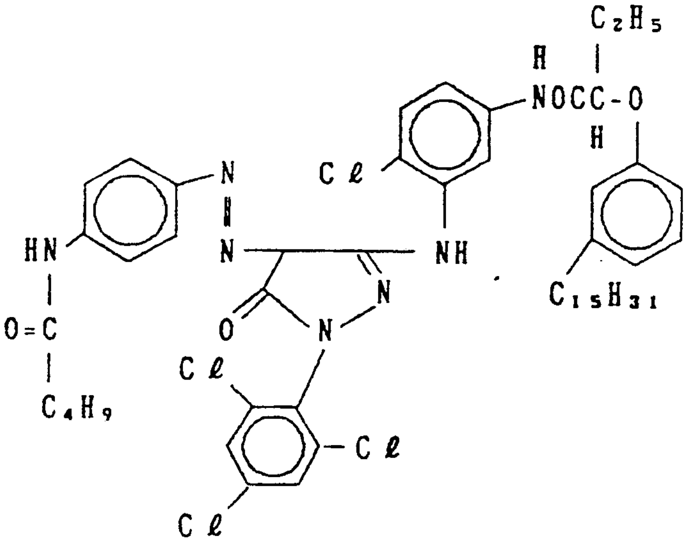
A density of the yellow filter is naturally depending on a colloidal silver halide grain, a yellow colored magenta coupler, a light absorption property and used amount of nondiffusing yellow organic dyes. To determine the density of the yellow filter layer readily and accurately, a filter layer, which has the same composition and coated amount as of the yellow filter layer in the silver halide color photographic material according to the present invention, is coated exclusively on a transparent support thereby obtaining a density as a correspondence.

Conventional yellow colored magenta couplers can be used in the present invention. Among these, the following compounds are particularly preferred.

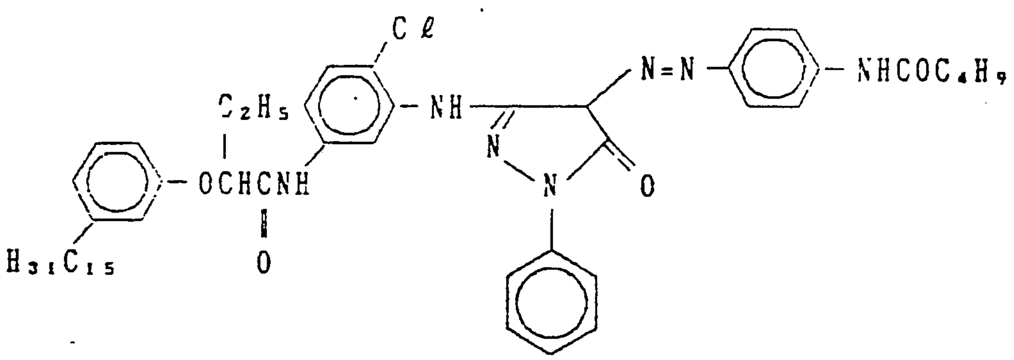
YD - 1



YD - 2



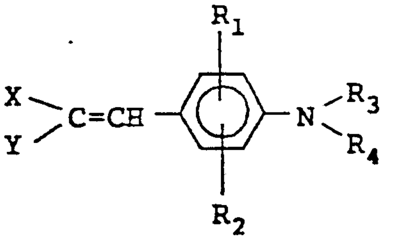
YD-3



The yellow colored magenta couplers can be introduced into the yellow filter of the present invention by conventional methods for introducing couplers into silver halide emulsion layers such as the method described in U.S. Patent No. 2,322,027. For example, they are dissolved in a solvent such as an alkyl phthalate (e.g., dibutyl phthalate, and dioctyl phthalate), a phosphoric ester (e.g., diphenyl phosphate, triphenyl phosphate, tricresyl phosphate, and dioctyl butyl phosphate), a citric ester (e.g., tributyl acetylcitrate), a benzoic ester (e.g., octyl benzoate), an alkylamides (e.g., diethyllaurylamide), a fatty acid ester (e.g., dibutoxyethyl succinate, and dioctyl azelate), a trimesic ester (e.g., tributyl ester of trimesic acid), or an organic solvent having a boiling point of about 30 to 150 °C such as a lower alkyl acetate (e.g., ethyl acetate, and butylacetate), an ethyl propionate, a secondary butyl alcohol, a methyl isobutyl ketone, a β-ethoxyethyl acetate and a methyl cellosolve acetate. The resulting solutions are dispersed in a hydrophilic colloid. If desired, mixtures of the above-described high-boiling organic solvents and the above-described low-boiling organic solvents can be used. Furthermore, dispersion methods using polymers such as those described in JP-B-51-39853 and JP-A51-59943 can be used.

The yellow colored magenta couplers in the form of an aqueous alkaline solution can be introduced into a hydrophilic colloid when they have an acid radical such as carboxylic acid or sulfonic acid.

The nondiffusing yellow organic dyes which may be used in the present invention can be arbitrarily selected from among conventional dyes. Dyes represented by the following general formula (I) are particularly preferred.

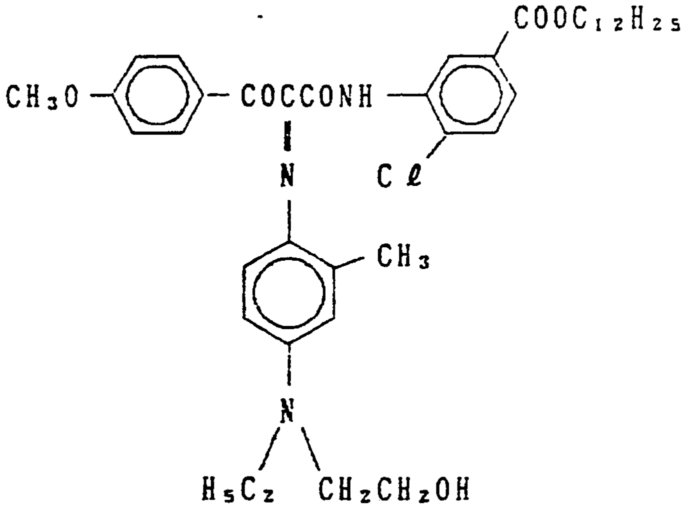


(I)

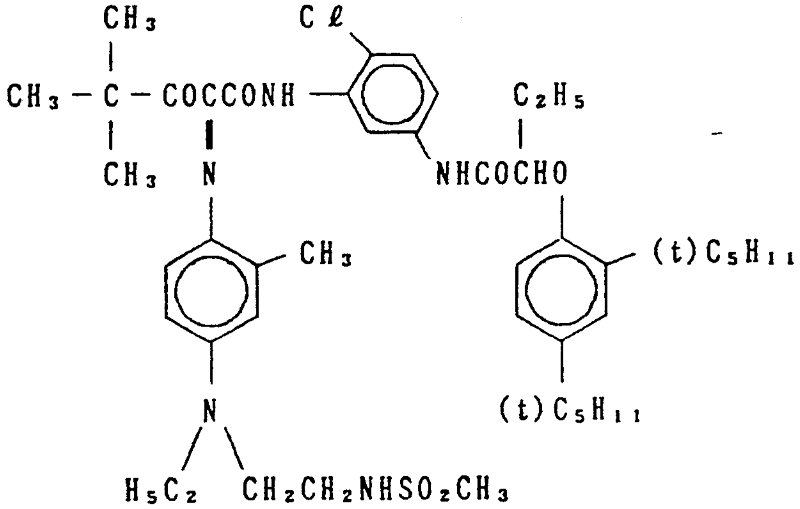
In the above formula, R_1 and R_2 may be the same or different and selected from a hydrogen atom, a halogen atom, an alkyl group, an alkoxy group, hydroxyl group, carboxyl group, a substituted amino group, a carbamoyl group, a sulfamoyl group, nitro group or an alkoxycarbamoyl group; R_3 and R_4 may be the same or different and selected from a hydrogen atom, an unsubstituted or substituted alkyl group, an unsubstituted or substituted alkenyl group, an unsubstituted or substituted aryl group, an acyl group or a sulfonyl group, and R_3 and R_4 may be combined together to form a 5-membered or 6-membered ring; and X and Y may be the same or different and are electron attractive groups.

Particularly preferred examples of the dyes include the following compounds.

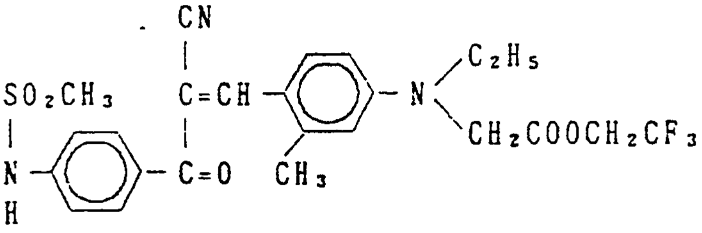
YD－4


COOC₁₂H₂₅
CH₃O
COCCONH
N
Cℓ
CH₃
N
H₅C₂
CH₂CH₂OH

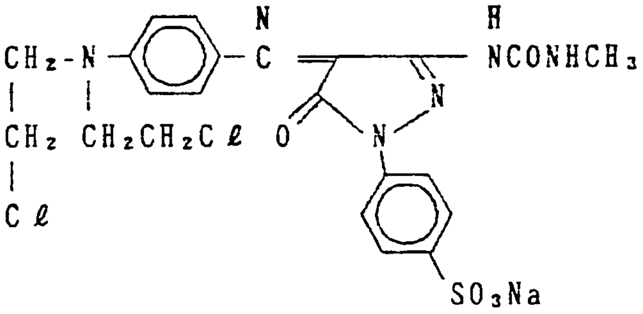
YD－5


CH₃
Cℓ
CH₃ − C − COCCONH
C₂H₅
CH₃
N
NHCOCHO
CH₃
(t)C₅H₁₁
N
(t)C₅H₁₁
H₅C₂
CH₂CH₂NHSO₂CH₃

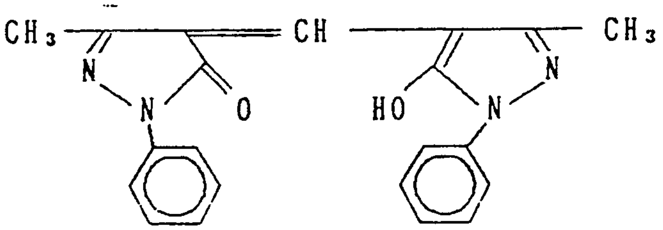
YD－6



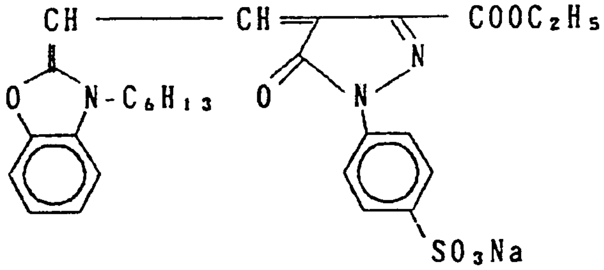
YD－7



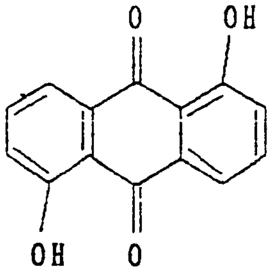
YD－8



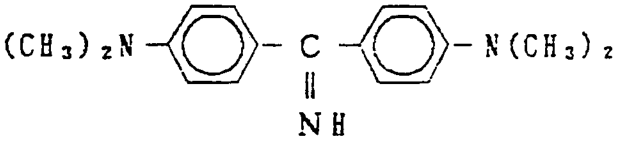
YD－9



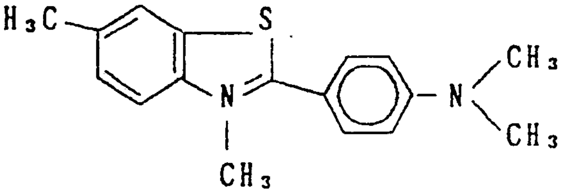
YD-10



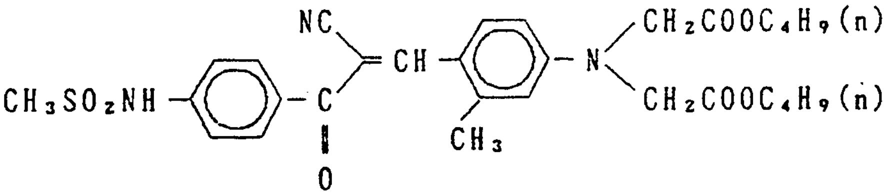
YD-11



YD-12



YD-13



The yellow filter containing the organic dye used in the present invention can be prepared by conventional methods. When the organic dyes are oil-sobluble, the yellow filter can be prepared in the same manner as the methods for introducing the above-described yellow colored magenta couplers. When the organic dyes are water-soluble, the dyes in the form of an aqueous alkaline solution can be introduced into hydrophilic colloid. The yellow filter layer of the present invention can be prepared in the same manner as the methods using colloidal silver. The amounts of colloidal silver, the yellow colored magenta coupler and the organic dye can be controlled so as to give a desired optical density.

The above-described yellow dyes provide not only a means for lowering the amount of silver by allowing the use of yellow colloidal silver to be omitted, but also have a unique sensitizing effect. The yellow dyes have such sharp light absorption characteristics that effective light is transmitted to the green-sensitive and red-sensitive silver halide emulsion layer without allowing the light to be absorbed. Accordingly, the dyes favor an increase in the sensitivity of the lower layers. Furthermore, theyellow dye filter can prevent physical development. Such physical development is often caused by adjoining colloidal silver. Thus, there is an advantage that high-sensitivity emulsions can be used for the blue-sensitive and green-sensitive layers without adverse effect, the emulsions having been sufficiently after-ripened.

Emulsions having a narrow grain size distribution are preferably used in the present invention, though emulsions having a wide grain size distribution can be used. Particularly, when normal crystal grains are used, a monodisperse emulsion can be used having such a grain size distribution that grains which account for 90% (by weight or in terms of the number of grains) of the total silver halide grains of each emulsion, have a grain size within ±40% of the mean grain size, preferably within ±30% of the mean grain size.

Twin grains are preferably used. It is preferred that the grains contain at least 30%, preferably at least 50%, more preferably at least 70% (in terms of projected area), of tabular (plate-form) grains having two or more parallel twin planes.

Emulsions having a clear layered structure, are preferably used in the present invention. They can be prepared by choosing appropriate methods from among various methods known in the field.

First, core grains are prepared by an acid process, neutral process or ammonia process. A soluble silver salt and a soluble halogen salt can be reacted in accordance with a single jet process, double jet process or a combination thereof. As a type of the double jet process, there can be used a controlled double jet process in which the pAg value in the liquid phase, in which silver halide is formed, is maintained constant. As another embodiment, there can be used a triple jet process (e.g., a soluble silver salt, a soluble bromine salt and a soluble iodine salt) in which soluble halogen salts having different compositions are independently added. Solvents such as ammonia, a Rhodan salt, thiourea, thioether and an amine for silver halide may be used during the course of preparative the core. Emulsions having a narrow grain size distribution are preferred as core grains. A monodisperse core emulsion is particularly preferred. It is desirable to use an emulsion in which individual grains are uniform in halogen composition, particularly iodine content at the stage of a core.

Whether the halogen compositions of individual grains is uniform or not can be determined using X-ray diffraction or EPMA. When the halogen composition of core grains is uniform, the diffraction breadth of X-ray diffraction is narrow and the peak is sharp.

Uniform silver iodobromide can be obtained by allowing silver iodobromide grains to be grown by a method wherein the addition rate is accelerated with time as disclosed in Irie and Suzuki's JP-B-48-36890, or a method wherein addition concentration is increased with time as disclosed in U.S. Patent No. 4,242,445 after the seed crystal of silver iodobromide having a high silver iodide content is prepared. These methods give particularly good results. In the method described in JP-B-48-36890, aqueous solutions of inorganic salts to be reacted are added at a given addition rate or higher, but at an addition rate Q which is not higher than an addition rate proportional to the total surface area of poorly soluble inorganic salt crystals during the course of growth in a method for preparing the poorly soluble inorganic crystal by a double composition reaction in which two or more aqueous inorganic salt solutions are simultaneously added by about equal amounts in the presence of a protective colloid. The addition is carried out at a rate of $Q = \gamma$ or higher, but at a rate not higher than $Q = \alpha t^2 + \beta t + \gamma$.

In the method described in U.S. Patent No. 4,242,445, the concentrations of aqueous solutions of inorganic salts to be reacted are increased in such a proportion that there is no significants formation of new crystal nucleus during the course of crystal growth. In the preparation of silver halide grains having a clear layer structure, it is preferred that the core emulsion is washed with water to carry out desilverization and then a shell is formed, though a shell can be formed on the core grains as formed.

It is preferred that the shell is formed by a double jet process, though the formation of the shell can be carried out by various conventional methods known in the field.

Conventional knowledge for preparing grains having a clear layer structure is useful when the emulsion is composed of fine grains. However, such knowledge is insufficient to increase the finish degree of the layer structure. First, it is necessary to determine carefully the halogen composition of the high iodine layer. Silver iodide and silver bromide are different in thermodynamically stable crystal structure; they do not form a mixed crystal in any composition ratio. The composition ratio of a mixed crystal varies depending on the temperature during the preparation of grains, but it is important that the optimum composition ratio is chosen from among the range of 15 to 45 mol%. The composition ratio of a stable mixed crystal varies depending on atmosphere, but it is believed that the ratio exists in the range of 30 to 45 mol%. When a low iodine layer is grown outside the high iodine layer, pl, pAg and stirring conditions are important factors. In addition thereof, it is important to determine the amount of protective collide when the low iodine layer is grown. It is desirable that the iodine layer is grown in the presence of compounds such as spectral sensitizing dyes, anti-fogging agents and stabilizers which are allowed to be adsorbed by the silver halide. Furthermore, it is effective that fine grains of silver halide are added in place of water-soluble silver salts and water-soluble alkali metal halides when a low iodine layer is formed.

The description "silver halide grains having a clear layer structure" means that substantially two or more areas having different halogen compositions exist within a grain wherein the central part of the grain forms a core and the outer part thereof forms a shell.

The description "substantially two ore more areas" means that there may optionally exist a third area (e.g., a layer existing between the central core part and the outermost shell part) in addition to the core and the shell. Such a third area optionally exists in such a range that the forms of two peaks corresponding to the high iodine layer and the low iodine layer are not substantially effected by the third layer when X-ray diffraction patterns are determined.

Therefore, silver halide grains having substantially two clear layer structures are grains in which there exist a core having a high iodine content, an intermediate part and a shell having a low iodine content; an X-ray diffraction pattern shows that there exist two peaks and one minimum part between these two peaks; the intensity of diffraction corresponding to the high iodine part is in the range of from 1/10 to 3/1, preferably 1/5 to 3/1, more preferably 1/3 to 3/1 of that corresponding to the low iodine part; and the minimum part is 90% or below, preferably 80% or below, particularly 70% or below of the smaller peak of the two peaks.

When a third area of the grain exists within the core, the grain has a similar structure to that described above.

In the emulsions which are preferably used in the present invention, silver halides having different compositions may be joined to each other by epitaxial joining, or silver halides may be joined to a compound such as silver rhodanide or lead oxide.

Grains having various crystal forms can be used, or the mixtures of grains having different crystal forms can be used.

Usually, silver halide emulsions are subjected to physical ripening, chemical ripening and spectral sensitization and then used. Additives which are used in these stages are described in Research Disclosure (RD) No. 17643 and ibid. No. 18716 and listed in the following Table. Conventional photographic additives which can be used in the present invention are described in the above two Research Disclosures and listed in the following Table.

Table

	Type of Additive	RD 17643	RD 18716
1.	Chemical Sensitizer	Page 23	Page 648, right column
2.	Sensitivity Increaser		- ditto -
3.	Spectral Sensitizing Agent, Supersensitizing Agent	Pages 23 to 24	Page 648, right column to page 649, right column
4.	Brightener	Page 24	
5.	Antifogging Agent and Stabilizer	Pages 24 to 25	Page 649, right column
6.	Light-Absorber, Filter Dye and UV Light Absorber	Pages 25 to 26	Page 649, right column to page 650, left column
7.	Antistaining Agent	Page 25, right column	Page 650, left column to right column
8.	Dye Image Stabilizer	Page 25	
9.	Hardening Agent	Page 26	Page 651, left column
10.	Binder	Page 26	- ditto -
11.	Plasticizer, Lubricant	Page 27	Page 650, right column
12.	Coating Aid, Surfactant	Pages 26 to 27	- ditto -
13.	Antistatic Agent	Page 27	- ditto -

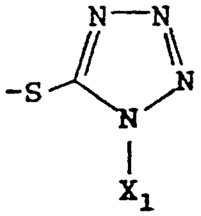
It is preferred that the emulsion layers of the present invention contain two equivalent type couplers.

It is particularly preferred to use compounds which release a diffusing restrainer or a precursor thereof by a coupling reaction with the oxidant of a developing agent. As such compounds, there are preferred compounds represented by the following formula (I′).

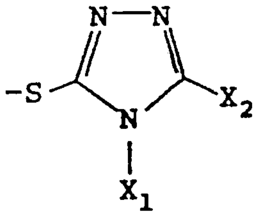
$A\text{-}(LINK)_n\text{-}B$ (I′)

In the above formula, A represents a residue of a coupler which releases $(LINK)_n\text{-}B$ by the coupling reaction with the oxidant of an aromatic primary developing agent; LINK represents a group which is attached to the coupling active site of A and is capable of releasing B after it is released from A by the coupling reaction; B represents a group represented by the following general formulae (IIa), (IIb), (IIc), (IId),-(IIe), (IIf), (IIg), (IIh), (IIi), (IIj), (IIk), (IIℓ), (IIm), (IIn), (IIo) or (IIp); and n represents an integer of 0 to 1 and when n = 0, B is directly attached to A.

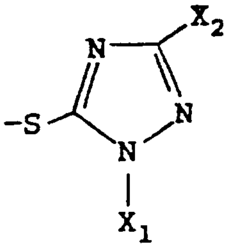
Formula (IIa)



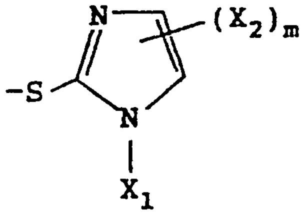
Formula (IIb)



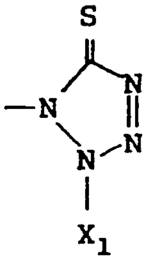
Formula (IIc)



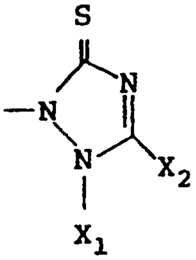
Formula (IId)



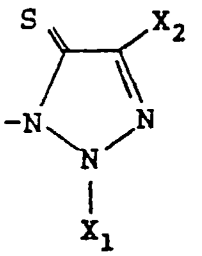
Formula (IIe)



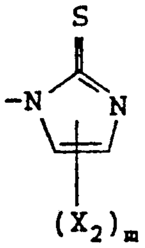
Formula (IIf)



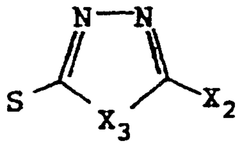
Formula (IIg)



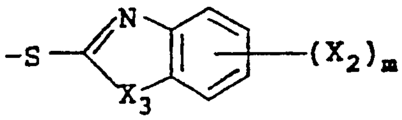
Formula (IIh)



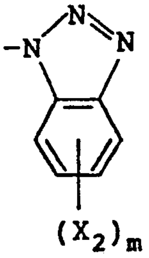
Formula (IIi)



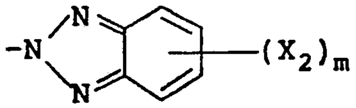
Formula (IIj)



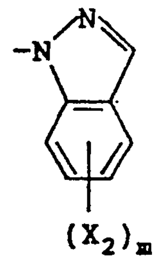
Formula (IIk)



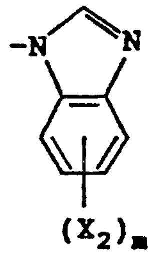
Formula (IIℓ)



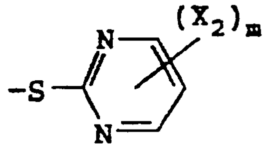
Formula (IIm)



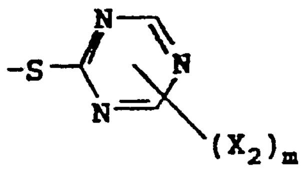
Formula (IIn)



Formula (IIo)



Formula (IIp)



In the above formulae, X_1 is a substituted or unsubstituted aliphatic group having from 1 to 4 carbon atoms wherein the substituent group has not more than 3 carbon atoms and is selected from the group consisting of an alkoxy group, an alkoxycarbonyl group, hydroxyl group, an acylamino group, a carbamoyl group, a sulfonyl group, a sulfonamido group, a sulfamoyl group, an amino group, an acylamino group, cyano group,a ureido group, an acyl group and an alkylthio group or X_1 is a substituted phenyl group wherein the substituent group has not more than 3 carbon atoms and is selected from the group consisting of 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, carboxyl group, cyano group, nitro group, an amino group and an acyl group; X_2 is hydrogen atom, an aliphatic group, halogen, 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, cyano group, nitro group, an amino group, an alkoxycarbonylamino group, an aryloxycarbonyl group or an acyl group; X_3 is oxygen atom, sulfur atom or an imino group having not more than 4 carbon atoms; m is an integer of 1 or 2; the sum total of carbon atoms of mX_2 is not more than 8; and when $m = 2$, two X_2 may be the same or different groups.

The residues of the couplers, represented by A in the formula (I) include residues of couplers, which form dyes (e.g., yellow, magenta, cyan dyes, etc.) by the coupling reaction with the oxidants of aromatic primary amine developing agents and residues of couplers, which give coupling reaction products having substantially no absorption in the region of visible light.

Examples of yellow dye image forming coupler residues represented by A include coupler residues (residues of couplers) such as pivaloylacetanilide type, benzoylacetanilide type, malonic diester type, malondiamide type, benzoylmethane type, benzthiazolylacetamide type, molonic ester monoamide type, benzthiazolyl acetate type, benzoxazolylacetamide type, benzoxazolyl acetate type, malonic diester type, benzmimidazolylacetamide type and benzimidazolyl acetate type residues; coupler residues derived from heterocyclic ring-substituted acetamides or heterocyclic ring-substituted acetates such as those described in U.S. Patent No. 3,841,880; coupler residues derived from cylacetamides such as those described in U.S. Patent No. 3,770,446, U.K. Patent No. 1,459,171, West German (OLS) 2,503,099, JP-A-50-139738 and Research Disclosure No. 15737; and heterocyclic ring type coupler residues such as those described in U.S. Patent No. 4,046,574.

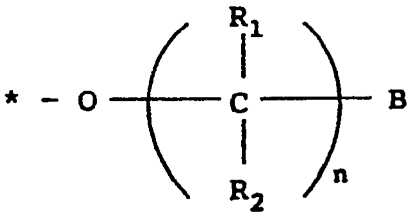
Preferred examples of magenta dye image forming coupler residues represented by A include residues having 5-oxo-2-pyrazoline nucleus, pyrazolo[1,5-a]benzimidazole nucleus, pyrazoloimidazole nucleus, pyrazolotriazole nucleus or pyrazolotetrazole nucleus and cyanoacetophenone type residues.

Preferred examples of cyan dye image forming coupler residues include residues having a phenol nucleus or α-naphthol nucleus.

The couplers have substantially the same effect as DIR couplers, even though a dye is substantially not formed after they release restrainers by the coupling reaction with the oxidants of developing agents. Other examples of the residues represented by A include those described in U.S. Patent Nos. 4,052,213, 4,088,491, 3,632,345, 3,958,993 and 3,961,959. The group A may also be residues of polymer couplers such as those described in U.S. Patent Nos. 3,451,820, 4,080,211 and 4,367,282 and U.K. Patent No. 2,102,173.

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

(1) Groups which utilize the cleavage reaction of hemi-acetal. An example thereof is a group represented by the following formula and described in U.S. Patent No. 4,146,396, and Japanese Patent Application Nos. 59-106223, 59-106224 and 59-75475.

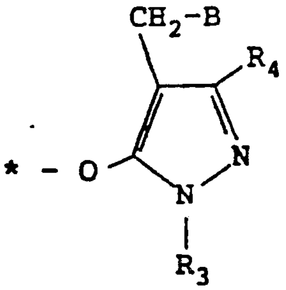


In the formula, the mark * represent a position at which the group is attached to the coupling position of A; R_1 and R_2 each represent a hydrogen atom or a substituent group; n represents 1 or 2; when n is 2, two R_1 groups may be the same or different and two R_2 groups may be the same or different, or any two of two R_1 and two R_2 groups may be combined to form a ring; and B is defined as above with respect to formula (I).

(2) Groups which allow a cleavage reaction to take place by utilizing an intramolecular nucleophilic substitution reaction. An example thereof is a timing group such as that described in U.S. Patent No. 4,248,962.

(3) Groups which allow a cleavage reaction to take place by utilizing an electron transfer reaction along conjugated system. Examples thereof include a group such as that described in U.S. Patent No. 4,409,323 and a group such as that represented by the following formula (see U.K. Patent No. 2,096,783A).

In the formula, the mark * represents a position at which the group is attached to the coupling position of A; R_3 and R_4 each represent a hydrogen atom or a substituent group; and B is the same as defined above with respect to formula (I). Examples of the group R_3 include an alkyl group having from 1 to 24 carbon atoms



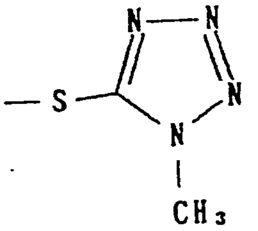
(e.g., methyl,ethyl, benzyl, and dodecyl) and an aryl group having from 6 to 24 carbon atoms (e.g., phenyl, 4-tetradecyloxyphenyl, 4-methoxyphenyl, 2,4,6-trichlorophenyl, 4-nitrophenyl, 4-chlorophenyl, 2,5-dichlorophenyl, 4-carboxyphenyl, and p-tolyl). Examples of the group R_4 include a hydrogen atom, an alkyl group having from 1 to 24 carbon atoms (e.g., methyl, ethyl, undecyl, and pentadecyl), an aryl group having from 6 to 36 carbon atoms (e.g., phenyl, and 4-methoxyphenyl), cyano group, an alkoxy group having from 1 to 24 carbon atoms (e.g., methoxy, ethoxy, and dodecyloxy), an amino group having from 0 to 36 carbon atoms (e.g., amino, dimethylamino, piperidino, dihexylamino, and anilino), a carbonamido group having from 1 to 24 carbon atoms (e.g., acetamido, benzamido, and tetradecanamido), a sulfonamido group having from 1 to 24 carbon atoms (e.g., methylsulfonamido, and phenylsulfonamido), carboxyl group, an alkoxycarbonyl having from 2 to 24 carbon atoms (e.g., methoxycarbonyl, ethoxycarbonyl, and dodecyloxycarbonyl) and a carbamoyl group having from 1 to 24 carbon atoms (e.g., carbamoyl, dimethylcarbamoyl, and pyrrolidinocarboxyl).

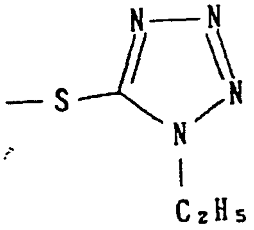
Substituent groups represented by X_1, X_2 and X_3 in formulae (IIa) to (IIp) are illustrated below.

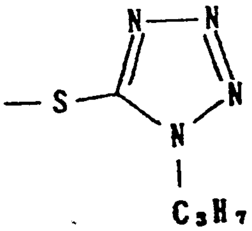
Examples of the group X_1 include methyl, ethyl, propyl, butyl, methoxyethyl, ethoxyethyl, isobutyl, allyl, dimethylaminoethyl, propargyl, chloroethyl, methoxycarbonylmethyl, methylthioethyl, 4-hydroxyphenyl, 3-hydroxyphenyl, 4-sulfamoylphenyl, 3-sulfamoylphenyl, 4-carbamoylphenyl, 3-carbamoylphenyl, 4-dimethylaminophenyl, 3-acetamidophenyl, 4-propaneamido, 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 the group X_2 include hydrogen atom, methyl, ethyl, benzyl, n-propyl, i-propyl, n-butyl, i-butyl, cyclohexyl, fluorine atom, chlorine atom, bromine atom, iodine atom, hydroxymethyl, hydroxyethyl, hydroxyl, methoxy, ethoxy, butoxy, allyloxy, benzyloxy, methylthio, ethylthio, methoxycarbonyl, ethoxycarbonyl, acetamido, propaneamido, butaneamido, octaneamido, benzamido, dimethylcarbamoyl, methylsulfonyl, methylsulfonamido, phenylsulfonamido, dimethylsulfamoyl, acetoxy, ureido, 3-methylureido, cyano, nitro, amino, 1-methyl-2-benzthiazolylideneamino, dimethylamino, methoxycarbonylamino, ethoxycarbonylamino, phenoxycarbonyl, methoxyethyl and acetyl. Examples of the group X_3 include oxygen atom, sulfur atom, imino, methylimino, ethylimino, propylimino and allylimino.

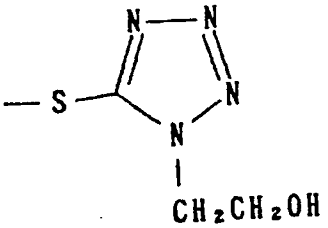
Among the groups represented by formulae (IIa) to (IIp), the groups represented by the formulae (IIa), (IIb), (IIi), (IIj), (IIk) and (IIℓ) are preferred. Among these, the groups represented by formulae (IIa), (IIi), (IIj) and (IIk) are particularly preferred.

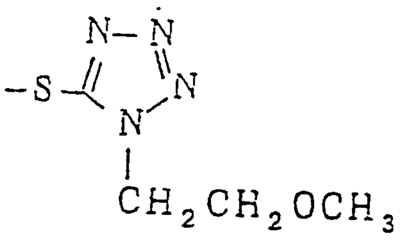
Examples of the group represented by B in the formula (I′) include the following groups.







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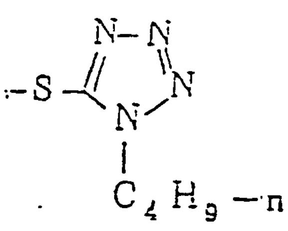
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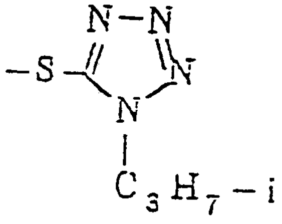
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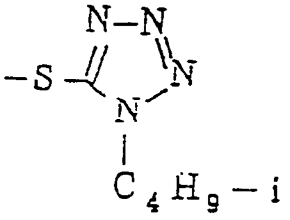
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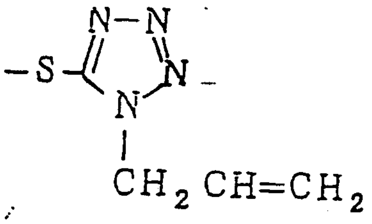
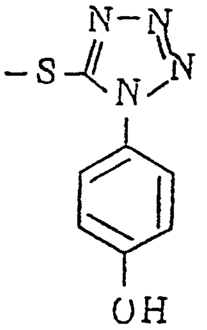
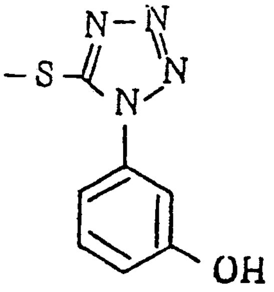

CH2CH=CH2


OH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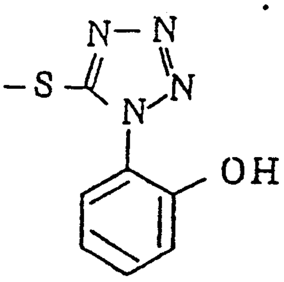
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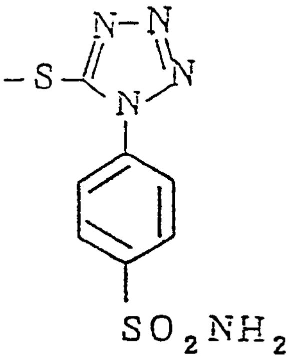
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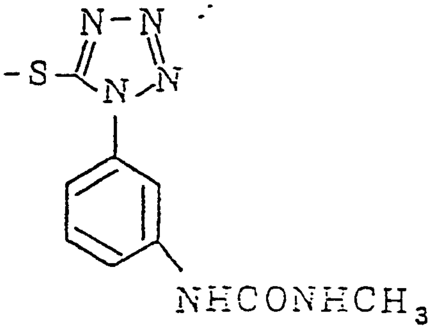
N
SO2NH2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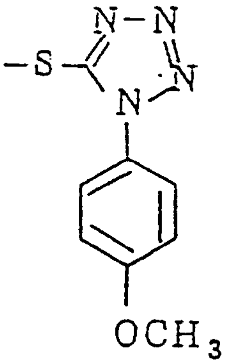
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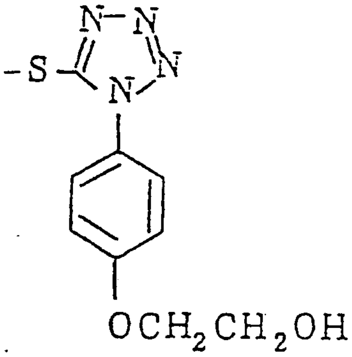
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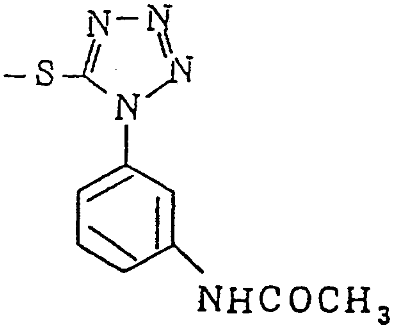
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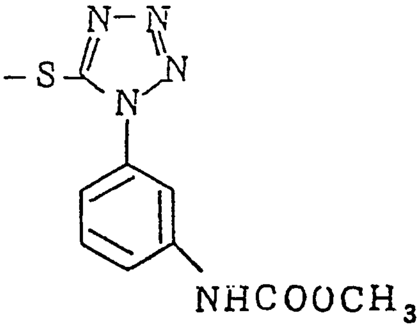
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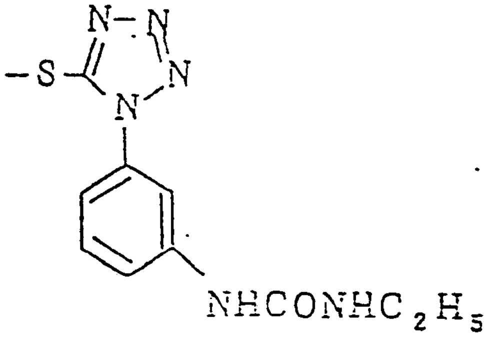
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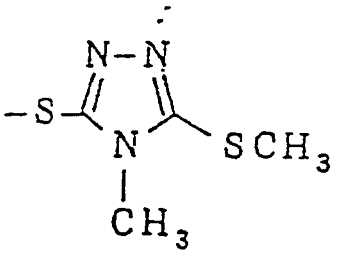
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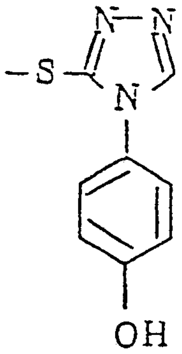
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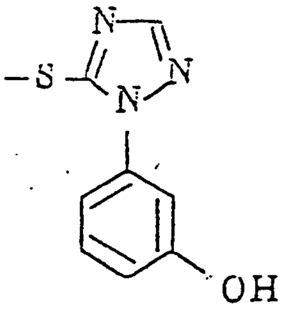
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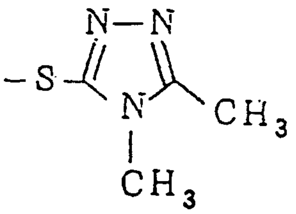
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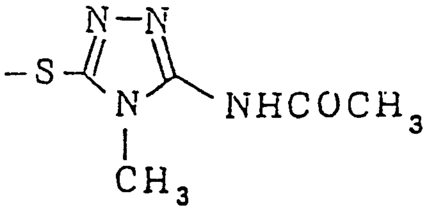
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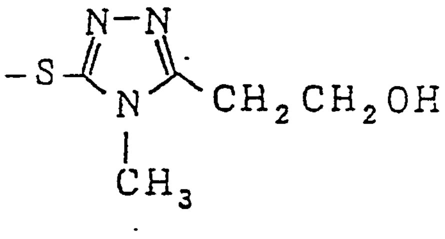

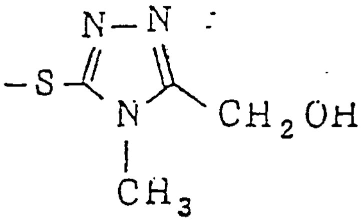

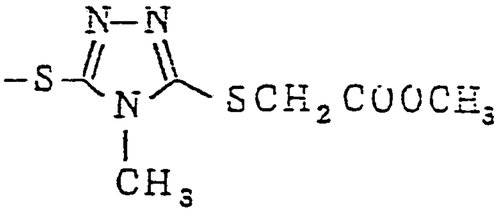

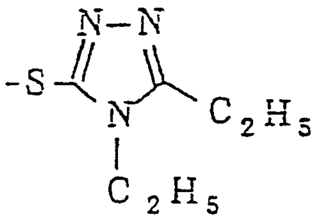

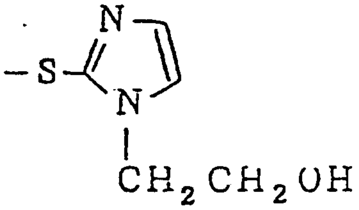

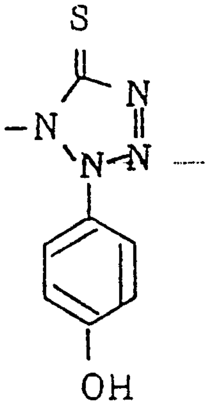

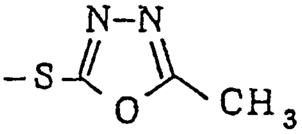

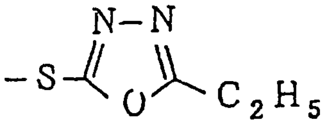

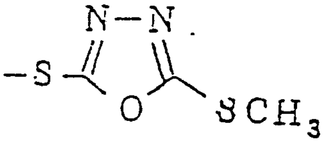

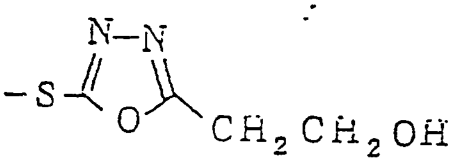

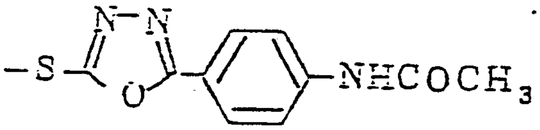

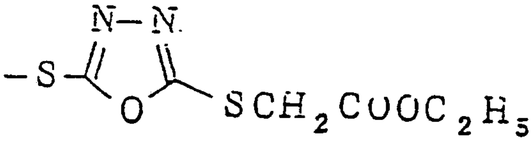

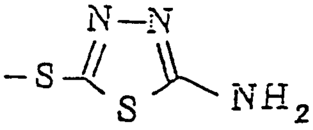

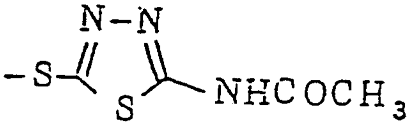

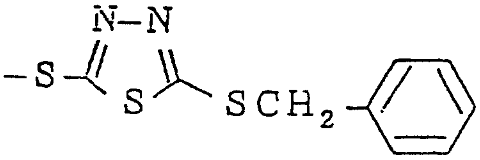

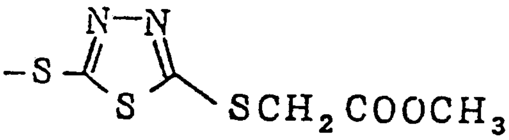

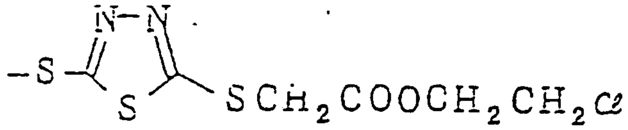

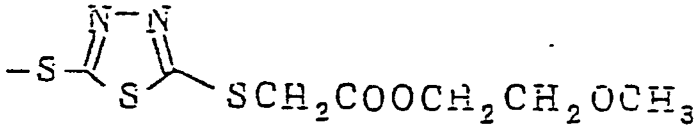

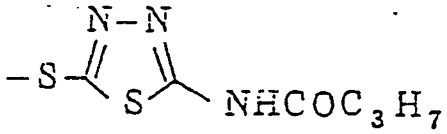

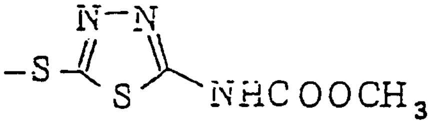

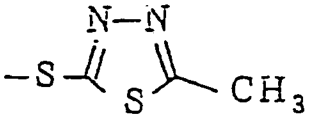

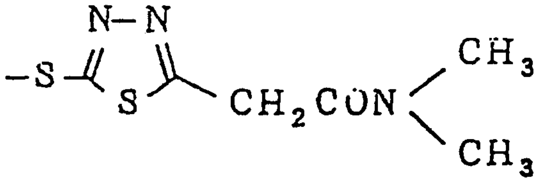

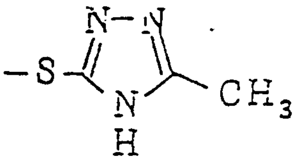

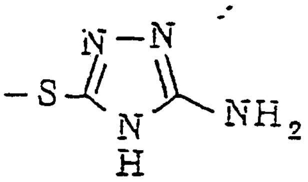

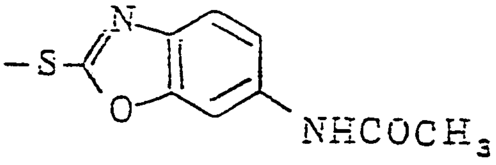

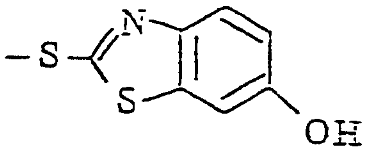

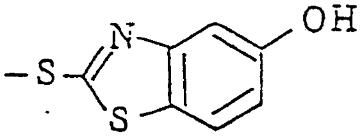

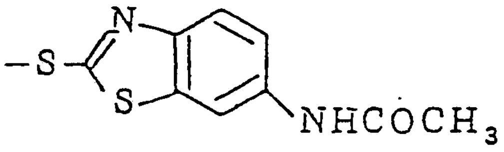

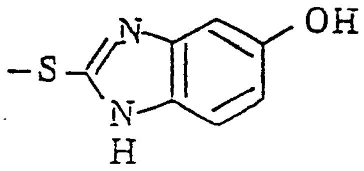

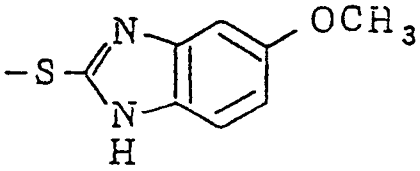

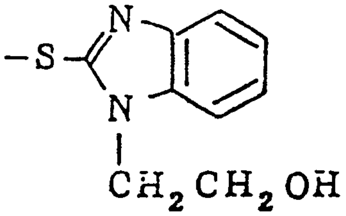

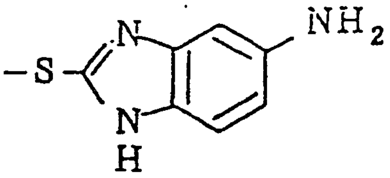

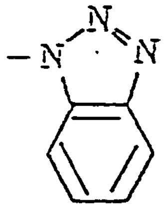
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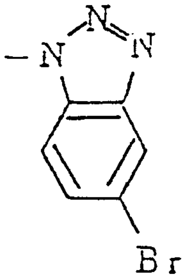
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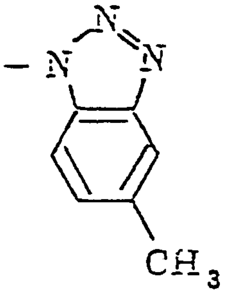
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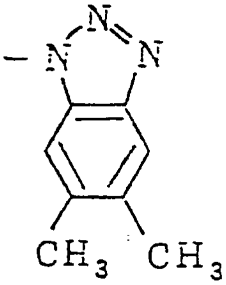
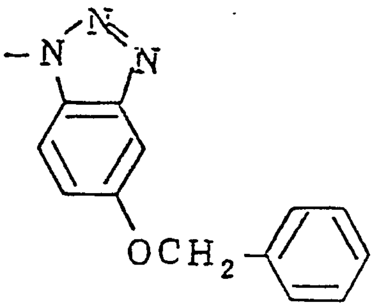
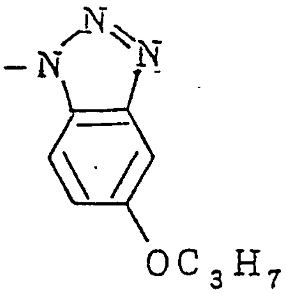
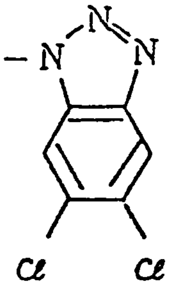
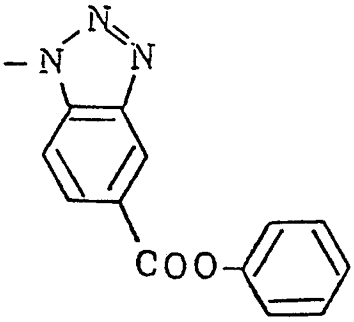
N
CH3

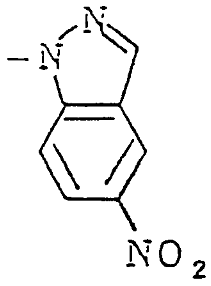

N
N
N
CH3
CH3

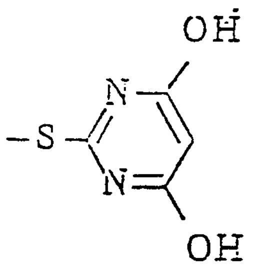

N
N
N
OCH2

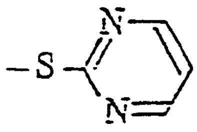

N
N
N
OC3H7

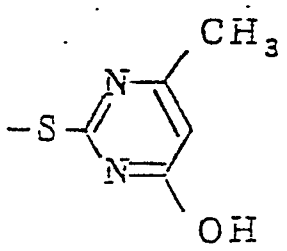

N
N
N
Cl
Cl

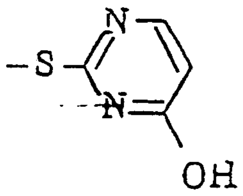

N
N
N
COO

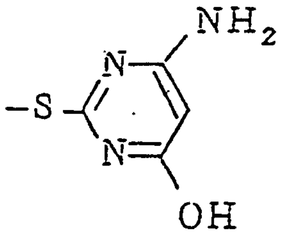


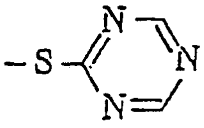


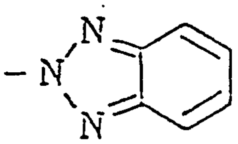


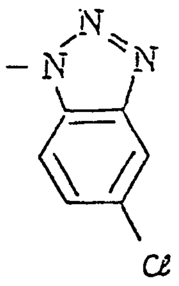


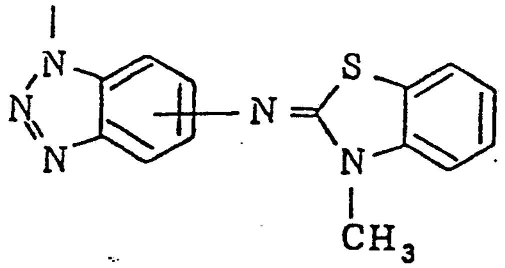






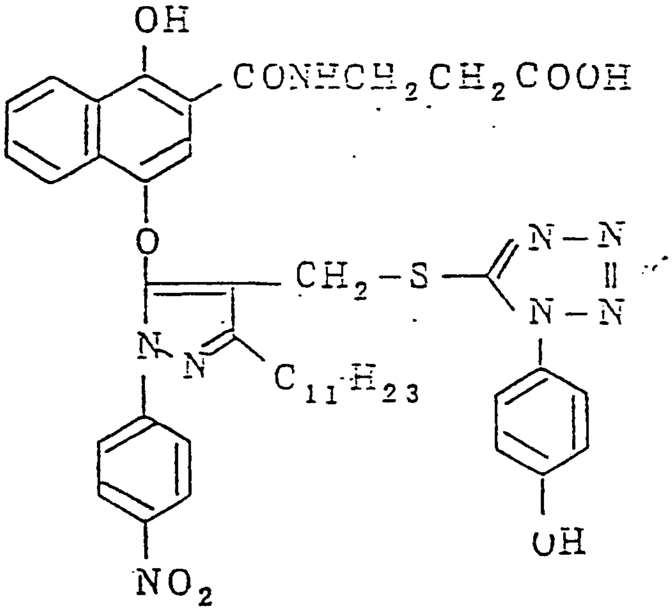




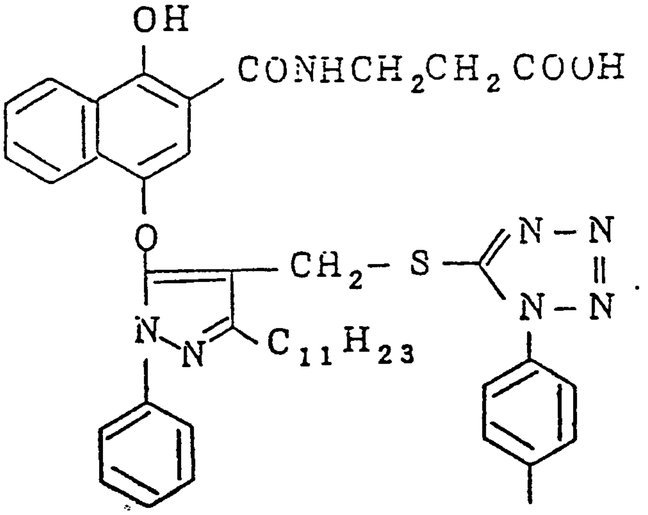


Examples of the couplers which are used in the present invention include, but are not limited to, the following compounds.

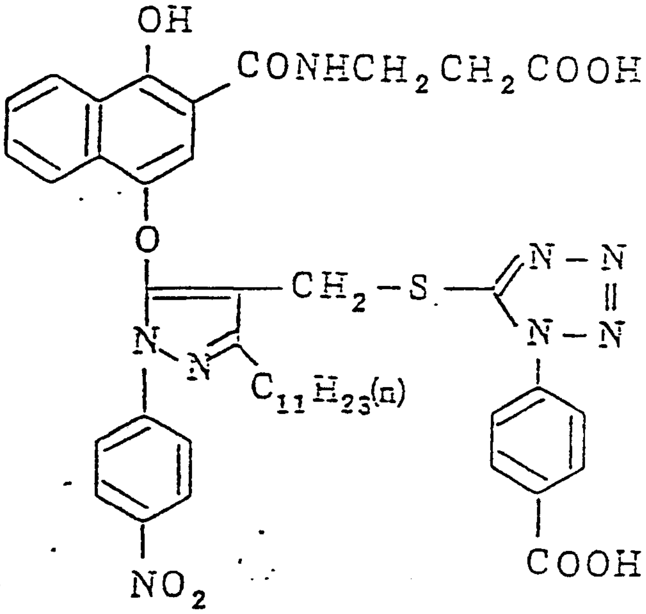
(D − 1)


OH
CONHCH2CH2COOH
O
CH2 − S
N − N
N − N
N
N
C11H23
NO2
OH

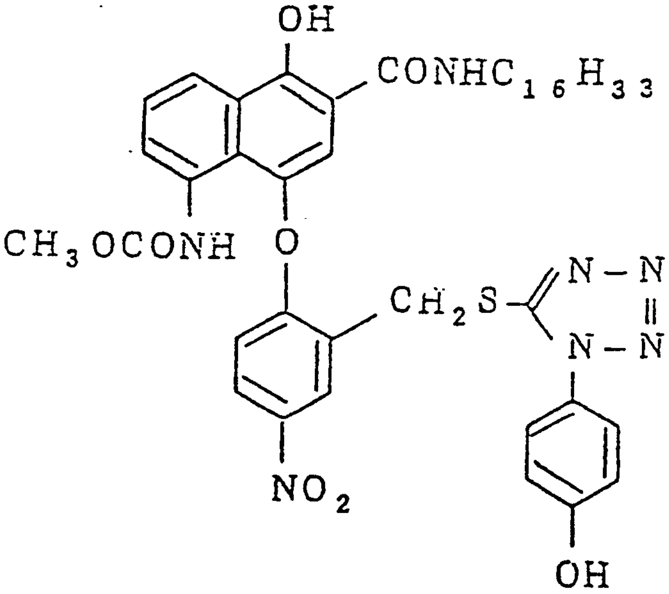
(D − 2)


OH
CONHCH2CH2COOH
O
CH2 − S
N − N
N − N
N
N
C11H23

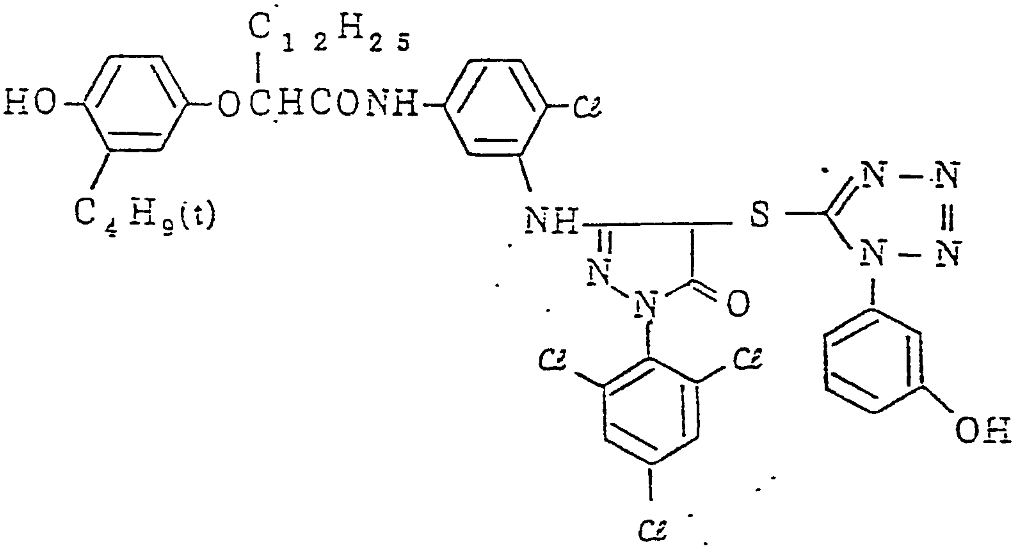
(D − 3)


OH
CONHCH₂CH₂COOH
O
CH₂−S
N−N
N−N
N
N
C₁₁H₂₃(n)
NO₂
COOH

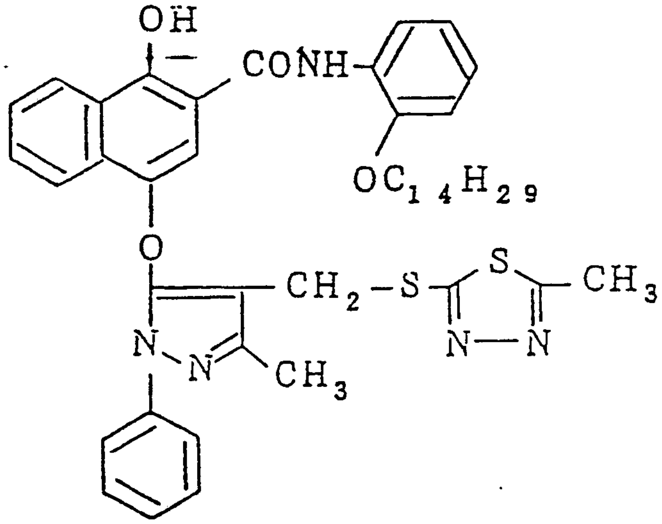
(D − 4)


OH
CONHC₁₆H₃₃
CH₃OCONH
O
CH₂S
N−N
N−N
NO₂
OH

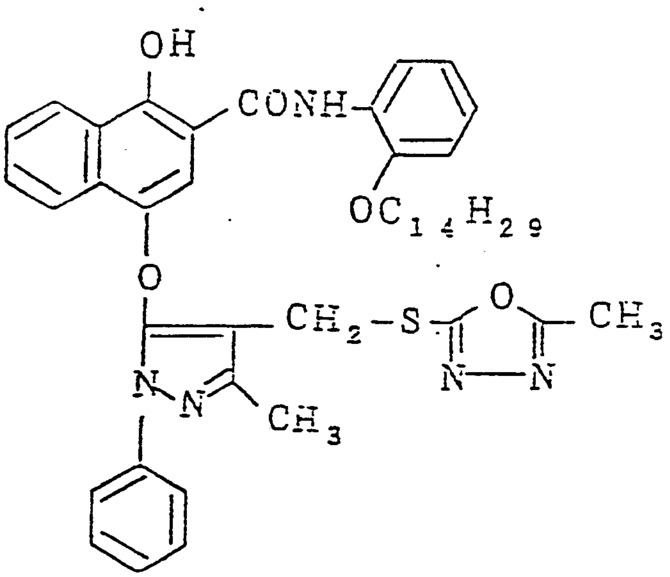
(D − 5)


HO
C12H25
OCHCONH
Cl
C4H9(t)
NH
S
N
O
OH

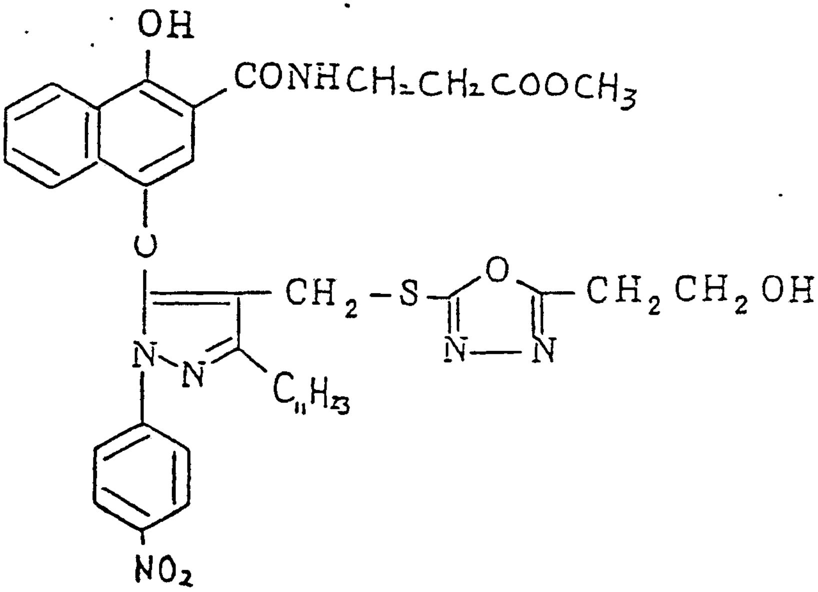
(D − 6)


OH
CONH
OC14H29
O
CH2−S
S
CH3
N
CH3

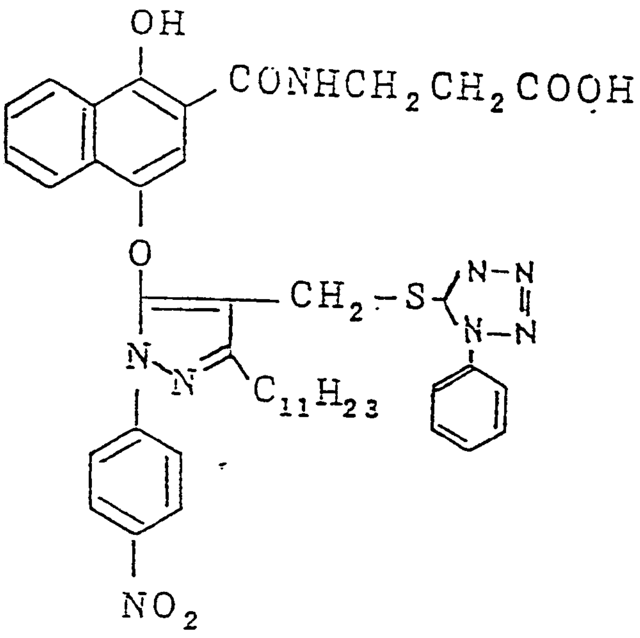
(D－7)


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

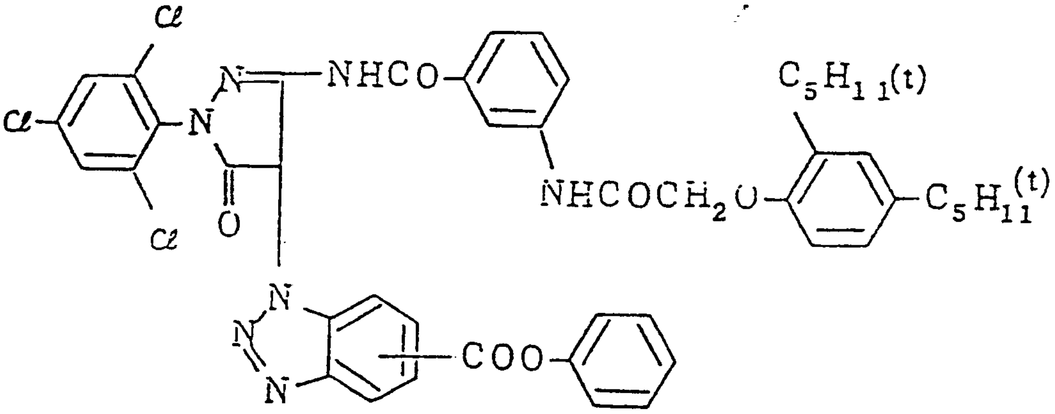
(D－8)


OH
CONHCH2CH2COOCH3
O
CH2－S
O
CH2CH2OH
N
N
N
N
C11H23
NO2

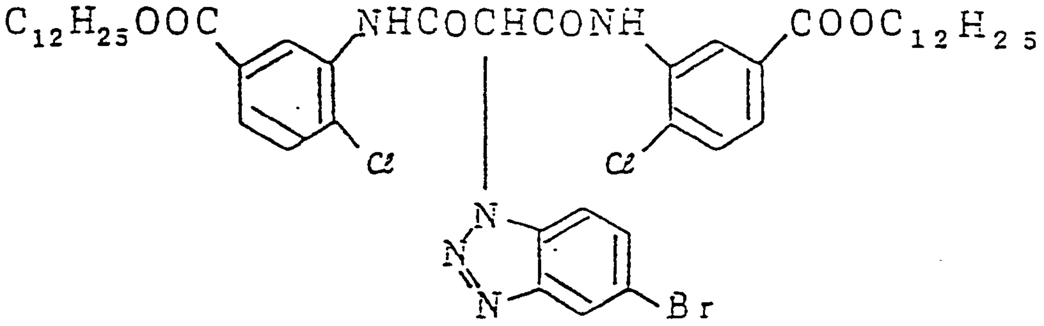
(D－9)


OH
CONHCH$_2$CH$_2$COOH
O
CH$_2$－S
N－N
N－N
N
N
C$_{11}$H$_{23}$
NO$_2$

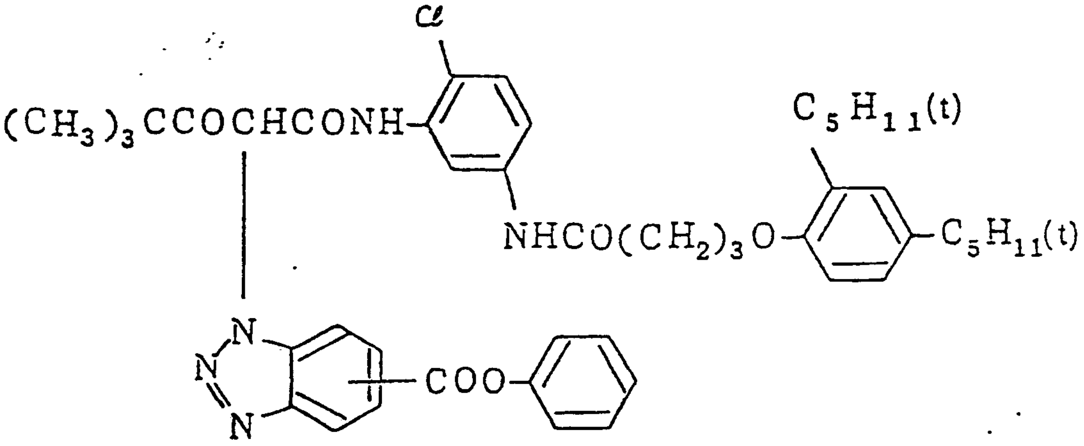
(D－10)


Cl
Cl
Cl
N
N
NHCO
O
NHCOCH$_2$O
C$_5$H$_{11}$(t)
C$_5$H$_{11}$(t)
N
N
N
COO

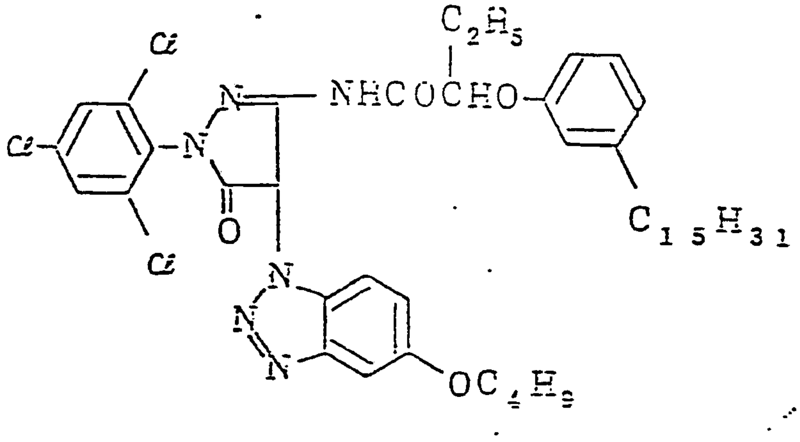
(D－11)


C12H25OOC
NHCOCHCONH
COOC12H25
Cl
Cl
N
N
N
Br

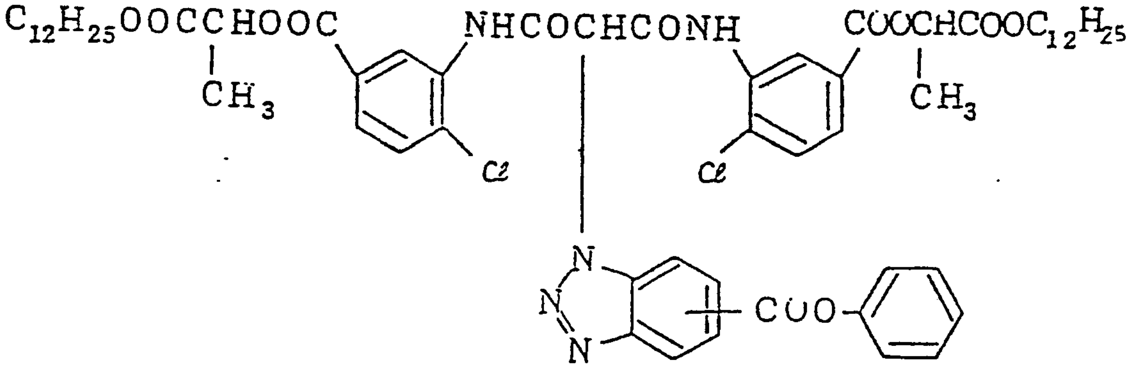
(D－12)


Cl
(CH3)3CCOCHCONH
C5H11(t)
NHCO(CH2)3O
C5H11(t)
N
N
N
COO

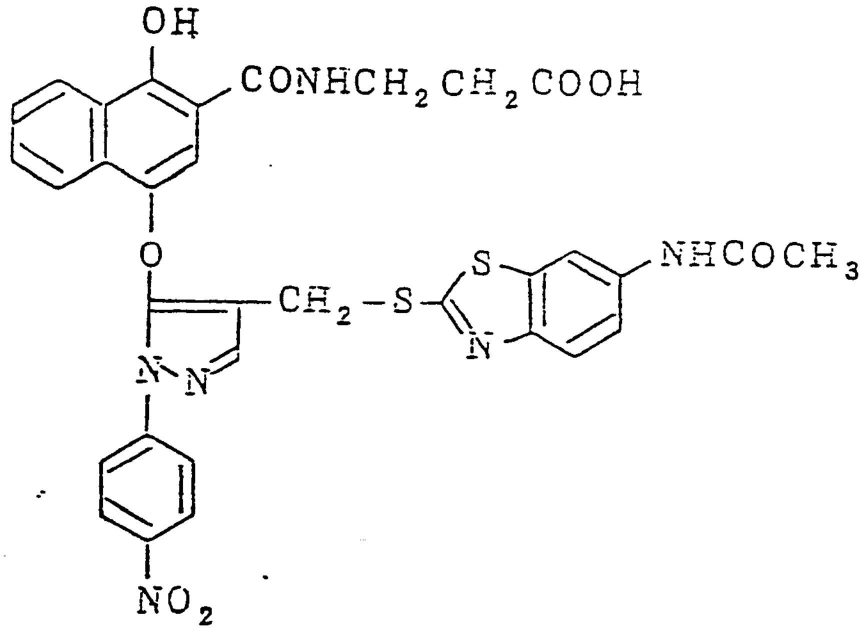
(D-13)


Cl
Cl
Cl
N
N
O
NHCOCHO
C2H5
C15H31
N
N
N
OC4H9

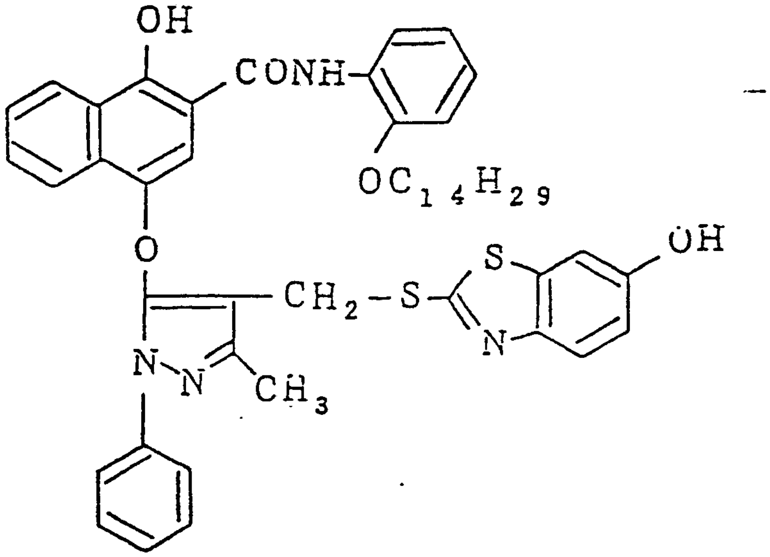
(D-14)


C12H25OOCCHOOC
CH3
NHCOCHCONH
COOCHCOOC12H25
CH3
Cl
Cl
N
N
N
COO

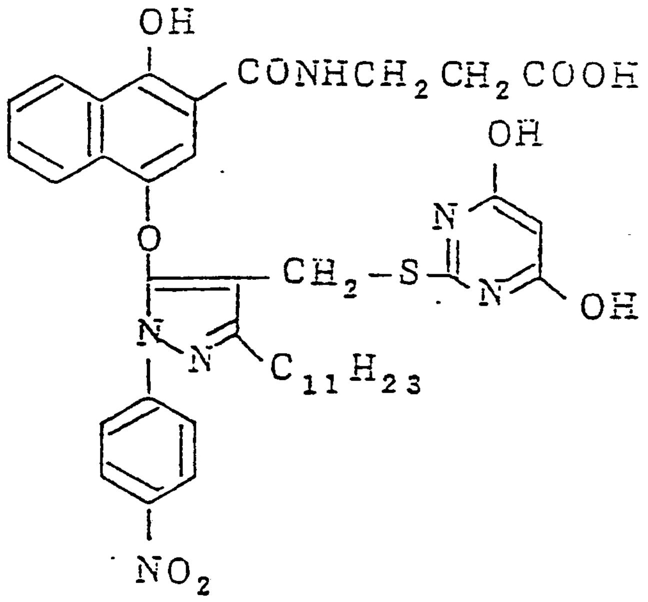
(D－15)


OH
CONHCH₂CH₂COOH
O
CH₂－S
S
N
NHCOCH₃
N
N
NO₂

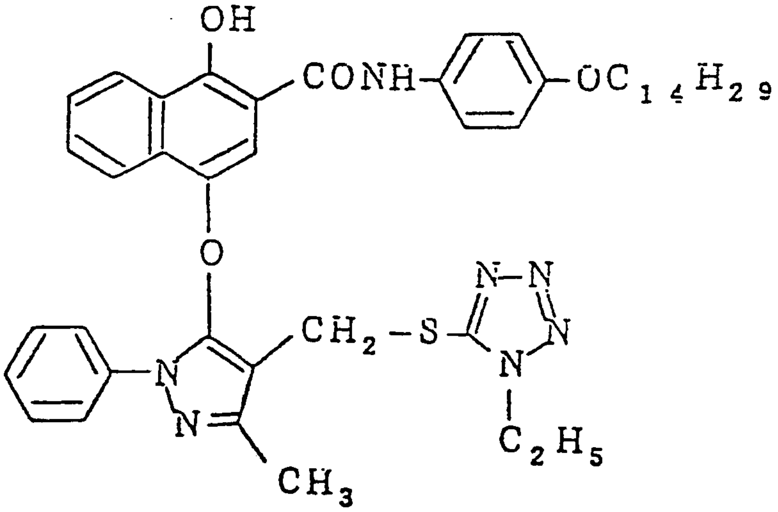
(D－16)


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

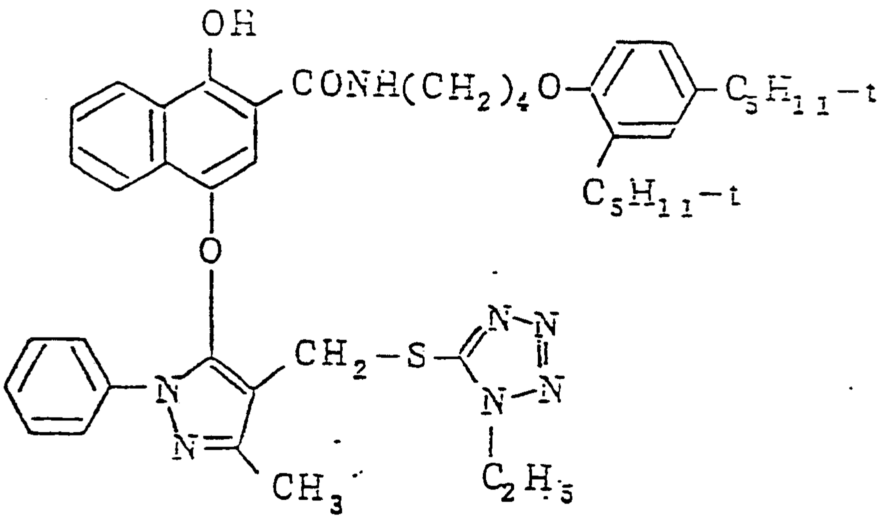
(D－17)


OH
CONHCH₂CH₂COOH
O
CH₂－S
N
N
OH
OH
N
N
C₁₁H₂₃
NO₂

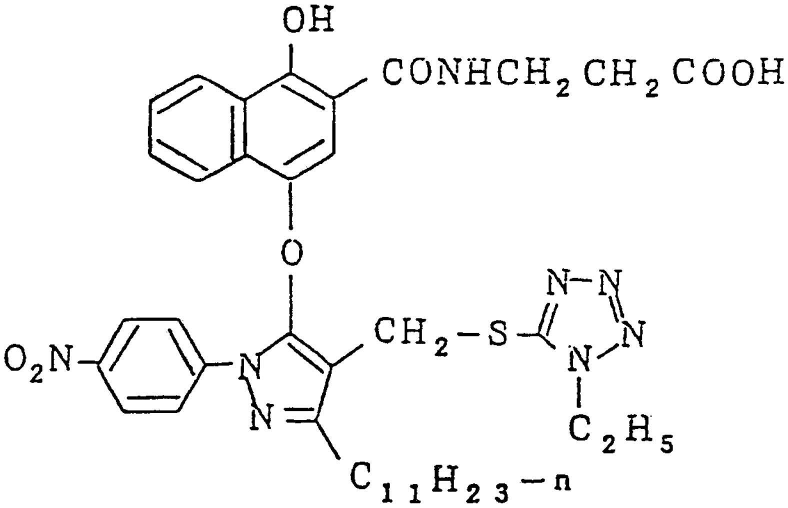
(D－18)


OH
CONH
OC₁₄H₂₉
O
CH₂－S
N－N
N
N
N
N
C₂H₅
CH₃

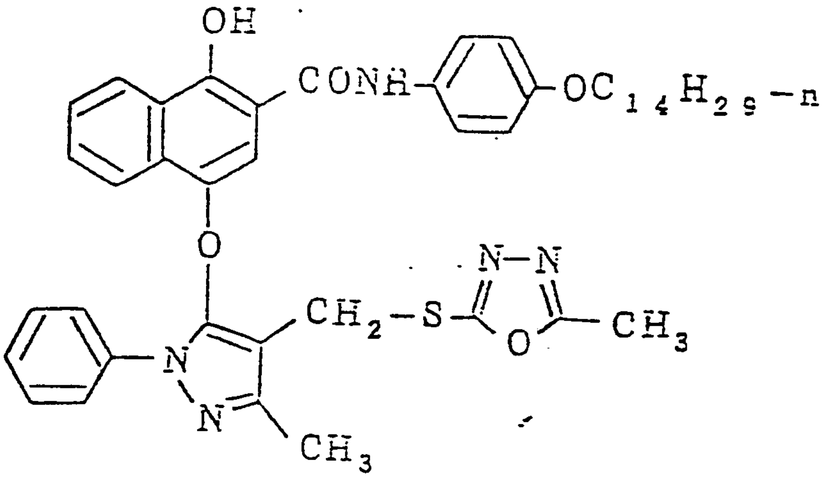
(D-19)


OH
CONH(CH2)4O
C5H11-t
C5H11-t
O
CH2-S
N
N
CH3
C2H5

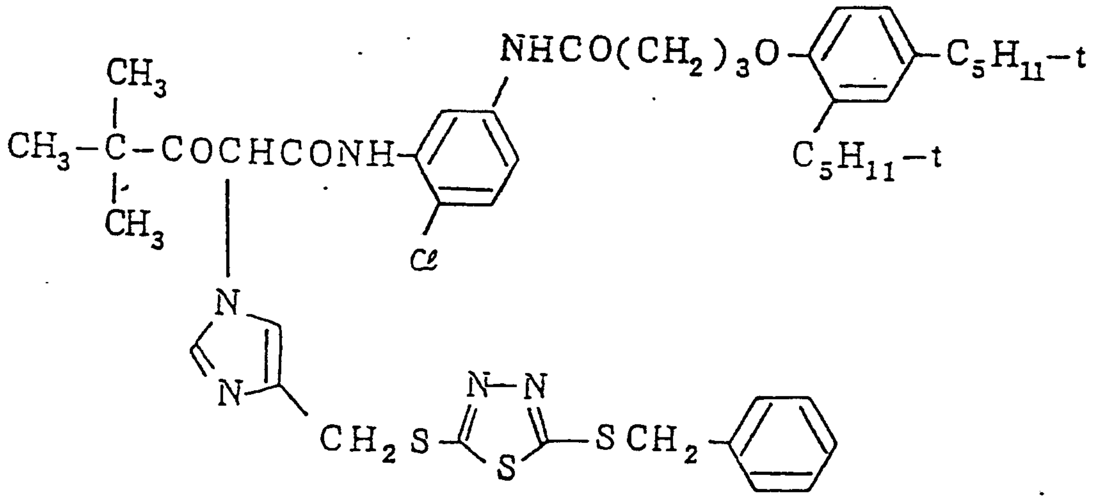
(D-20)


OH
CONHCH2CH2COOH
O
O2N
CH2-S
N
C2H5
C11H23-n

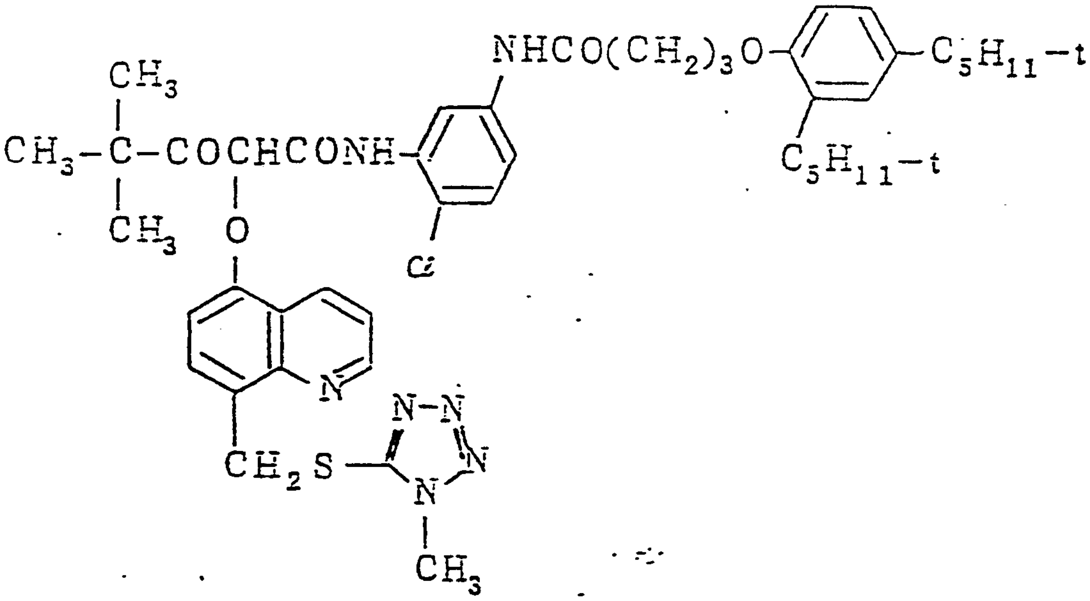
(D-21)


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

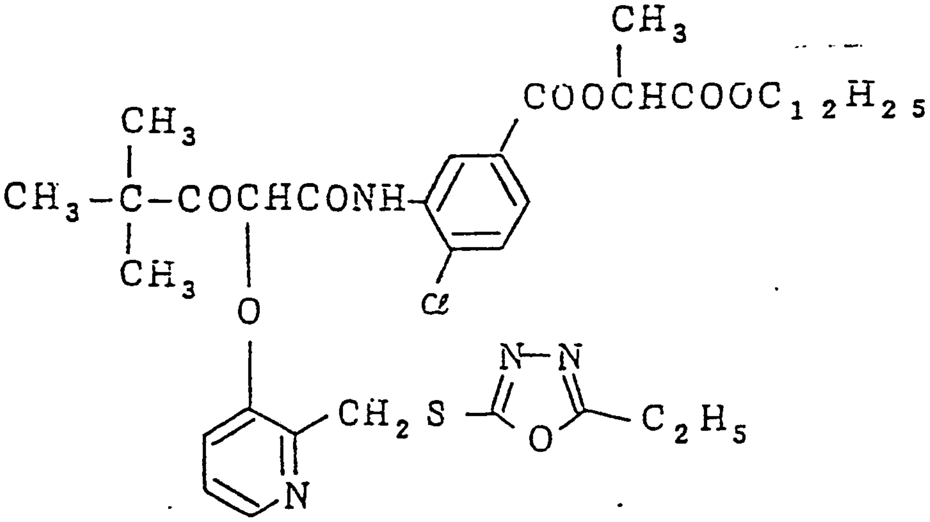
(D-21)


NHCO(CH2)3O
C5H11-t
C5H11-t
CH3
CH3-C-COCHCONH
CH3
Cl
N
N
N—N
CH2S
S
SCH2

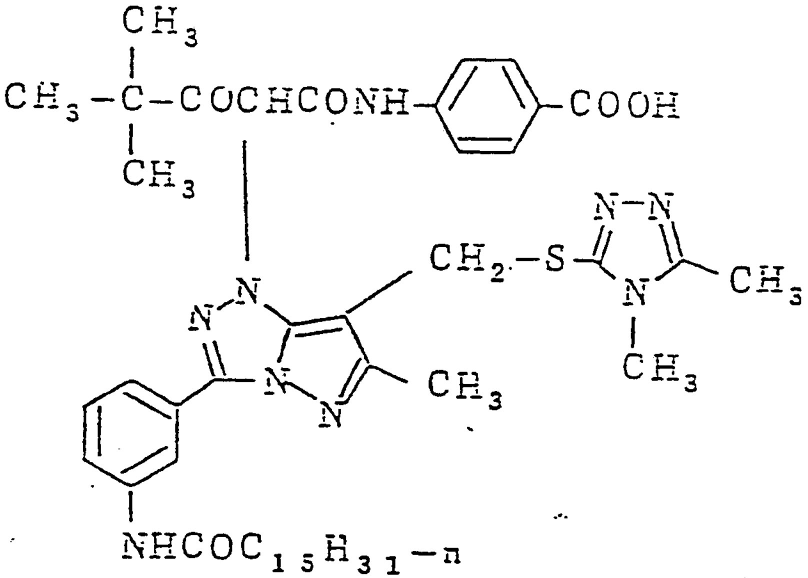
(D-22)



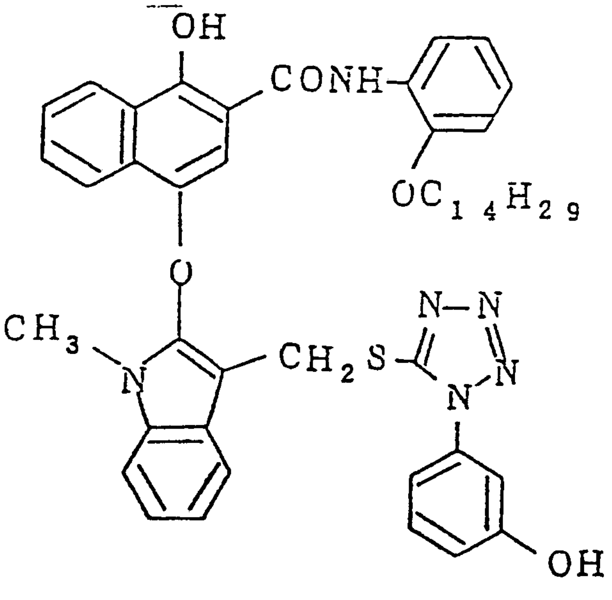
(D-23)



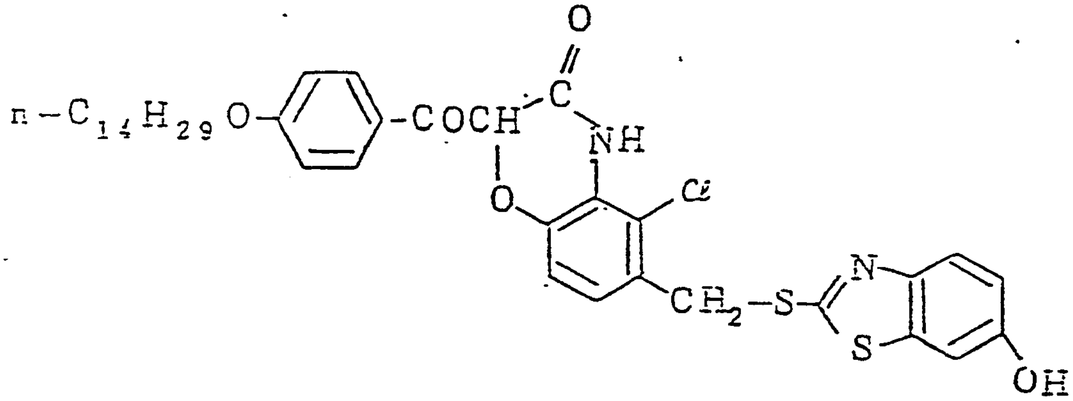
(D-24)


CH3
CH3-C-COCHCONH
CH3
COOH
N-N
CH2-S
N
CH3
CH3
N-N
N
N
N
CH3
NHCOC15H31-n

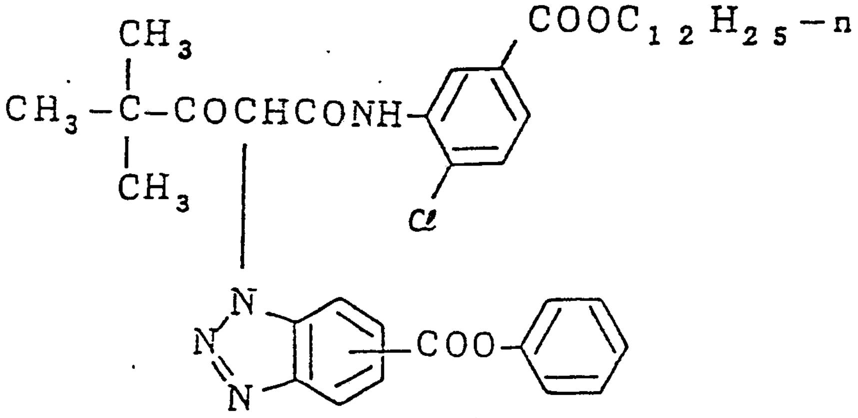
(D-25)


OH
CONH
OC14H29
O
CH3
N
CH2S
N-N
N
N
OH

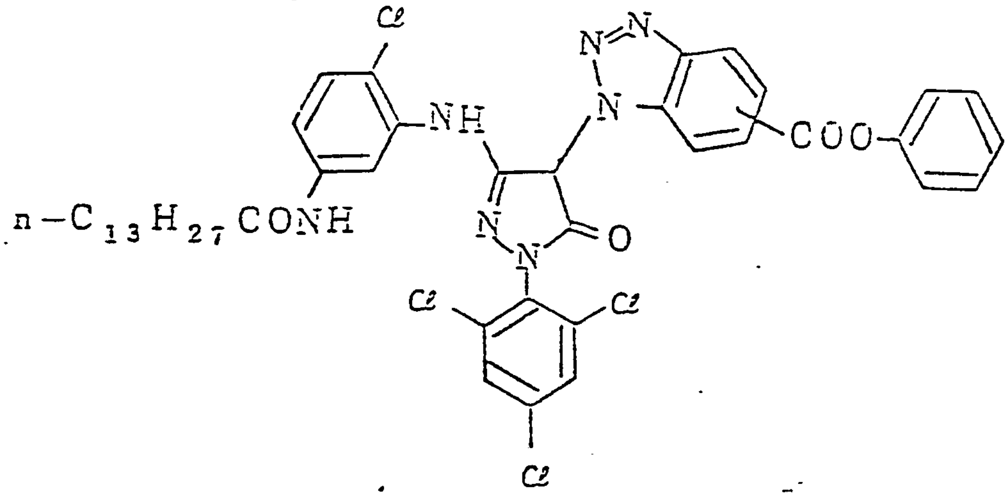
(D-26)



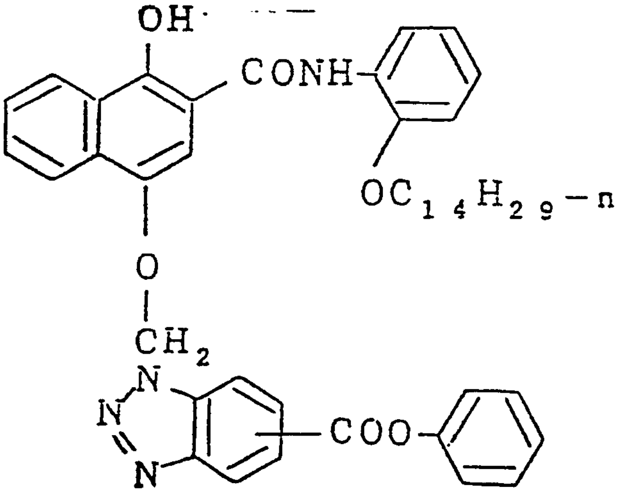
(D-27)



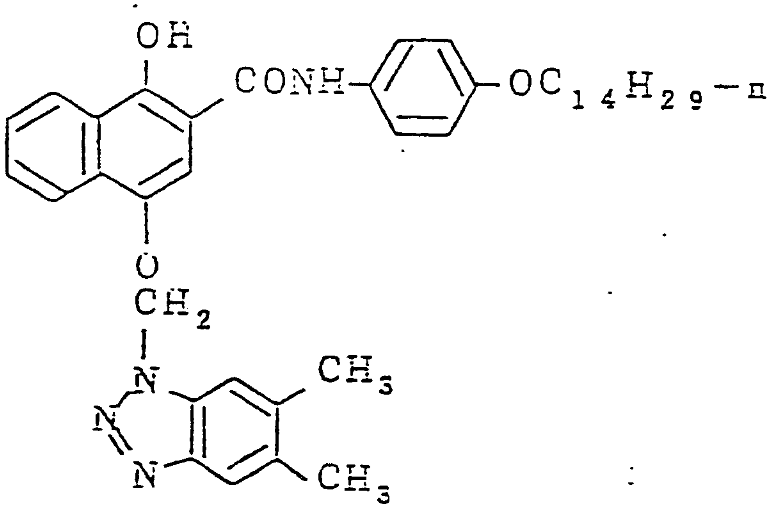
(D-28)


Cl
NH
N=N
N
COO
n-C13H27CONH
N
N
O
Cl
Cl
Cl

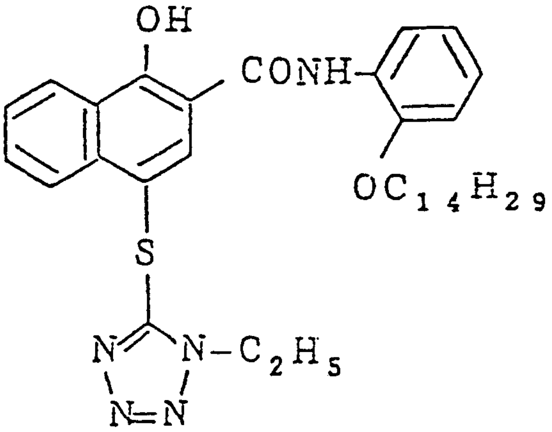
(D-29)


OH
CONH
OC14H29-n
O
CH2
N
N
N
COO

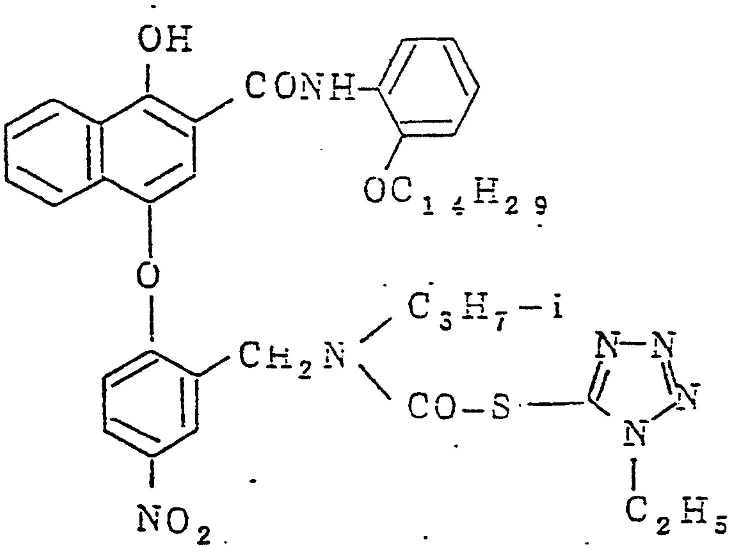
(D-30)



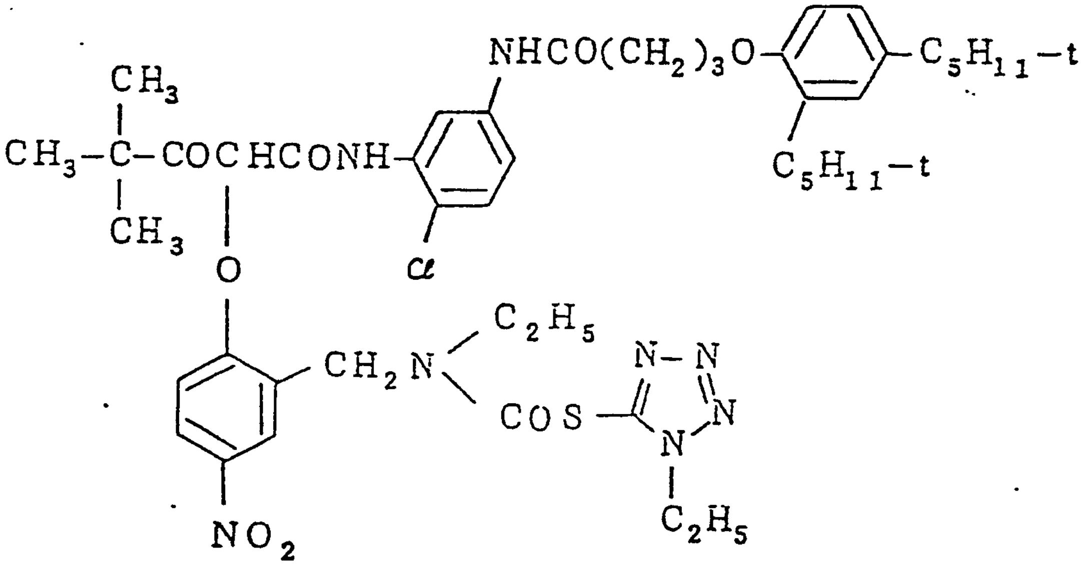
(D-31)



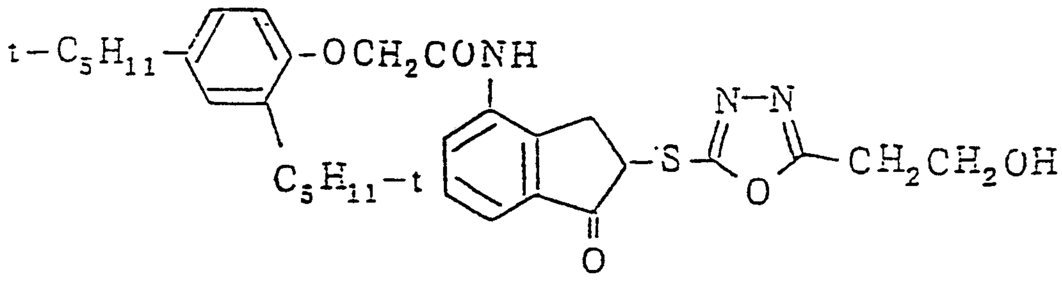
(D-32)


OH
CONH
$OC_{14}H_{29}$
O
C_3H_7-i
CH_2N
CO-S
N-N
N
N
NO_2
C_2H_5

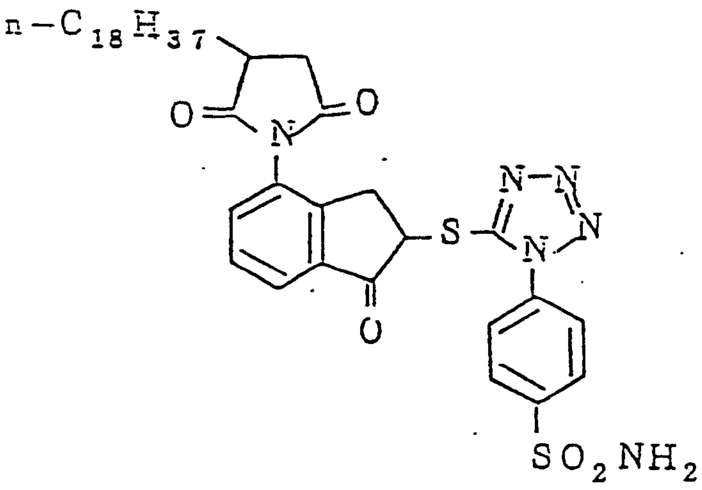
(D-33)


$NHCO(CH_2)_3O$
$C_5H_{11}-t$
CH_3
$CH_3-C-COCHCONH$
CH_3
$C_5H_{11}-t$
O
Cl
C_2H_5
CH_2N
N-N
COS
N
N
NO_2
C_2H_5

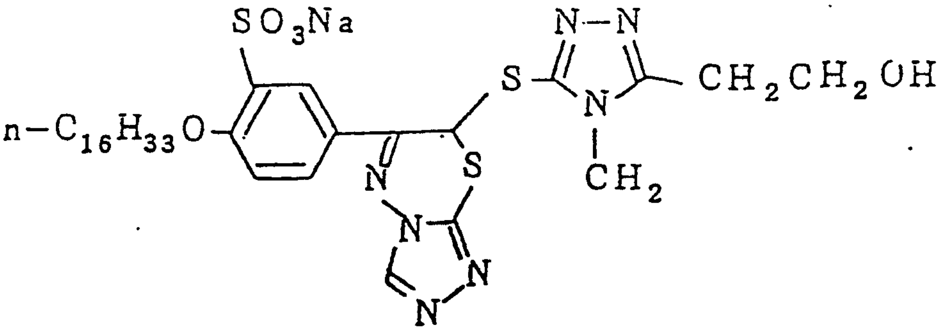
(D-34)



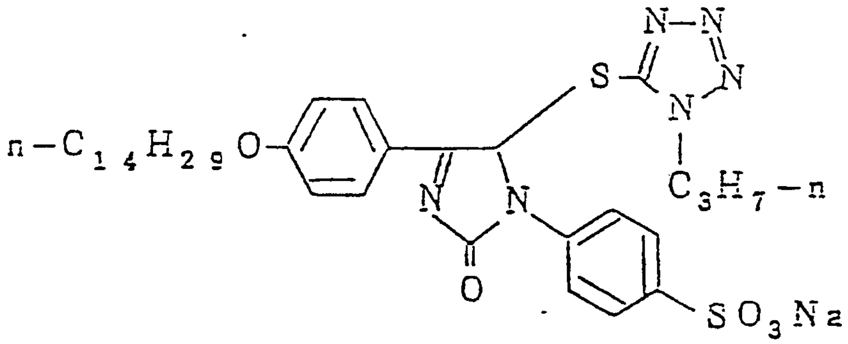
(D-35)



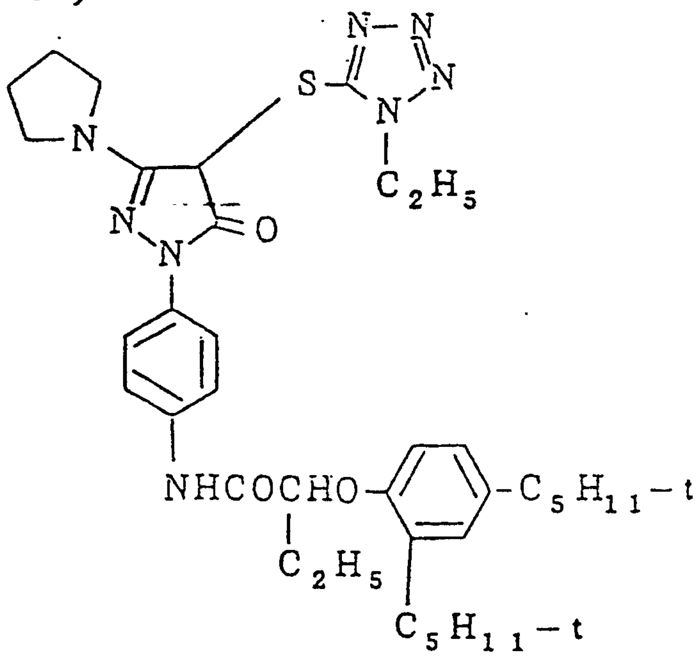
(D-36)



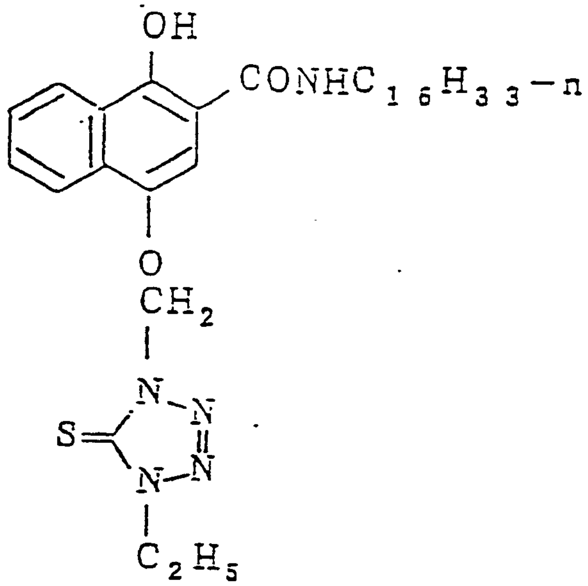
(D-37)



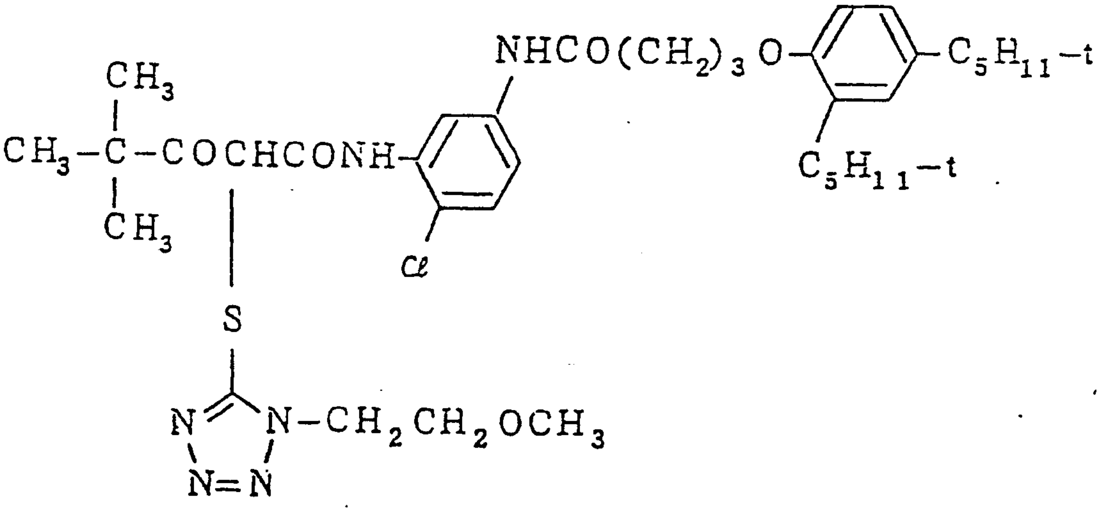
(D-38)



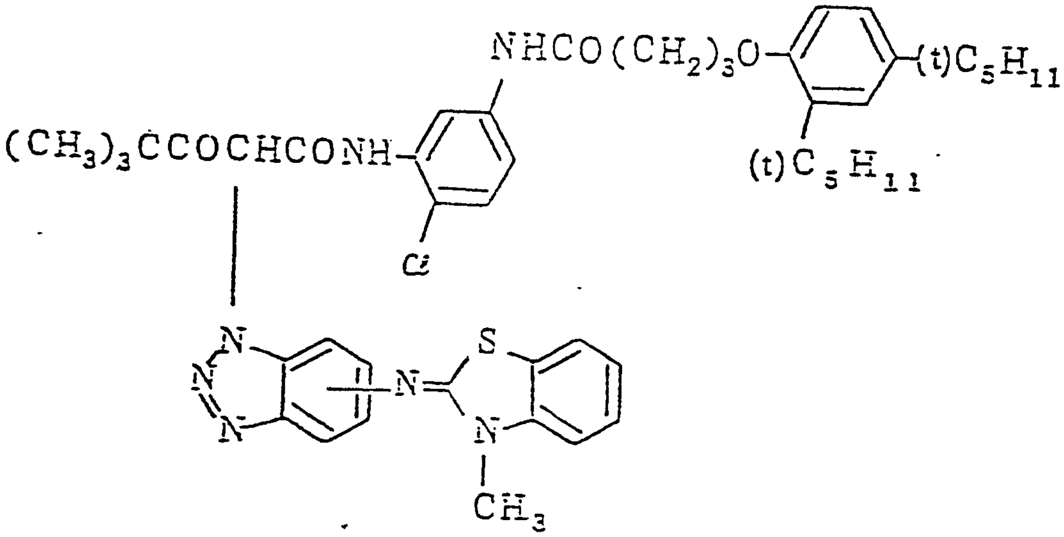
(D-39)


OH
CONHC16H33-n
O
CH2
N
S
C2H5

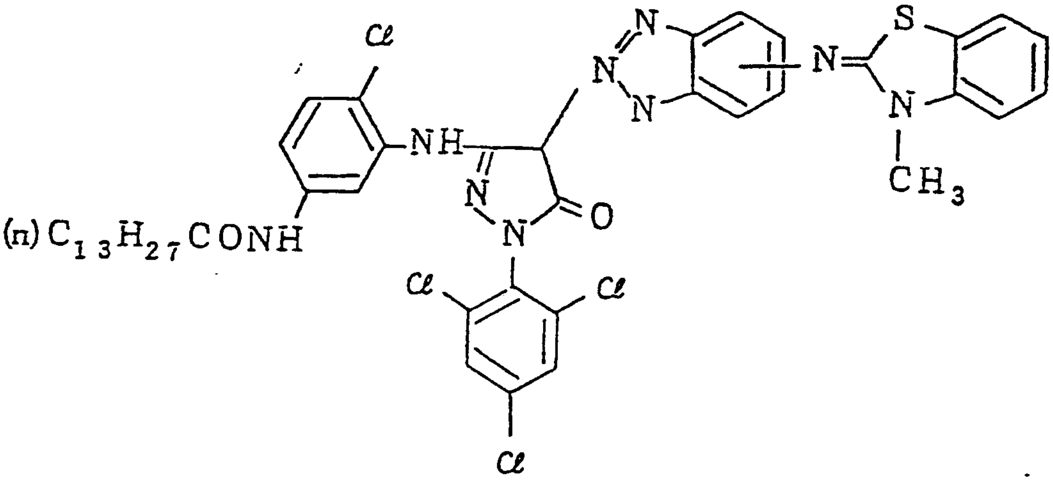
(D-40)


NHCO(CH2)3O
C5H11-t
CH3
CH3-C-COCHCONH
CH3
Cl
S
N-CH2CH2OCH3
C5H11-t

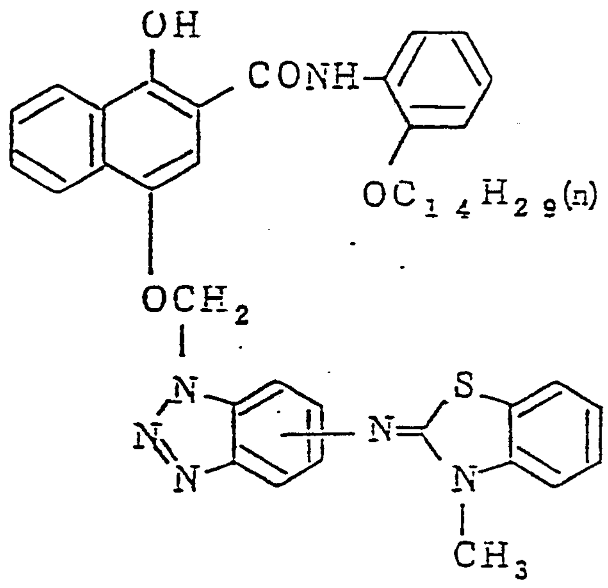
(D-41)


NHCO(CH2)3O
(t)C5H11
(CH3)3CCOCHCONH
(t)C5H11
Cl
N
N
N
N=
S
N
CH3

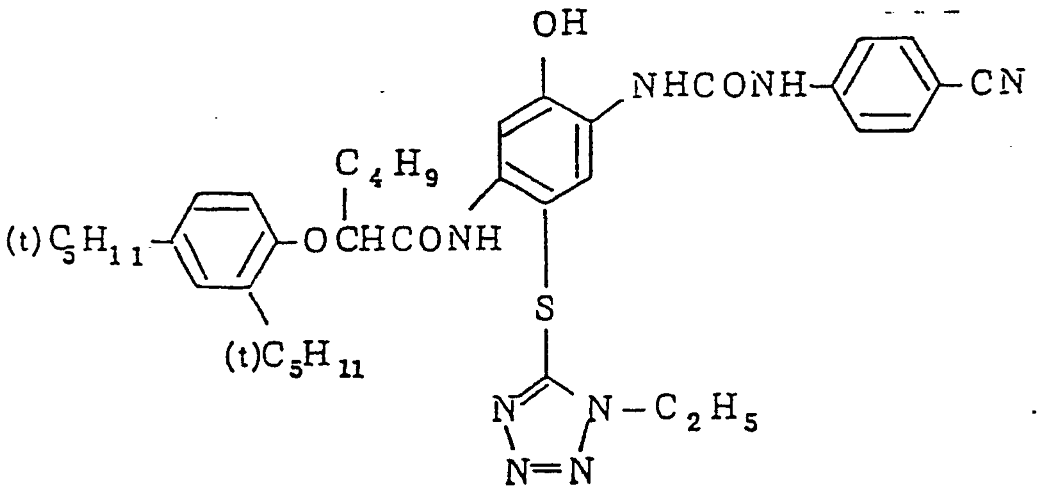
(D-42)


Cl
N
N
N
N=
S
N
CH3
NH
N
N
O
(n)C13H27CONH
Cl
Cl
Cl

(D - 43)



(D - 44)



The compounds represented by the formula (I) can be prepared according to the methods described in U.S. Patent Nos. 4,174,966, 4,183,752, 4,421,845 and 4,447,563, and JP-A-54-145135, JP-A-57-151944, JP-A-57-154234, JP-A-57-188035, JP-A-58-98728, JP-A-58-162949, JP-A-58-209736, JP-A-58-209737, JP-A-58-209738 and JP-A-58-209740.

The compounds having the formula (I′) are incorporated in at least one layer of the silver halide material, i.e., at least one of the silver halide emulsion layers, the intermediate layers, the filter layers (yellow filter layer, magenta filter layer, etc.), the undercoat layer, the antihalation layer, the protective layer and other auxiliary layers of the photographic material. It is preferred that the compounds are incorporated in a sensitive silver halide layer or a sensitive layer adjacent thereto, particularly a layer containing the emulsion grains of the present invention or a layer sensitive to the same color as the layers and adjacent to the layers.

The compounds having the formula (I′) can be added to the photographic material in the same manner as coupler dispersion method described hereinafter. The compounds are used in an amont of 10^{-6} to 10^{-3} mol/m^2, preferably 3×10^{-6} to 5×10^{-4} mol/m^2 and more preferably 5×10^{-6} to 2×10^{-4} mol/m^2.

It is preferred from the viewpoint of improving development activity and sharpness of color reproducibility, to use a compound which cleaves the restrainer by the reaction of the compound with an oxidant of a developing agent and then the reaction of the resulting cleaved compound with another one molecule of the oxidant of the developing agent.

The compound which cleaves the restrainer by the reaction of said compound with the oxidant of a developing agent and then the reaction of the resulting cleaved compound with another one molecule of the oxidant of the developing agent, can be represented by the following general formula [I″]

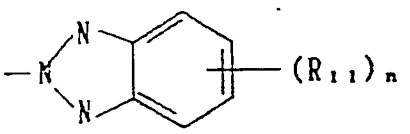
A′-P-Z [I″]

In the above formula, A′ represents a coupling component capable or reacting with the oxidants of color developing agents and a component capable of releasing the -P-Z group by reaction with the oxidants of the color developing agents; Z represents a development restrainer whose diffusion can be freely chosen (preferably Z is a restrainer whose ability as the restrainer is rapidly deactivated when it flows out into developing agents); and -P-Z represents a group which forms a restrainer through the reaction with the oxidants of the developing agents after cleavage from the group A′.

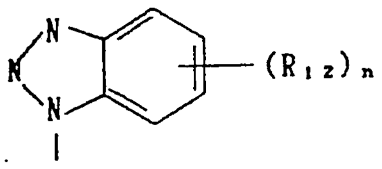
Restrainers represented by Z include restrainers described in Research Disclosure No. 17643 (December 1978), preferably mercaptotetrazole, selenotetrazole, mercaptobenzthiazole, selenobenzthiazole, mercaptobenzoxazole, selenobenzoxazole, mercaptobenzimidazole, selenobenzimidazole, benztriazole, mercaptotriazole, mercaptooxadiazole, mercaptothiadiazole and derivatives thereof.

Preferred examples of the restrainers include those represented by the following general formulas.

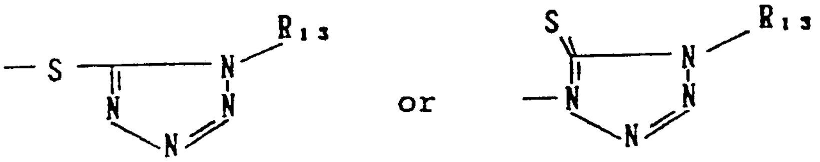
(Z - 1)



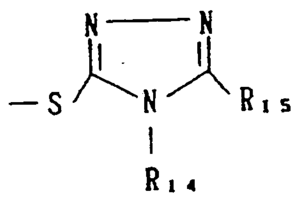
(Z - 2)



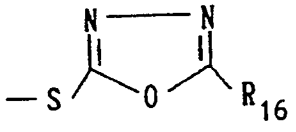
(Z - 3)



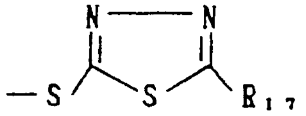
(Z - 4)



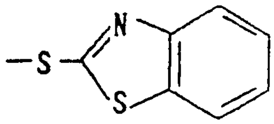
(Z - 5)



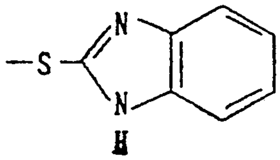
(Z − 6)



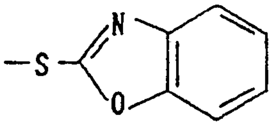
(Z − 7)



(Z − 8)



(Z − 9)



In the formulae (Z-1) and (Z-2), R_{11} and R_{12} are each an alkyl group, an alkoxy group, an acylamino group, a halogen atom, an alkoxycarbonyl group, a thiazolylideneamino group, an aryloxycarbonyl group, an acyloxy group, a carbamoyl group, an N-alkylcarbamoyl group, an N,N-dialkylcarbamoyl group, nitro group, anamino group, an N-arylcarbamoyloxy group, a sulfamoyl group, a sulfonamido group, an N-alkylcarbamoyloxy group, a ureido group, hydroxyl group, an alkoxycarbonylamino group, an aryloxy group, an alkylthio group, an arylthio group, an anilino group, an aryl group, an imido group, a heterocyclic group, cyano group, an alkylsulfonyl group or an aryloxycarbamoylamino group; and n is 1 or 2. When n is 2, each of R_{11} and R_{12} may be the same or different. The sum total of carbon atoms of n R_{11} or n R_{12} is 0 to 20.

In the formulae (Z-3), (Z-4), (Z-5) and (Z-6), R_{13}, R_{14}, R_{15}, R_{16} and R_{17} are each an alkyl group, an aryl group or a heterocyclic group.

The alkyl group represented by R_{11} to R_{17} may be a substituted or unsubstituted, linear or cyclic alkyl group. Examples of substituent groups include halogen, nitro group, cyano group, an aryl group, an alkoxy group, an aryloxy group, an alkoxycarbonyl group, an aryloxycarbonyl group, a sulfamoyl group, a carbamoyl group, hydroxyl group, an alkanesulfonyl group, an arylxulfonyl group, an alkylthio group and an arylthio group.

The aryl group represented by R_{11} to R_{17} may be optionally be substituted. Examples of substituent groups include an alkyl group, an alkenyl group, an alkoxy group, an alkoxycarbonyl group, a halogen atom, nitro group, an amino group, a sulfamoyl group, hydroxyl group, a carbamoyl group, an aryloxycarbonylamino group, an alkoxycarbonylamino group, an acylamino group, cyano group and a ureido group.

The heterocyclic group represented by R_{11} to R_{17} may be a 5-membered or 6-membered, monocyclic or condensed ring containing a nitrogen atom, oxygen atom or sulfur atom as the hetero-atom. Examples of the heterocyclic group include pyridyl group, quinolyl group, furyl group, benzthiazolyl group, oxazolyl group, imidazolyl group, thiazolyl group, triazolyl group, benztriazolyl group, imido group and oxazine group. These groups may optionally be substituted by one or more substituent groups already described above for the aryl group.

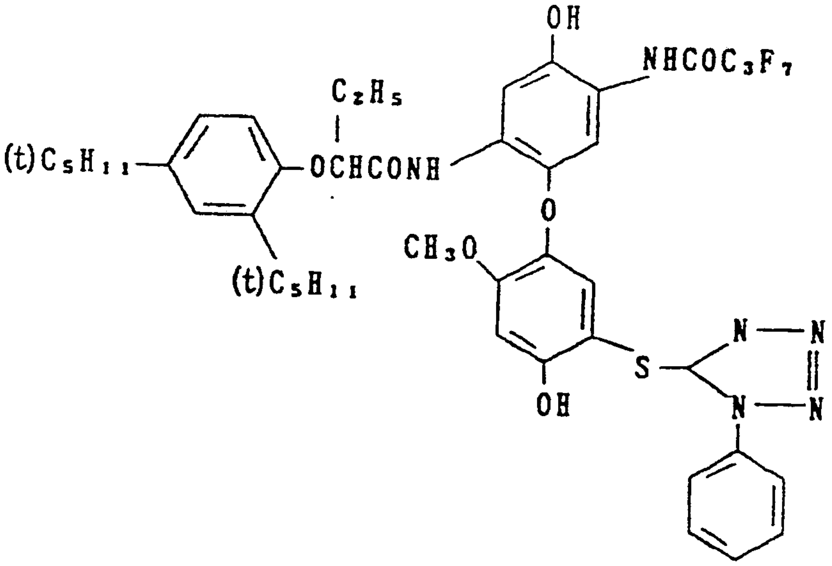
In the formulae (Z-1) and (Z-2), the number of carbon atoms of R_{11} or R_{12} is 1 to 20, more preferably 7 to 20.

In the formulae (Z-3), (Z-4), (Z-5) and (Z-6), the sum total of carbon atoms of each of R_{13} to R_{17} is 1 to 20, more preferably 4 to 20.

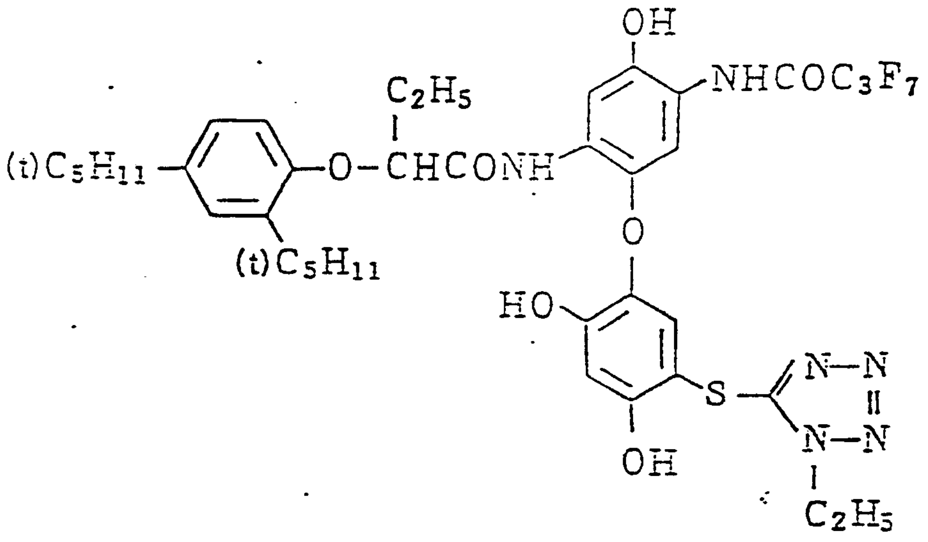
These compounds which can be used in the present invention can be easily synthesized by the methods described in JP-A-60-185950, JP-A-61-240240, JP-A-61-249052, JP-A-61-266550 and JP-A-61-236551.

Examples of these compounds include, but are not limited to, the compounds having the following formulas.

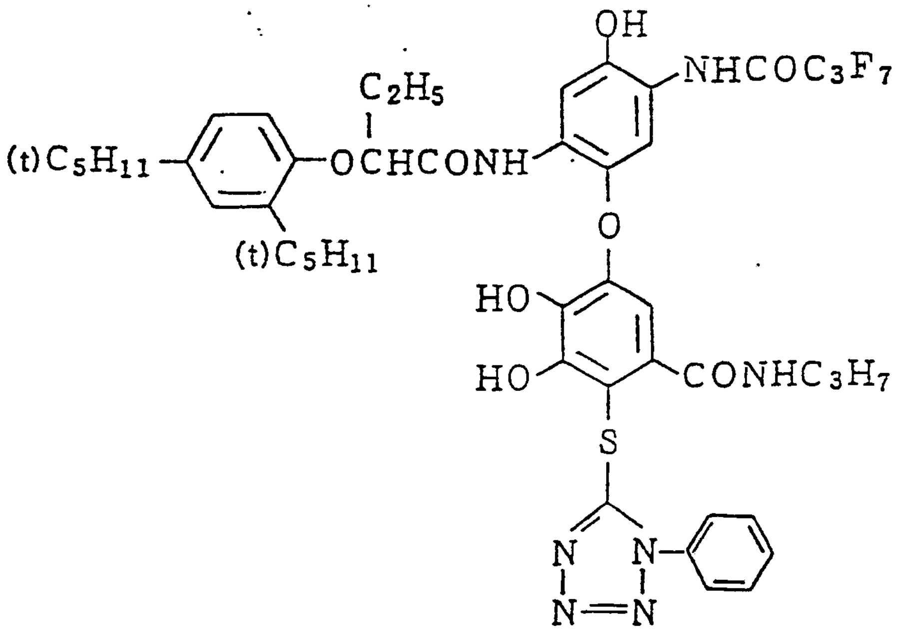
T − 1



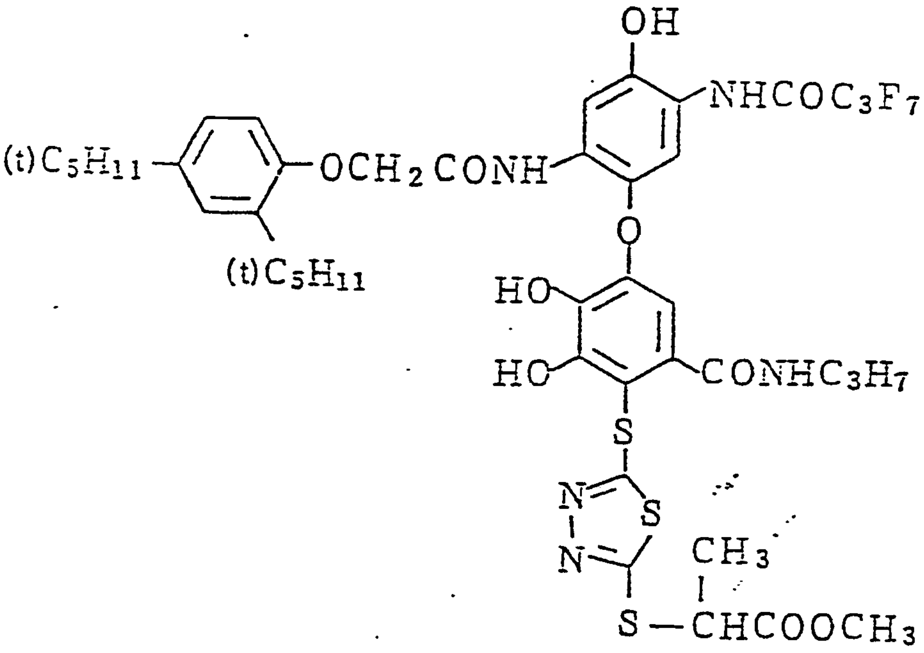
T − 2



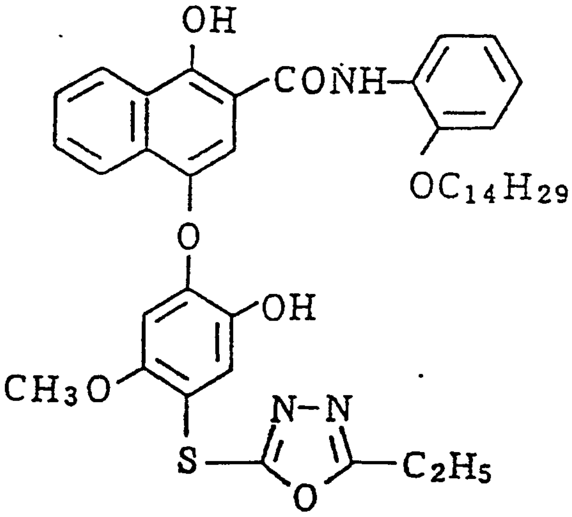
T − 3



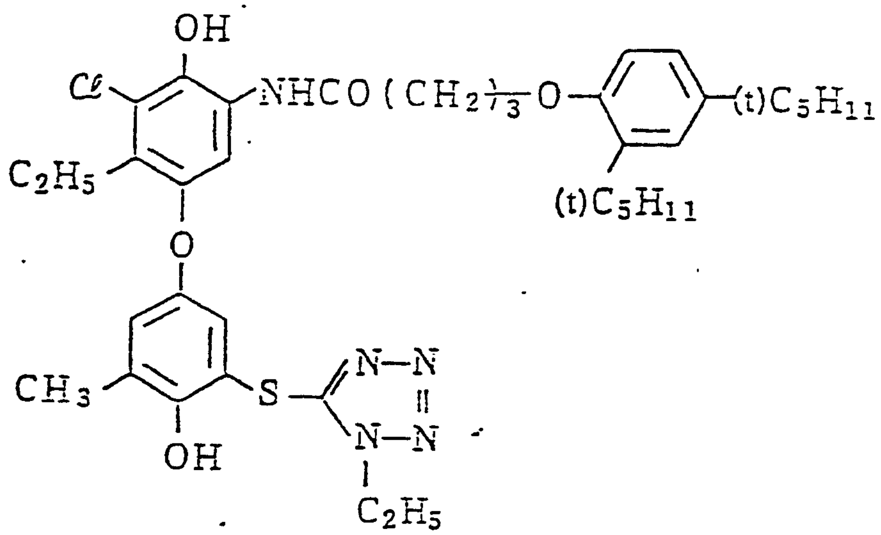
T − 4



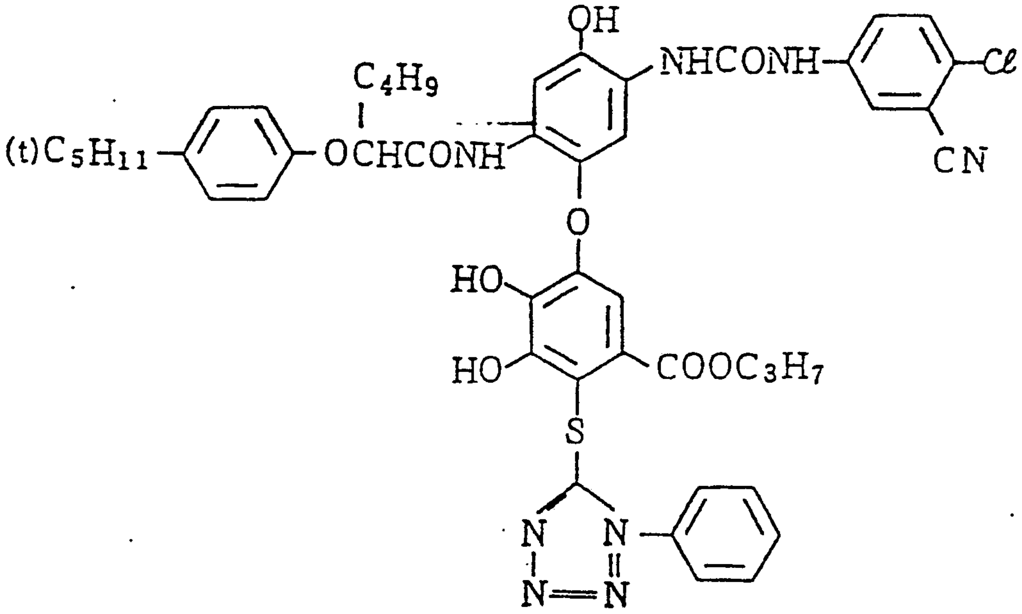
T − 5



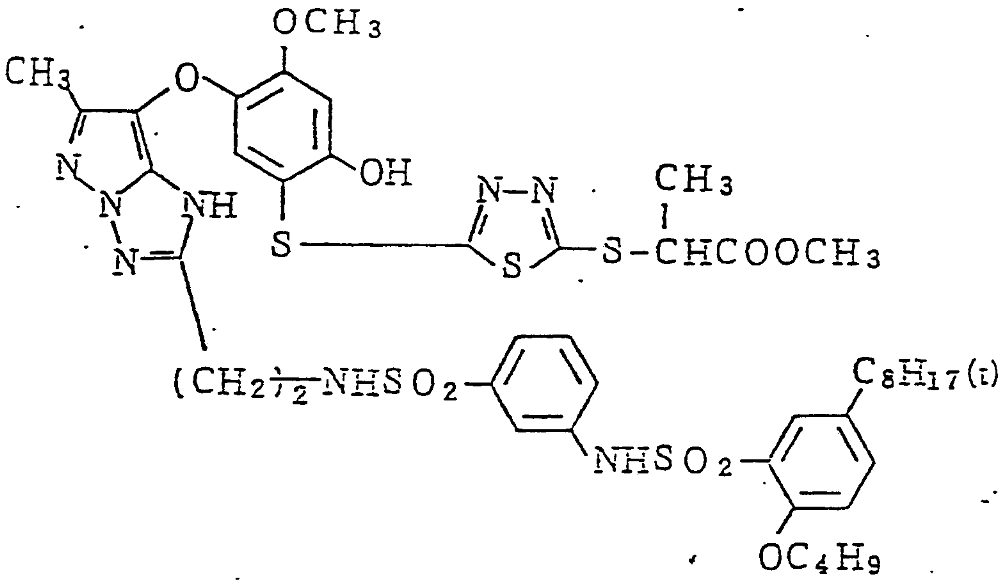
T — 6


OH
Cl
NHCO(CH2)3O
(t)C5H11
C2H5
(t)C5H11
O
N—N
CH3
S
N—N
OH
C2H5

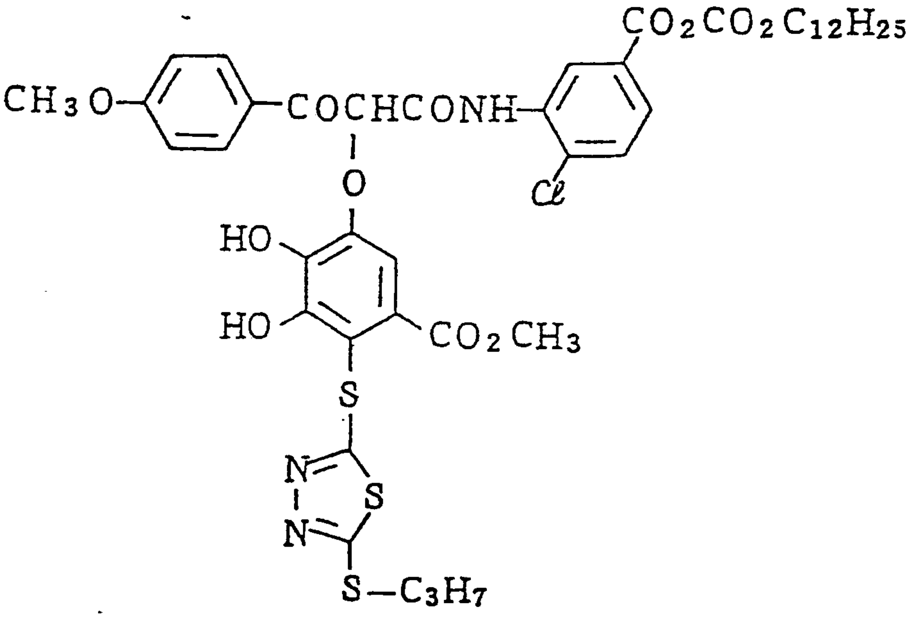
T — 7


OH
NHCONH
Cl
C4H9
(t)C5H11
OCHCONH
CN
O
HO
HO
COOC3H7
S
N
N
N
N

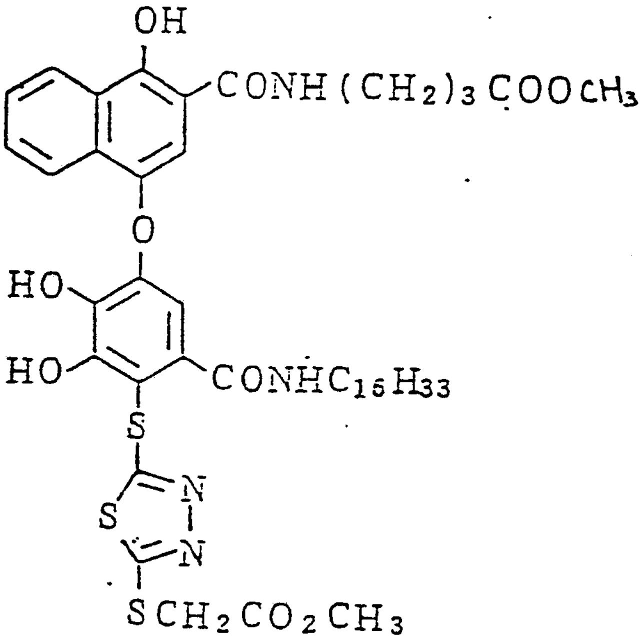
T − 8



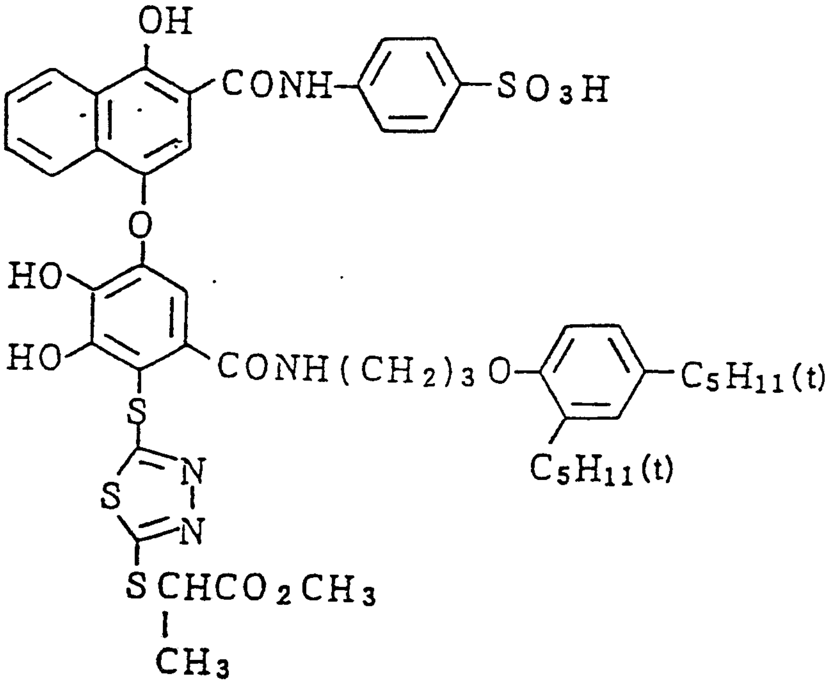
T − 9



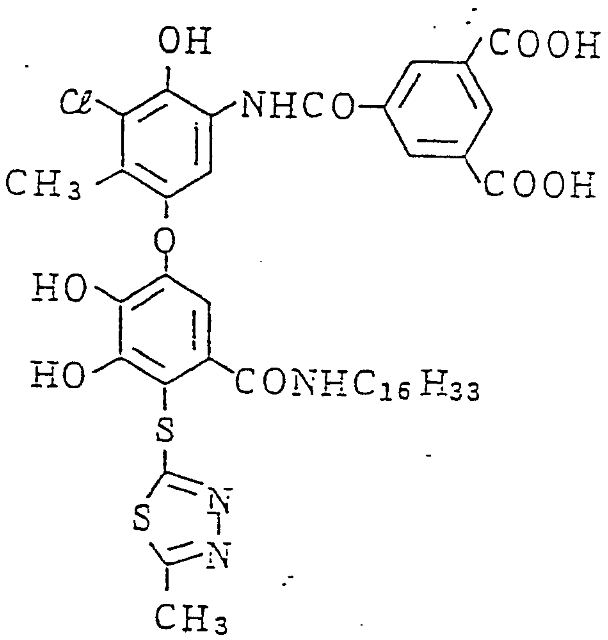
T－10



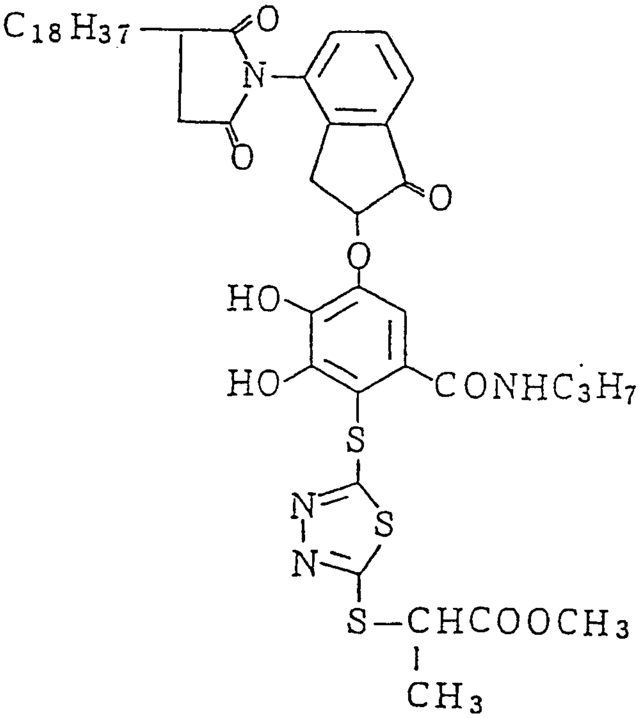
T－11



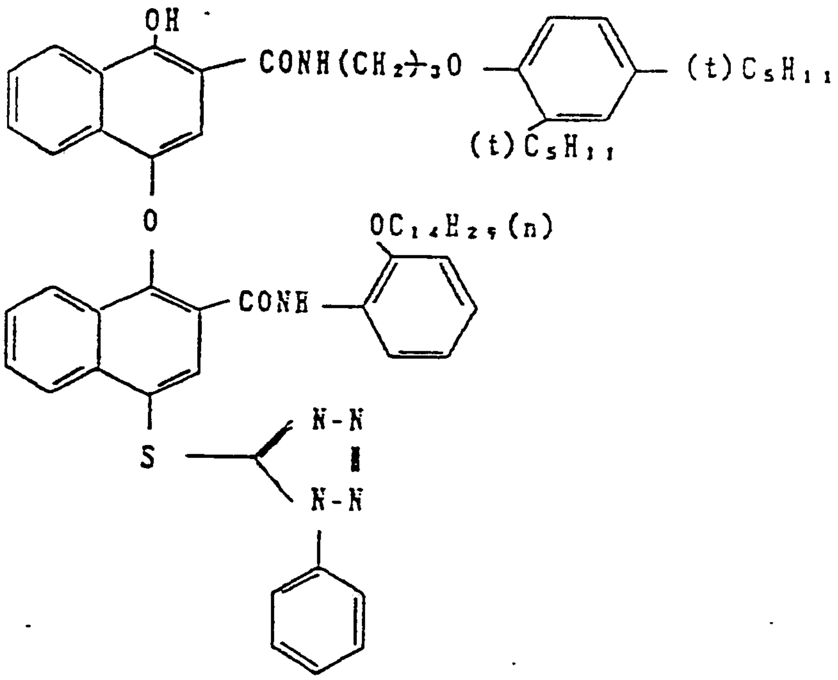
T — 12



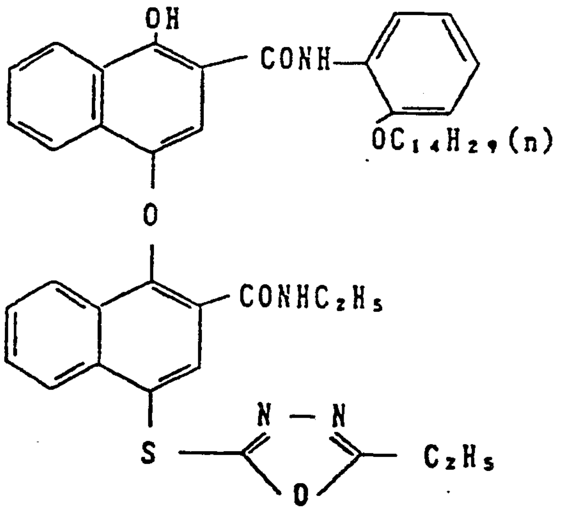
T — 13



T - 14



T - 15



The above-described restrainer-releasing compounds can be added to the silver halide emulsion layers or the non-sensitive intermediate layers of the silver halide color photographic material. The restrainer-releasing compounds should be used in an amount of 10^{-6} to 10^{-3} mol/m^2, preferably 5×10^{-6} to 3×10^{-4} mol/m^2.

When there is an emphasis on an improvement in sharpness in the present invention, the following methods are preferred. First, the photographic material is thin-layered. The thickness thereof from the surface of the support to the surface of the protective layer is preferably not more than 23 μm, more preferably not more than 18 μm. Secondly, for the upper layer of the silver halide emulsion layers, there are used tubular (plate-form) silver halide grains having an average aspect ratio of not lower than 5 and good light transmission, or monodisperse silver halide grains having a grain size within which light in the region of visible light is scarcely scattered.

Furthermore, the above methods may be used in combination with methods wherein unsharp mask compounds are used to enhance sharpness as described in JP-A-62-35355 and JP-A-62-25756.

There may be used methods wherein nondiffusing color absorbing dyes are added to the sensitive layers or the non-sensitive layers as described in JP-A-61-295550 and JP-A-61-292636.

In the present invention, it is preferred that compounds capable of reacting with formaldehyde for fixing (see e.g., U.S. Patent Nos. 4,411,987 and 4,435,503) are added to the photographic material to prevent photographic performance from being deteriorated by formaldehyde gas.

Various color couplers can be used in the present invention. Specific examples thereof include those couplers described in the Patent Specifications cited in the Research Disclosure (RD) No. 17643, VII-C to G.

Preferred examples of yellow couplers include those described in U.S. Patent Nos. 3,933,501, 4,022,620, 4,326,024 and 4,401,752, JP-B-58-10739, U.K. Patent Nos. 1,425,020 and 1,476,760, U.S. Patent Nos. 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 compounds are described in U.S. Patent Nos. 4,310,619 and 4,351,897, European Patent 73,636, U.S. Patent Nos. 3,061,432 and 3,725,064, Research Disclosure No. 2422 (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. Patent Nos. 4,500,630, 4,540,654 and 4,556,630.

Cyan couplers include phenol couplers and naphthol couplers. Preferred examples of cyan couplers include those compounds described in U.S. Patent Nos. 4,052,212, 4,146,396, 4,228,238, 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 Laid-Open No. 3,329,729, European Patent Nos. 121,365A and 249,453A, U.S. Patent Nos. 3,446,622, 4,333,999, 4,753,871, 4,451,559, 4,427,767, 4,690,889, 4,254,212 and 4,296,199, and JP-A-61-42658.

Colored couplers for correcting the unnecessary absorption of color forming dyes include those described in Research Disclosure No. 17643, item VII-G, U.S. Patent 4,163,670, JP-B-57-39413, U.S. Patent Nos. 4,004,929 and 4,138,258 and U.K. Patent No. 1,146,368. It is preferred that there are used couplers for correcting the unnecessary absorption of color forming dyes by fluorescent dye released during coupling, described in U.S Patent No. 4,774,181, or couplers having, as an eliminable group, a dye precursor group capable of forming a dye by the reaction with developing agent such as those described in U.S. Patent No. 4,777,120.

As couplers whose color forming dyes are properly diffusing, there are preferred those couplers described in U.S. Patent No. 4,366,237, U.K. Patent 2,125,670, European Patent No. 96,570 and West German Patent Laid-Open No. 3,234,533.

Typical examples of dye forming polymer couplers are described in U.S. Patent Nos. 3,451,820, 4,080,211, 4,367,282, 4,409,320 and 4,576,910, and U.K. Patent 2,102,173.

Couplers which release photographically useful residues by coupling are preferably used in the present invention. Preferred examples of DIR couplers which release a restrainer include those decribed in Patent Specifications cited in the afore-mentioned Research Disclosure (RD) No. 17643, item VII-F, JP-A-60-184248, JP-A-63-37346 and U.S. Patent No. 4,782,012 in addition to the compounds represented by the general formula (I).

As couplers which release imagewise a nucleating agent or a development accelerator during development, there are preferred the compounds described in U.K. Patent Nos. 2,097,140 and 2,131,188, JP-A-59-157638 and JP-A-59-170840.

Other examples of couplers which can be used in the photographic material of the present invention include couplers which release a dye capable of restoring its color to the original one after elimination such couplers are described in European Patent No. 173,302A. Other useful couplers incluse releasing bleaching accelerators such as those described in JP-A-61-201247; couplers releasing ligands such as those described in U.S. Patent No. 4,553,477; couplers releasing leuco dyes such as those described in JP-A-63-75747; and couplers releasing fluorescent dyes such as those described in U.S. Patent No. 4,774,181.

The couplers can be introduced into the photographic material of the present invention by conventional dispersion methods.

Examples of high-boiling solvents for use in oil-in-water dispersion methods are described in U.S. Patent No. 2,322,027.

Examples of the high-boiling organic solvents which are suitable for use in the oil-in-water dispersion methods and have a boiling point of not lower than 175°C under atmospheric pressure include phthalic esters such as dibutyl phthalate, dicyclohexyl phthalate, di-2-ethylhexyl phthalate, decyl phthalate, bis(2,4-di-t-amylphenyl) phthalate, bis(2,4-di-t-amylphenyl) isophthalate and bis(1,1-diethylpropyl) phthalate; phosphoric or phosphonic esters such as triphenyl phosphate, tricresyl phosphate, 2-ethylhexyl diphenyl phosphate, tricyclohexyl phosphate, tri-2-ethylhexyl phosphate, tridodecyl phosphate, tributoxyethyl phosphate, trichloropropyl phosphate and di-2-ethylhexyl phenyl phosphonate; benzoic esters such as 2-ethylhexyl benzoate, dodecyl benzoate and 2-ethylhexyl p-hydroxybenzoate; amides such as N,N-diethyldodecaneamide, N,N-diethyllaurylamide and N-tetradecylpyrrolidone; alcohols or phenols such as isostearyl alcohol and 2,4-di-t-amylphenol; aliphatic carboxylic esters such as bis(2-ethylhexyl) sebacate, dioctyl azelate, glycerol tributyrate, isostearyl lactate and trioctyl citrate; aniline derivatives such as N,N-dibutyl-2-butoxy-5-t-octylaniline; and hydrocarbons such as paraffin, dodecylbenzene and diisopropylnaphthalene. Organic solvents having a boiling point of not lower than about 30° C, preferably from 50 to 160° C can be used as co-solvents. Typical examples thereof include ethyl acetate, butyl acetate, ethyl propionate, methyl ethyl ketone, cyclohexanone, 2-ethoxyethyl acetate and dimethylformamide.

The stages and effects of latex dispersion methods and examples of impregnating latexes are described in U. S. Patent No. 4,199,363, and West Germany Patent Application (OLS) Nos. 2,541,274 and 2,541,230.

The present invention can be applied to various color photographic materials. Typical examples thereof include cinema and general-purpose color negative films and reversal color films for slide and TV.

Supports suitable for use in the present invention are described in, for example, the above-described RD No. 17643 (page 28) and *ibid.* No. 18716 (right column of page 647 to left column of page 648).

Preferably, the photographic material of the present invention has such properties that the sum total of the layer thicknesses of the entire hydrophilic colloid layers on the side having the emulsion layers is not more than 28 μm and a layer swelling rate $T_{\frac{1}{2}}$ is not larger than 30 seconds. The term "layer thickness" as used herein means a layer thickness measured by air conditioning at 25° C and 55% RH (two days). The layer swelling rate $T_{\frac{1}{2}}$ can be measured by conventional methods, for example, by using a swellometer described in A. Grren, et al., *Photographic Science and Engineering*, Vol. 19, No. 2, pages 124-129. $T_{\frac{1}{2}}$ is defined as the time taken to reach a saturated layer thickness which is referred to be 90% of the maximum swelling layer thickness attainable when processed with a color developing solution at 30° C for 3 min 15 sec.

The layer swelling rate $T_{\frac{1}{2}}$ can be controlled by adding a hardening agent to gelatin as a binder, or by changing conditions with time after coating. The swelling ratio is preferably in the range of 150 to 400%. The swelling ratio can be calculated from the maximum swelling layer thickness under the conditions described above. That is, the swelling ratio can be calculated by the following equation.

$$\text{Swelling Ratio} = \frac{\text{Maximum Swelling Layer Thickness} - \text{Layer Thickness}}{\text{Layer Thickness}}$$

The color photographic material of the present invention can be developed by conventional methods such as those described in RD No. 17643 (pages 28-29) and *ibid.* No. 18716 (page 615 left column to right column).

The color developing solutions which can be used in the present invention are preferably aqueous alkaline solutions prinarily 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.

These compounds may be used either alone or in combination of two or more.

Generally, the color developing solutions contain pH buffering agents such as alkali metal carbonates, borates and phosphates, restrainers such as 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, hydrazine, sulfites, phenylsemicarbazides, triethanolamine, catecholsulfonic acids and triethylenediamine (1,4-diazabicyclo[2,2,2]octane); organic solvents such as ethylene glycol and diethylene glycol; development accelerators such as benzyl alcohol polyethylene glycol, quaternary ammonium salts and amines; fogging agents such as color forming couplers, competitive couplers and sodium boron hydride; auxiliary developing agents such as 1-phenyl-3-pyrazolidone; tackifiers; and chelating agents such as polyamino carboxylic acids, polyaminophosphonic acids, alkylphosphonic acids and phosphonocarboxylic acids, for example, ethylenediaminetetraacetic acid, nitrilotriacetic acid, diethylenetriaminepentaacetic acid, cyclohexanediaminetetraacetic acid, hydroxyethylimidinoacetic 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.

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 m^2 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 replenishment is to be reduced, it is desirable that the contact with air of the area of the layer to be processed is reduced to prevent the solution from being evaporated or oxidized by air. The replenishment rate can be reduced by using a means for inhibiting the accumulation of bromide ion in the developing solution.

Color development time is generally from 2 to 5 minutes. However, the processing time can be shortened when the color developing agent is used at a higher concentration, and processing is carried out at a higher temperature and at a higher pH.

After color development, the photographic emulsion layer is generally bleached. Bleaching may be carried out simultaneously with fixing (bleaching-fixing treatment) or they may be separately carried out. After bleaching, a bleaching-fixing treatment may be conducted to expedite processing. A bleaching-fixing bath composed of two consecutive baths may be used. 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), cobalt(III), chromium(VI) and copper(II), peracids, quinones and nitro compounds. Typical examples of the bleaching agents include ferricyanates; dichromates; organic complex salts of iron(III) and cobalt(III) such as complex salts of polyaminocarboxylic acids (e.g., ethylenediaminetetraacetic acid, diethylenetriaminepentaacetic acid, cyclohexanediaminetetraacetic acid, methyliminodiacetic acid, 1,3-diaminopropanetetraacetic acid, and glycol ether diaminetetraaacetic acid) citric acid, tartaric acid, and malic acid; persulfates; bromates; permanganates; and nitrobenzenes. Among these, ion(III) complex salts of polyaminocarboxylic acids such as (ethylenediaminetetraacetonato)iron(III) complex and persulfates are preferred from the viewpoint of rapid processing and prevention of environmental pollution. Furthermore, iron(III) complex salts of polyaminocarboxylic acids are useful for bleaching solutions and bleaching-fixing solutions. The pH of the bleaching solutions containing the iron(III) complex salts of the polyaminocarboxylic acids and the bleaching-fixing solutions containing the iron(III) complex salts is generally in the range of 5.5 to 8. A lower pH may be used to expedite processing.

If desired, the bleaching solution, the bleaching-fixing solution and the previous bath thereof may contain bleaching accelerators. Examples of the bleaching accelerators include compounds having a mercapto group or disulfide group such as those described in U.S. Patent No. 3,893,858, West German Patent Nos. 1,290,812 and 2,059,988, JP-A-53-32736, JP-A-53-57831, JP-A-53-37418, JP-A-53-72623, JP-A-53-95630, JP-A-53-95631, JP-A-53-104232, JP-A-53-124424, JP-A-53-141623, JP-A-53-28426 and Research Disclosure No. 17129 (July 1978): thiazolidine derivatives such as those described in JP-A-50-140129; thiourea derivatives such as those described in JP-B-45-8506, JP-A-52-20832, JP-A-53-32735 and U.S. Patent No. 3,706,561; iodides such as those described in West German Patent No. 1,127,715 and JP-A-58-16235; polyoxyethylene compounds such as those described in West German Patent Nos. 996,410 and 2,748,430; polyamine compounds such as those described in JP-B-45-8836; compounds described in JP-A-49-42434, JP-A-49-59644, JP-A-53-94927, JP-A-54-35727, JP-A-55-26506 and JP-A-58-163940; and bromide ions. Among these, the compounds having mercapto group or disulfide group are preferred from the viewpoint of high accelerating effect. Particularly, the compounds described in U.S. Patent No. 3,893,858, West German Patent No. 1,290,812 and JP-A-53-95630 are preferred. Furthermore, compounds such as those described in U.S. Patent No.4 , 552,834 are preferred. These bleaching accelerator may be incorporated in the photographic materials. These bleaching accelerators are particularly effective in conducting the bleaching-fixing of the color photographic materials for photography.

Examples of fixing agents include thiosulfates, thiocyanates, thioether compounds, thioureas and various iodides. Thiosulfates are widely used as fixing agents. Particularly, ammonium thiosulfate is the most widely used. Sulfites, bisulfites and carbonyl bisulfite adducts are preferred as preservatives for the bleaching-fixing solutions.

Usually, the silver halide color photographic materials of the present invention will be subjected to washing and/or stabilization after desilverization. The amount of rinsing water in the washing stage varies widely depending on the characteristics of the material (e.g., depending on materials used such as couplers), use, the temperature of rinsing water, the number of rinsing tanks (the number of stages), the 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 literature, the amount of rinsing water can be greatly reduced. However, there is problem in that the residence time of water in the tanks is prolonged. As a result, bacteria grows and the resulting suspended matter is deposited on the photographic material. A method for reducing calcium ion and magnesium ion described in JP-A-62-288838 can be effectively used for the color photographic materials of the present invention to solve the above-mentioned problem. Furthermore, isothiazolone compounds, thiabendazole compounds, chlorine-containing germicides such as sodium chlorinated isocyanurate and benztriazole such as those described in JP-A-57-8542 and germicides such as those described in Chemistry of Germicidal Antifungal Agent, written by Hiroshi Horiguchi, Sterilization, Disinfection, Antifungal Technique, edited by Sanitary Technique Society and Antiacterial and Antifungal Cyclopedie, edited by Nippon Antibacterial Antifungal Society, can be used.

The pH of the rinsing water in the treatment of the photographic materials of the present invention ranges from 4 to 9, preferably 5 to 9. The temperature of the rinsing water and washing time will vary depending on the characteristics of the photographic materials, use, etc., 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 the rinsing water. Such stabilizing treatment can be carried out by conventional methods such as those described in JP-A-57-8543, JP-A-58-14834 and JP-A-60-220345.

A stabilizing treatment subsequent to the rinsing may be conducted. The stabilizing treatment may be used as the final bath for the color photographic materials for photography. An example thereof include a stabilizing bath containing formalin and a surfactant. 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 a desilverization stage.

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 such as those described in U.S. Patent No. 3,342,597; Schiff base-type compounds such as those described in U.S. Patent No. 3,342,599 Research Disclosure No. 14850 and ibid., No. 15159; aldol compounds such as those described in Research Disclosure No. 13924; metal complex salts such as those described in U.S. Patent No. 3,719,492; and urethane compounds such as those 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, it is possible that higher temperatures can be used to accelerate processing and to shorten processing time, while lower temperatures can be used to improve image quality and to improve the stability of the processing solutions. If desired, treatments using cobalt intensification or hydrogen peroxide intensification such as those described in West German Patent No. 2,226,770 and U.S. Patent No. 3,674,499 may be carried out to save silver.

The silver halide photographic materials of the present invention can be applied to heat-developing photosensitive materials such as those described in U.S. Patent No. 4,500,626, JP-A-60-133449, JP-A-59-218443, JP-A-61-238056, and European Patent 210,660A2.

The present invention will now be illustrated in greater detail by reference to the following examples. These examples, however, should not be construed to be in any way limiting.

EXAMPLE 1

Comparative sample 101 was prepered. This sample was a photographic material which has a spectral sensitive distribution similar to that disclosed in U.S. Patent No. 3,672,898 and had a low multi-layer effect.

An undercoated cellulose triacetate film support was coated with the following layers having the following compositions to prepare multi-layer color photographic material, Sample 101.

Compositions of Sensitive Layers

The coating weights of silver halide and colloidal silver are represented by the unit of g/m^2 in terms of silver. The amounts of couplers, additives and gelation are represented by the unit of g/m^2. The amounts of sensitizing dyes are represented by moles per one mole of silver halide in the same layer.

First Layer : Antihalation Layer	
Black colloidal silver	0.2
Gelatin	1.3
Colored coupler C-1	0.06
Ultraviolet light absorber UV-1	0.1
Ultraviolet light absorber UV-2	0.2
Dipersion oil Oil-1	0.01
Dipersion oil Oil-2	0.01

Second Layer : Interlayer	
Fine silver bromide grains (mean grain size: 0.07 μ)	0.15
Gelatin	1.0
Colored coupler C-2	0.02
Dispersion oil Oil-1	0.1

Third Layer : First Red-sensitive Emulsion Layer	
Silver iodobromide emulsion (silver iodide: 2 mol%, mean grain size: 0.3 μ)	0.3
Gelatin	0.6
Sensitizing dye I	3.0×10^{-4}
Sensitizing dye II	1.0×10^{-4}.
Coupler C-3	0.06
Coupler C-4	0.06
Coupler C-5	0.01
Coupler C-8	0.04
Coupler C-2	0.03
Dispersion oil Oil-1	0.03
Dispersion oil Oil-3	0.012

Fourth Layer : Second Red-sensitive Emulsion Layer	
Silver iodobromide emulsion (silver iodide: 5 mol%, mean grain size: 0.5 μ)	0.5
Sensitizing dye I	2.0×10^{-4}
Sensitizing dye	0.6×10^{-4}
Coupler C-3	0.24
Coupler C-5	0.02
Coupler C-4	0.24
Coupler C-8	0.04
Coupler C-2	0.04
Dispersion oil Oil-1	0.15
Dispersion oil Oil-3	0.02

Fifth Layer : Third Red-sensitive Emulsion Layer	
Silver iodobromide emulsion (silver iodide: 10 mol%, mean grain size: 0.7 μ)	1.0
Gelatin	1.0
Sensitizing dye I	1.5×10^{-4}
Sensitizing dye II	0.5×10^{-4}
Coupler C-6	0.05
Coupler C-7	0.1
Dispersion oil Oil-1	0.01
Dispersion oil Oil-2	0.05

Sixth Layer : Interlayer	
Gelatin	1.0
Compound Cpd-A	0.03
Dispersion oil Oil-1	0.05

Seventh Layer : First Green-sensitive Emulsion Layer	
Silver iodobromide emulsion (silver iodide: 4 mol%, mean grain size: 0.3 μ)	0.10
Sensitizing dye III	2×10^{-4}
Sensitizing dye IV	4×10^{-4}
Sensitizing dye V	1×10^{-4}
Gelatin	1.0
Coupler C-9	0.2
Coupler C-1	0.03
Dispersion oil Oil-1	0.5

Eighth Layer : Second Green-sensitive Emulsion Layer	
Silver iodobromide emulsion (silver iodide: 5 mol%, mean grain size: 0.5 μ)	0.10
Sensitizing dye III	1.2×10^{-4}
Sensitizing dye IV	2.8×10^{-4}
Sensitizing dye V	0.6×10^{-4}
Coupler C-9	0.25
Coupler C-1	0.03
Coupler C-10	0.015
Dispersion oil Oil-1	0.2

Ninth Layer : Third Green-sensitive Emulsion Layer	
Silver iodobromide emulsion (silver iodide: 6 mol%, mean grain size: 0.7 μ)	0.3 silver
Gelatin	1.0
Sensitizing dye III	1.0×10^{-4}
Sensitizing dye IV	2.0×10^{-4}
Sensitizing dye V	0.5×10^{-4}
Coupler C-11	0.01
Coupler C-12	0.03
Coupler C-13	0.20
Coupler C-1	0.02
Coupler C-15	0.02
Dispersion oil Oil-1	0.20
Dispersion oil Oil-2	0.0.5

Tenth Layer : Yellow Filter Layer	
Gelatin	1.2
Yellow colloidal silver	0.04
Compound Cpd-B	0.1
Dispersion oil Oil-1	0.3

Eleventh Layer : First Blue-sensitive Emulsion Layer	
Monodisperse silver iodobromide emulsion (silver iodide: 4 mol%, mean grain size: 0.3 μ)	0.2 silver
Gelatin	1.0
Sensitizing dye VI	2×10^{-4}
Coupler C-3	0.01
Coupler C-14	0.9
Dispersion oil Oil-1	0.2

Twelfth Layer : Second Blue-sensitive Emulsion Layer	
Silver iodobromide emulsion (silver iodide: 10 mol%, mean grain size: 1.5 µ)	0.4 silver
Gelatin	0.6
Sensitizing dye VI	1×10^{-4}
Coupler C-14	0.25
Dispersion oil Oil-1	0.07

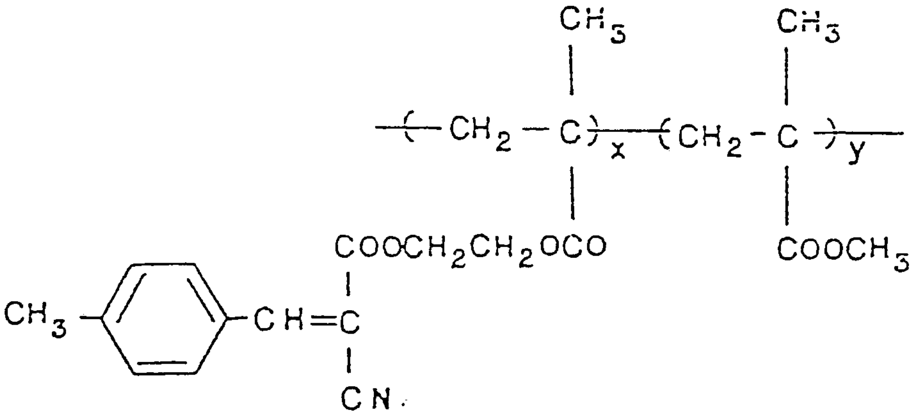
Thirteenth Layer : First Protective Layer	
Gelatin	0.8
Ultraviolet light absorber UV-1	0.1
Ultraviolet light absorber UV-2	0.2
Dispersion oil Oil-1	0.01
Dispersion oil Oil-2	0.02

Fourteenth Layer : Second Protective Layer	
Fine silver bromide grains (mean grain size: 0.07 µ)	0.5
Gelatin	0.45

In addition to the above-described ingredients, a surfactant component was added to each layer. The thus prepared sample was referred to as Sample 101.

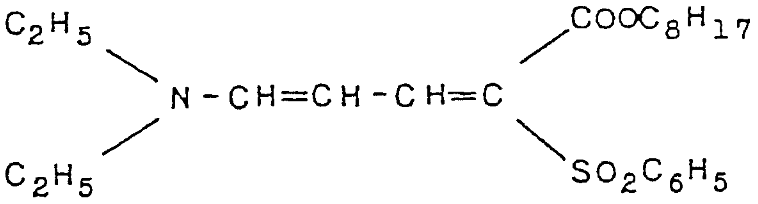
The chemical structural formulas and the chemical names of the compounds used for the preparation of the sample are as follows.

UV-1



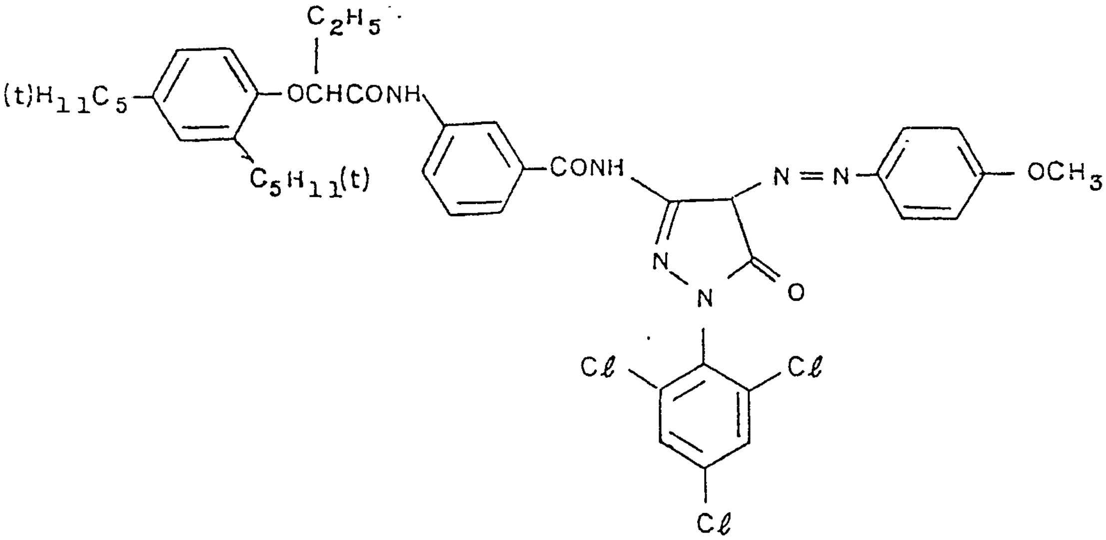
x/y=7/3 (by weight)

UV-2

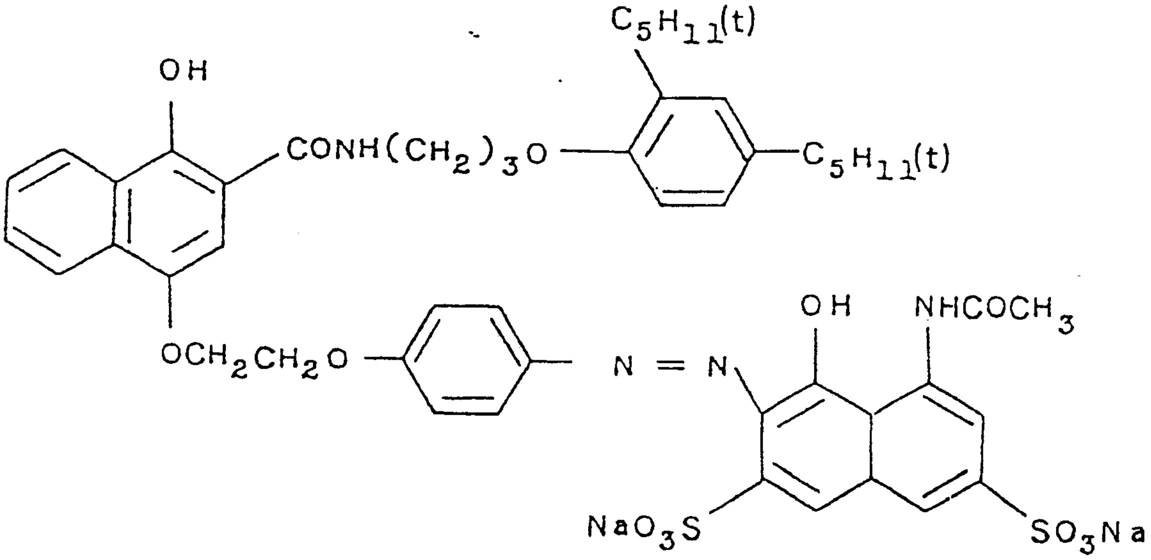


Oil-1 Tricresyl phosphate
Oil-2 Dibutyl phthalate
Oil-3 Bis(2-ethylhexyl) phthalate

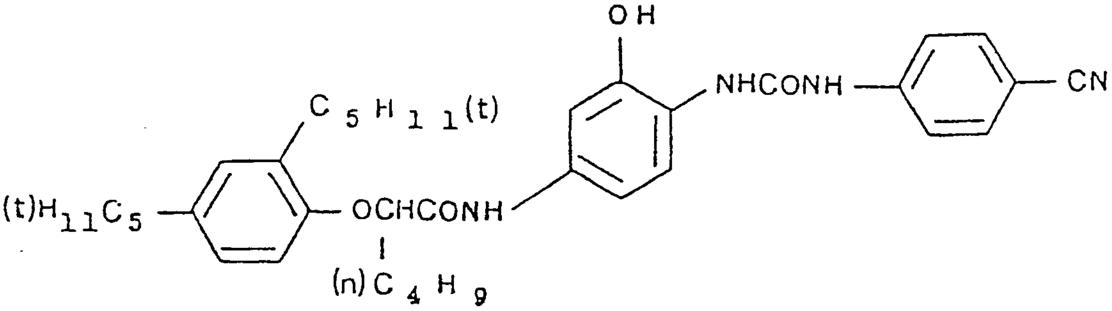
C − 1



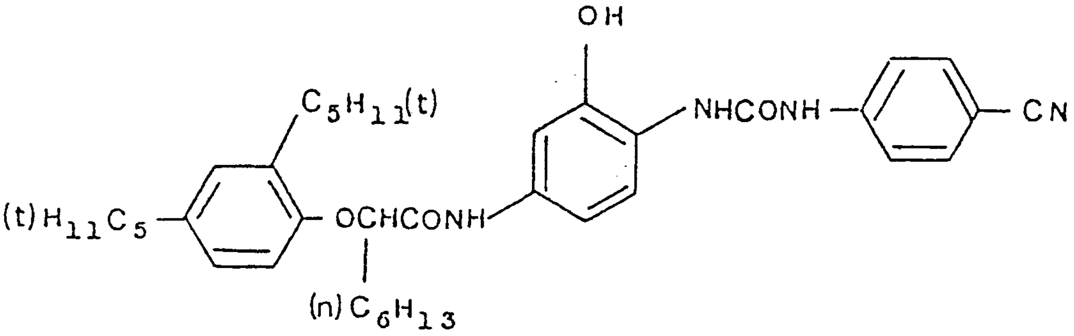
C − 2


OH
CONH(CH2)3O
C5H11(t)
C5H11(t)
OCH2CH2O
N = N
OH
NHCOCH3
NaO3S
SO3Na

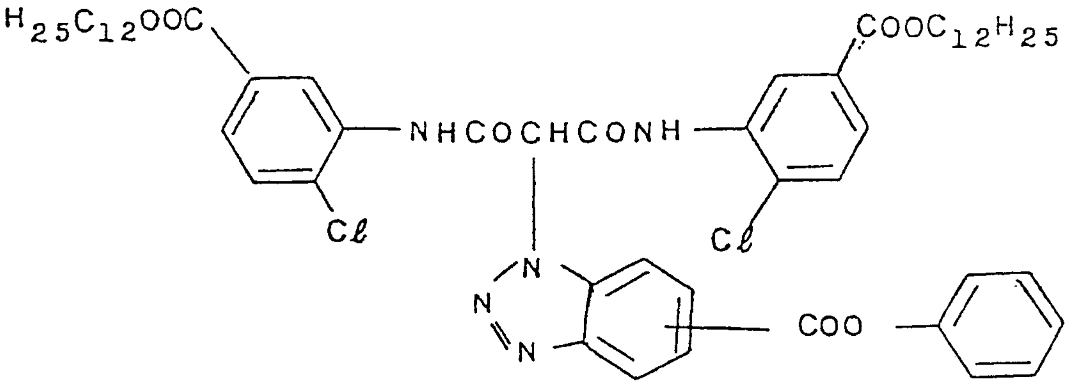
C − 3


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

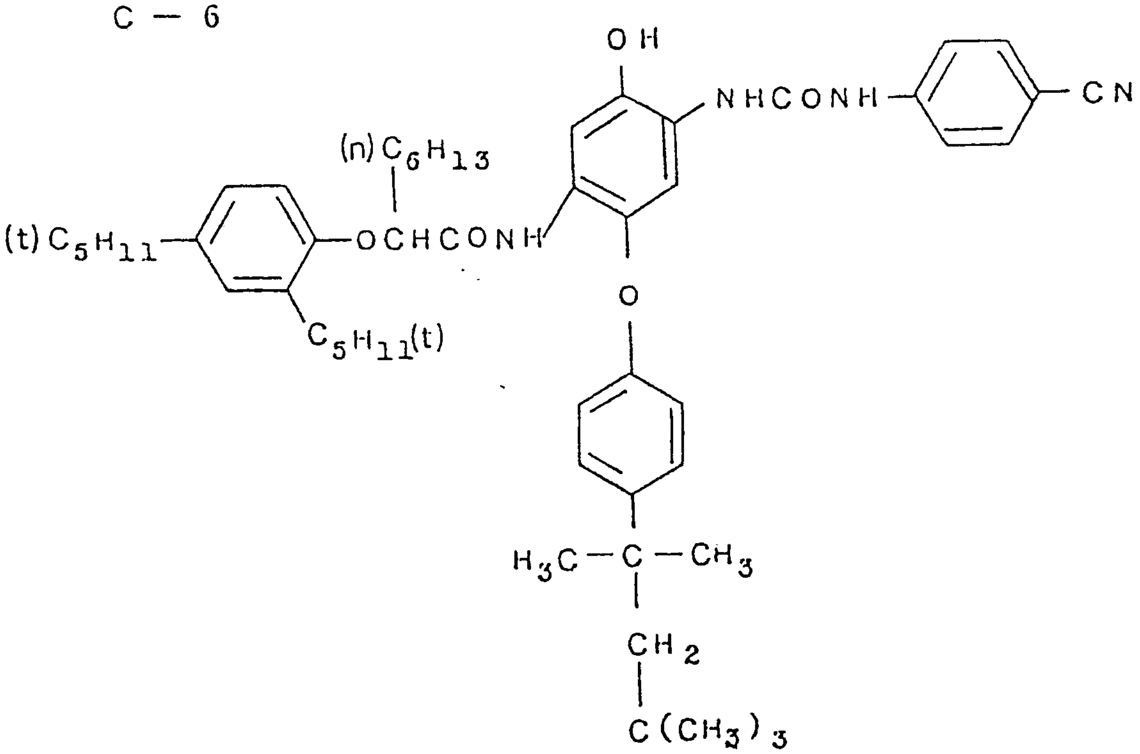
C − 4


OH
NHCONH
CN
C5H11(t)
(t)H11C5
OCHCONH
(n)C6H13

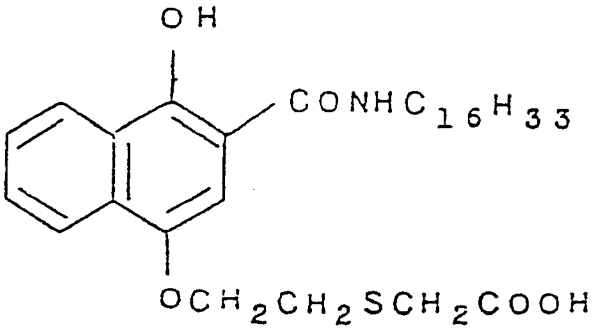
C — 5



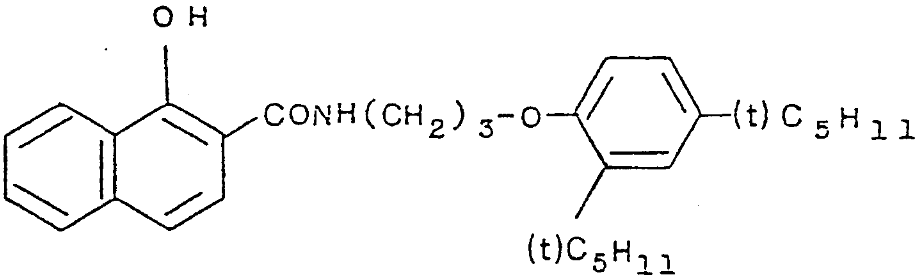
C — 6



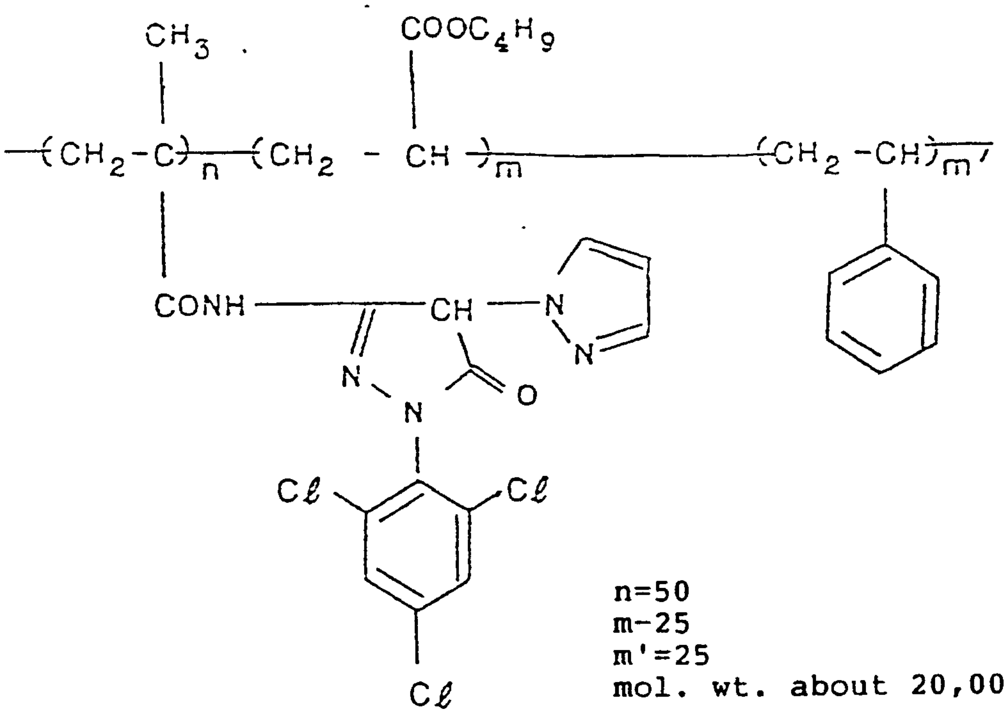
C — 7


OH
CONHC16H33
OCH2CH2SCH2COOH

C — 8

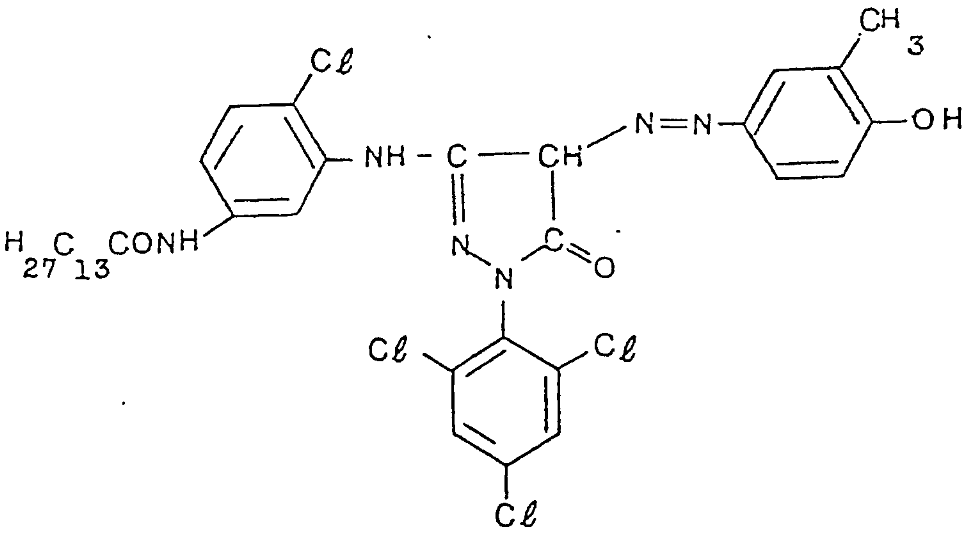

OH
CONH(CH2)3-O
(t)C5H11
(t)C5H11

C－9

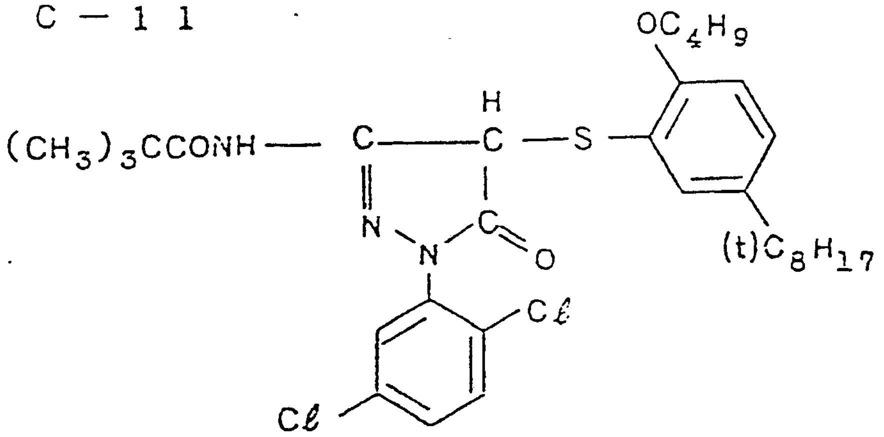


n=50
m-25
m'=25
mol. wt. about 20,000

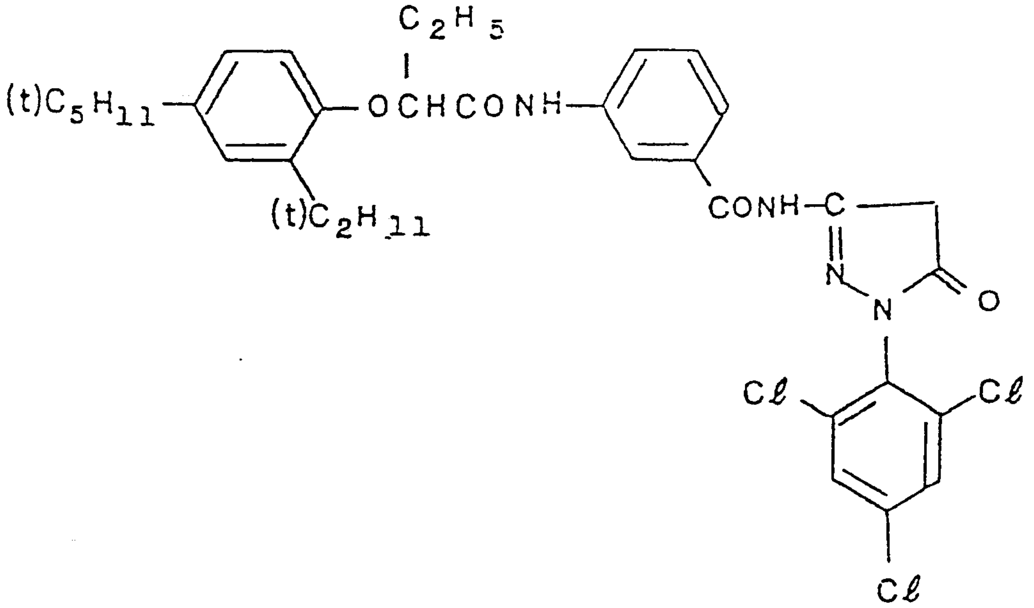
C－10



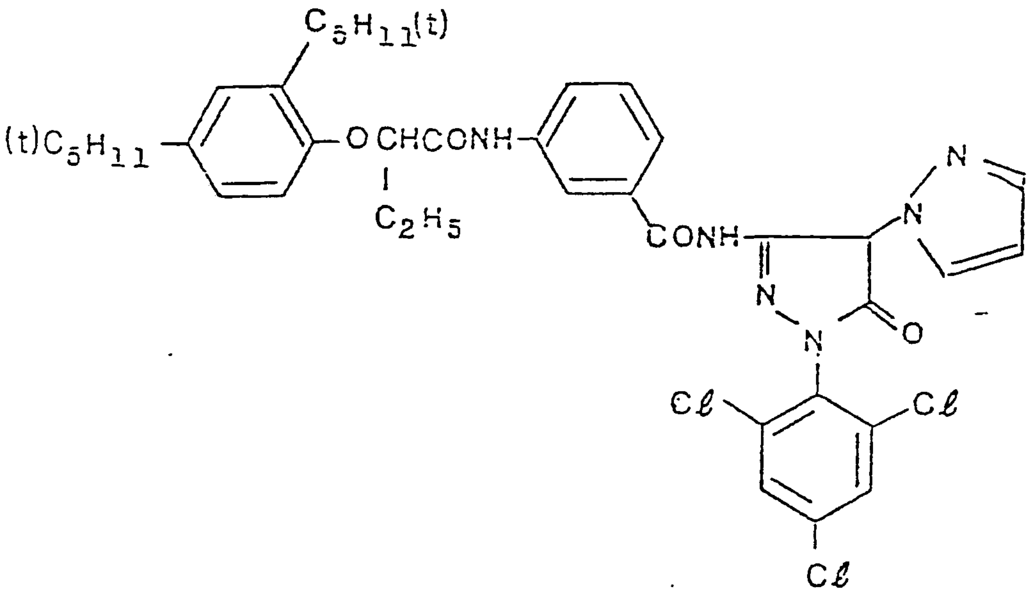
C－１１


OC4H9
H
(CH3)3CCONH
C
C
S
N
N
C
O
(t)C8H17
Cℓ
Cℓ

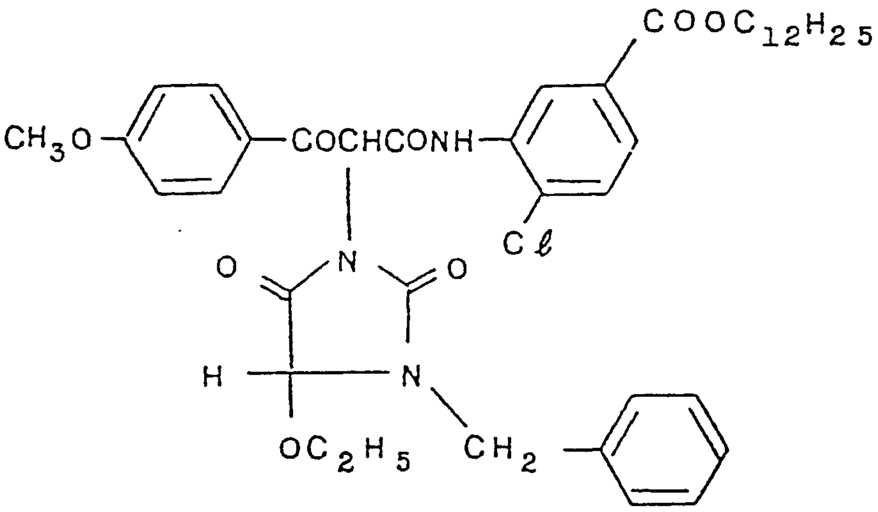
C－１２


C2H5
(t)C5H11
OCHCONH
(t)C2H11
CONH
C
N
N
O
Cℓ
Cℓ
Cℓ

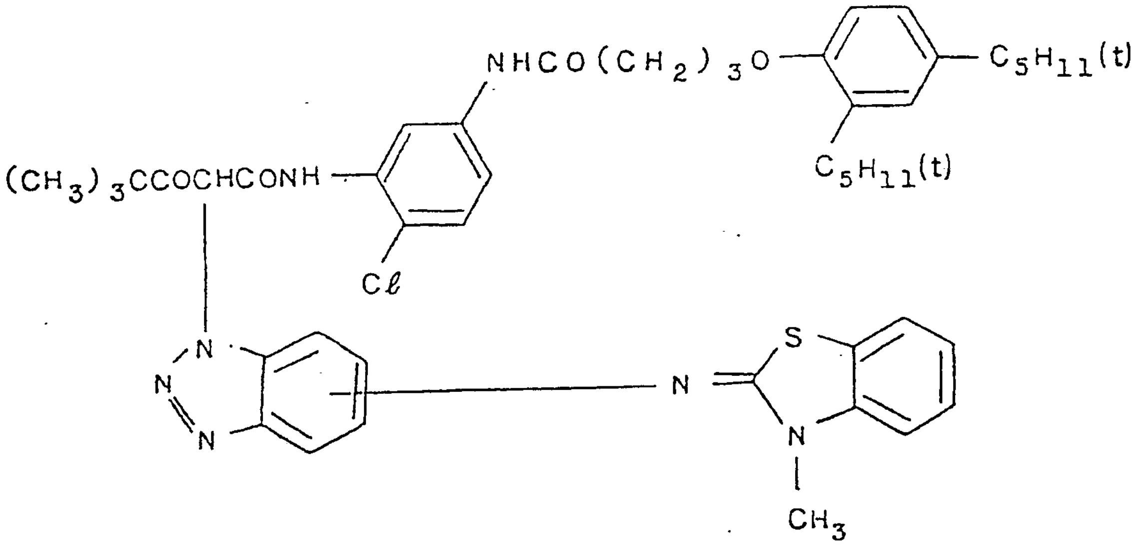
C－１３



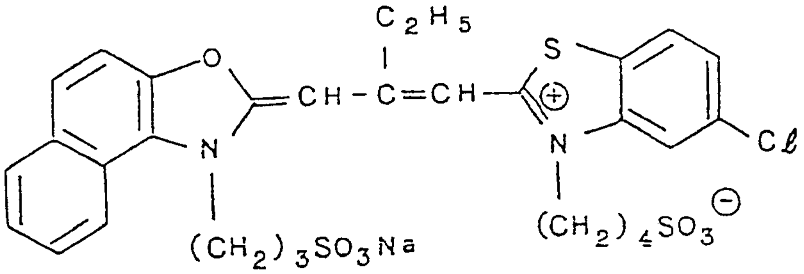
C－１４



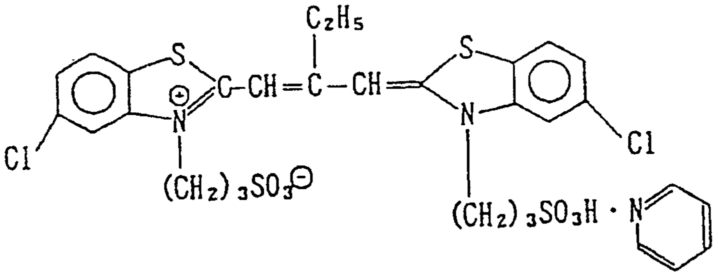
C-15



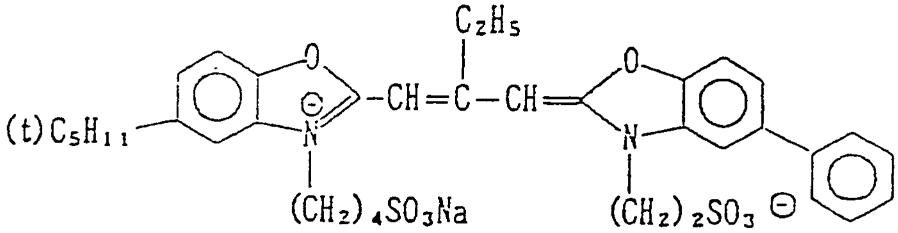
Sensitizing dye I



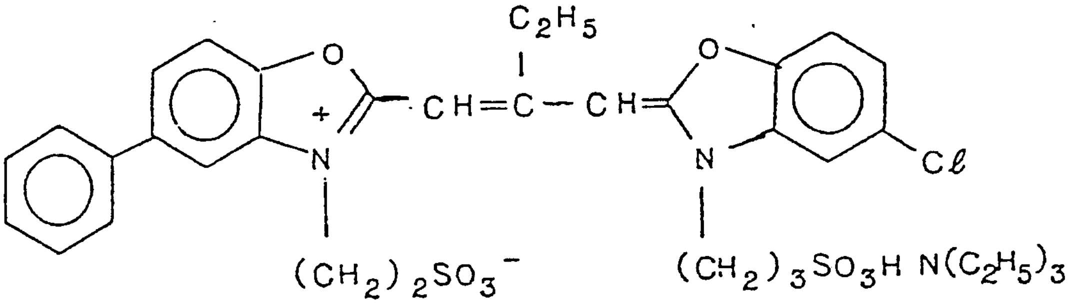
Sensitizing dye II



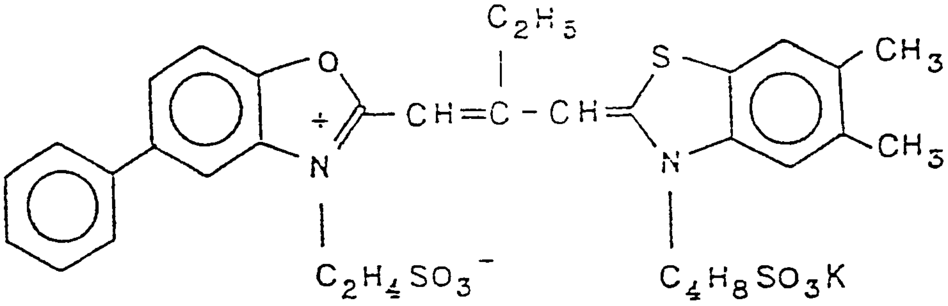
Sensitizing dye III



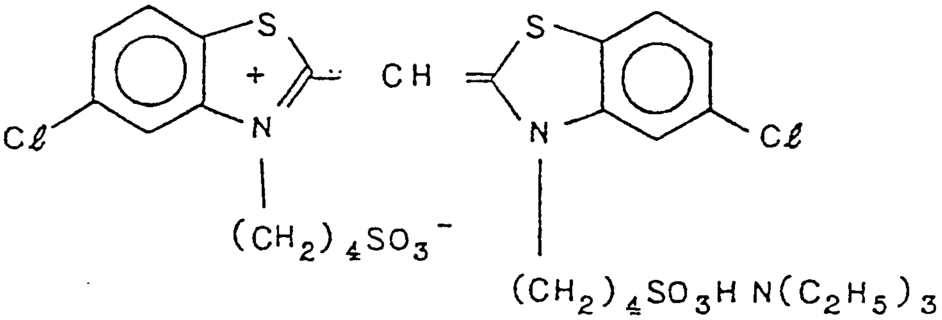
Sensitizing dye IV



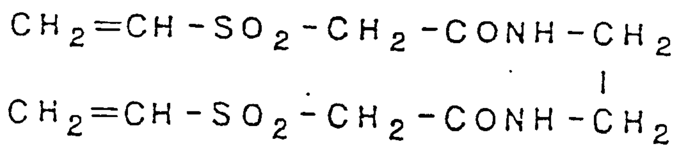
Sensitizing dye V



Sensitizing dye VI

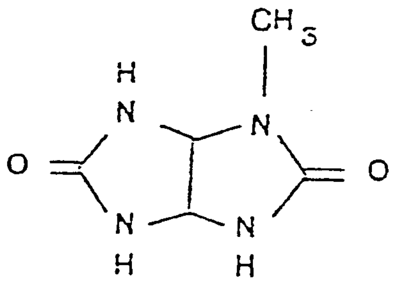


H — 1

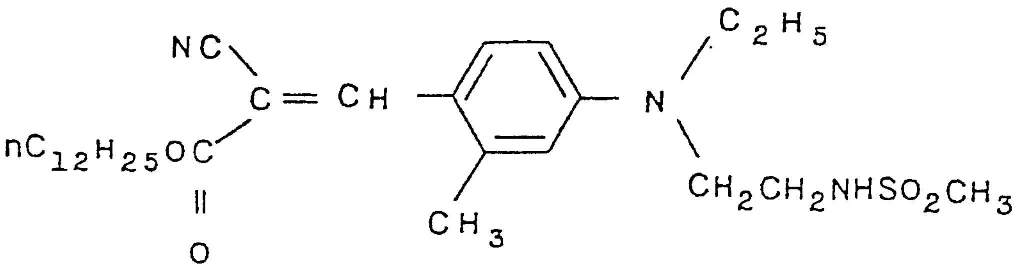


$$\begin{array}{r}\mathrm{CH_2{=}CH{-}SO_2{-}CH_2{-}CONH{-}CH_2}\\ |\\ \mathrm{CH_2{=}CH{-}SO_2{-}CH_2{-}CONH{-}CH_2}\end{array}$$

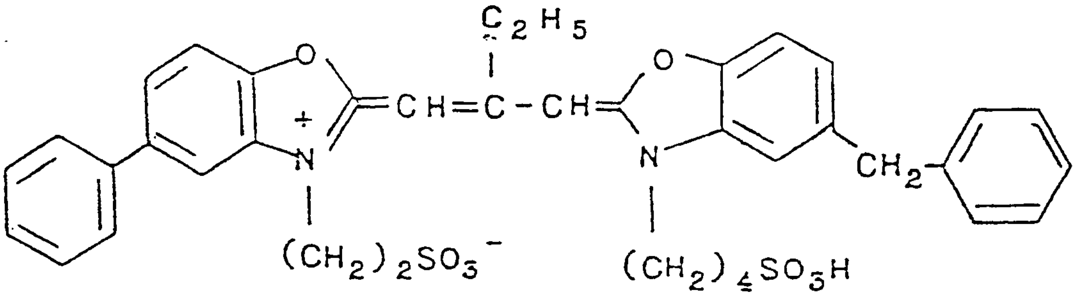
S — 1



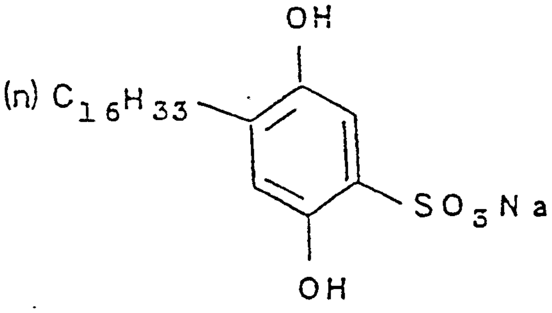
Y — 1



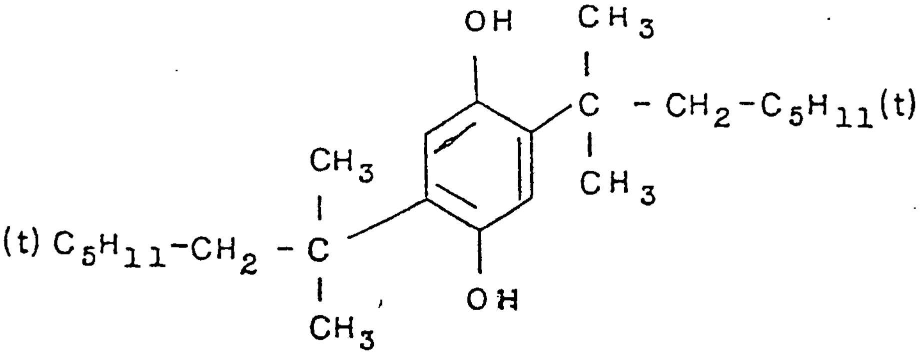
S — 6



Cpd A



Cpd B



Comparative Sample 102 was prepared by using DIR coupler to enhance the chroma of a reproduced color. This sample was prepared in the same manner as Sample 101, but with the following modifications.

(1) DIR coupler C-5 in an amount of 0.03 g/m^2 was added to the seventh layer and the amount of the whole of the seventh layer was increased 70%.

(2) DIR coupler C-5 in an amount of 0.01 g/m^2 was added to the eighth layer and the amount of the whole of the eighth layer was increased by 50%.

(3) DIR coupler C-5 in an amount of 0.03 g/m^2 was added to the eleventh layer and the amount of the whole of the eleventh layer was increased by 60%.

(4) The amont of the whole of each of the third layer and the fourth layer was increased by 40%.

(5) The amount of the whole of the twelfth layer was increased by 10%.

Comparative Sample 103 in which the concentration of yellow filter layer was increased was prepared to improve blue color reproducibility. This sample was prepared in the same manner as Sample 102, except with the following modifications.

(1) The coating weight of the yellow colloidal silver in the tenth layer was doubled.

(2) The silver iodobromide emulsion in the fifth layer was replaced with one having a mean grain size of 0.75 μ and the amount of the whole of the fifth layer was increased by 5%.

(3) The silver iodobromide emulsion in the ninth layer was replaced with one having a mean grain size of 0.85 μ and the amount of the whole of the ninth layer was increased by 10%.

Comparative sample 104 was prepared in the same manner as Sample 102, except that the following modifications were made to prepare the sample 104.

(1) The amount of the sensitizing dyes in the seventh layer were changed to the following amounts.

Sensitizing dye III	3.0×10^{-4}
Sensitizing dye IV	3.0×10^{-4}
Sensitizing dye V	1.0×10^{-4}

(2) The amounts of the sensitizing dyes in the eighth layer were changed to the following amounts.

Sensitizing dye III	2.0×10^{-4}
Sensitizing dye IV	2.0×10^{-4}
Sensitizing dye V	0.6×10^{-4}

(3) The amounts of the sensitizing dyes in the ninth layer were changed to the following amounts, and the amount of the whole of the ninth layer was increased by 5%.

Sensitizing dye III	1.5×10^{-4}
Sensitizing dye IV	1.5×10^{-4}
Sensitizing dye V	0.5×10^{-4}

Comparative sample 105 was prepared in the same manner as Sample 102, except that the following modifications were made to prepare the sample 105.

(1) The amount of the sensitizing dyes in the seventh layer were changed to the following amounts.

Sensitizing dye III	4.0×10^{-4}
Sensitizing dye IV	2.5×10^{-4}
Sensitizing dye V	0.5×10^{-4}

(2) The amounts of the sensitizing dyes in the eighth layer were changed to the following amounts, and the amount of the whole of the eighth layer was increased by 10%.

Sensitizing dye III	2.6×10^{-4}
Sensitizing dye IV	1.7×10^{-4}
Sensitizing dye V	0.3×10^{-4}

(3) The amounts of the sensitizing dyes in the ninth layer were changed to the following amounts, and the amount of the whole of the ninth layer was increased by 10%.

Sensitizing dye III	1.8×10^{-4}
Sensitizing dye IV	1.4×10^{-4}
Sensitizing dye V	0.3×10^{-4}

Comparative sample 106 was prepared in the same manner as Sample 102, except that the following modifications were made to prepare the sample 106.

(1) The amount of the sensitizing dyes in the seventh layer were changed to the following amounts.

Sensitizing dye III	4.5×10^{-4}
Sensitizing dye IV	2.0×10^{-4}
Sensitizing dye V	0.5×10^{-4}

(2) The amounts of the sensitizing dyes in the eighth layer were changed to the following amounts, and the amount of the whole of the eighth layer was increased by 20%.

Sensitizing dye III	3.0×10^{-4}
Sensitizing dye IV	1.3×10^{-4}
Sensitizing dye V	0.3×10^{-4}

(3) The amounts of the sensitizing dyes in the ninth layer were changed to the following amounts, and the amount of the whole of the ninth layer was increased by 15%.

Sensitizing dye III	2.2×10^{-4}
Sensitizing dye IV	1.0×10^{-4}
Sensitizing dye V	0.3×10^{-4}

Comparative sample 107 and Samples 108 and 109 representing the invention were prepared in the same manner as Samples 104 to 106 except with the following modifications were made to prepare the samples 107 to 109 respectively.

(1) The amont of the yellow colloidal silver in the tenth layer were increased to double thereof.

(2) The average particle size of the silver iodobromide emulsion in the fifth layer were changed to 0.75 μm, and the amount of the whole of the fifth layer was increased by 5%.

(3) The average particle size of the silver iodobromide emulsion in the ninth layer was changed to 0.85 μm, and the amount of the whole of the ninth layer was increased by 10%.

Sample 110 representing the invention was prepared in the same manner as Sample 109, except that the amount of the yellow colloidal silver was decreased by 30% to prepare the sample 110.

Sample 111 representing the invention was prepared in the same manner as Sample 109, except that nondiffusing yellow dye YD-13 in an amount of 0.17 g/m^2 was used in place of yellow colloidal silver in the tenth layer.

Sample 112 representing the invention was prepared in the same manner as Sample 111, except that the silver iodobromide emulsion in the twelfth layer was changed to 5 mol% of silver iodide and the average particle size to 1.7 μm.

Comparative sample 113 was prepared in the same manner as Sample 112, except that the following modifications were made to prepare sample 113.

(1) The average particle size of the silver iodobromide in ninth layer was changed to 0.95 μm, and the amount of the whole of the ninth layer was increased by 5%.

(2) The sensitizing dyes in the eleventh layer was omitted.

(3) The sensitizing dyes in the twelfth layer was omitted.

ISO sensitivity S of each of Samples 101 to 112 and S_G^{480} - S_B^{480} after uniform exposure were determined by the above-described method. Interference filter of Line double Filter, DEPIL 0.5 (manufactured by Shott Glass-werre) was used to obtain monochromatic light of 480 nm. Half width was 8 nm. Development was carried out in the following stages.

Stage	Processing Time	Processing Temperature
Color development	3 min 15 sec	38° C
Bleaching	6 min 30 sec	38° C
Rinse	2 min 10 sec	24° C
Fixing	4 min 20 sec	38° C
Rinse (1)	1 min 5 sec	24° C
Rinse (2)	2 min 10 sec	24° C
Stabilization	1 min 5 sec	38° C
Drying	4 min 20 sec	55° C

Each processing solution had the following composition.

Color Developing Solution	Unit: g
Diethylenetriaminepentaacetic acid	1.0
1-Hydroxyethylidene-1,1-diphosphonic acid	3.0
Sodium sulfite	4.0
Potassium carbonate	30.0
Potassium bromide	1.4
Potassium iodide	1.5 mg
Hydroxylamine sulfite	2.4
4-(N-Ethyl-N-β-hydroxyethylamino)-2-methylaniline sulfate	4.5
Add water	1.0 ℓ
pH	10.05

Bleaching Solution	Unit: g
Ethylenediaminetetraacetic acid iron(III) sodium trihydrate	100.0
Disodium ethylenediaminetetraacetate	10.0
Ammonium bromide	140.0
Ammonium nitrate	30.0
Ammonia water (27%)	6.5 ml
Add water	1.0 ℓ
pH	6.0

Fixing Solution	Unit: g
Disodiumethylenediaminetetraacetate	0.5
Sodium sulfite	7.0
Sodium bisulfite	5.0
Ammonium thiosulfate (70% aqueous solution)	170.0 ml
Add water	1.0 ℓ
pH	6.7

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

The results are shown in Table 1.

Each of the Samples 101 to 112 was processed into a Leica size for camera photography. Color rendition charts (manufactured by Macbeth) were photographed and printing was made on color paper (Fuji Color Paper AGL #653-258) so that a grey sheet having an optical density of 0.7 reproduced lightness as well as hue.

The chroma and fidelity of Blue and the fidelity of Bluish Green were visually evaluated.

As seen in the results in Table 1, the comparative sample 101 shows the fidelity of Bluish Green well enough, but insufficient, and the fidelity and chroma of Blue so insufficient. The comparative sample 102 shows the chroma in acceptable level, however, the fidelity of Bluish Green so worse. Among the comparative samples 103 to 107 and 113, none of the samples satisfies requirements of the chroma and fidelity simultaneously.

On the contrary, the sample 108 to 112 according to the present invention produce excellent color and satisfy all three requirements, i.e. the chloma and fidelity of Blue, and the fidelity of Bluish Green.

Table 1

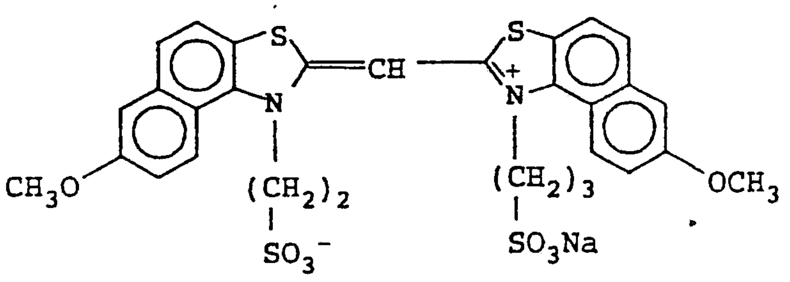
Sample No.	Kind	ISO Sensitivity	$S_G^{4\;80}$-$S_G^{4\;80}$	Chroma of Blue	Fidelity of Blue	Fidelity of Bluish Green	Peak Density of Yellow Filter Layer
101	Comp. Ex.	75	-0.80	0.85	××	×	○-△
102	"	80	-0.95	0.85	○	○-△	×-××
103	"	78	-1.20	1.70	○	○-◎	××
104	"	73	-0.65	0.85	○-△	△	○
105	"	77	-0.50	0.85	○-△	△-×	○-◎
106	"	75	-0.35	0.85	△	×	◎
107	"	71	-0.90	1.70	○	○-◎	×
108	Invention	76	-0.80	1.70	○	○-◎	○
109	"	74	-0.65	1.70	○	○-◎	○
110	"	80	-0.75	1.20	○	○	○
111	"	82	-0.55	1.80	○	◎	◎
112	"	83	-0.15	1.80	○	◎	○
113	Comp. Ex.	87	+0.30	1.80	△	○	×

◎: Very superior
○: Superior
△: Slightly inferior
×: Inferior
××: Very inferior

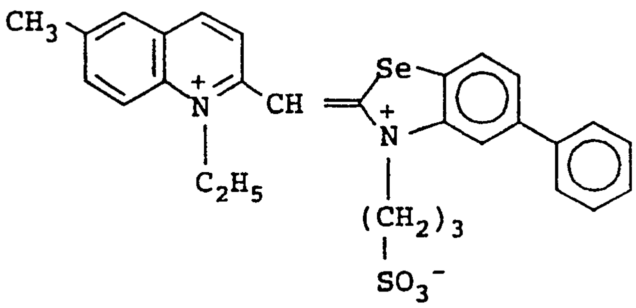
EXAMPLE 2

Samples 201 to 204 were prepared in the same manner as in the preparation of the Samples 109 and 111 except that equimolar amounts of the following sensitizing dyes were used in place of sensitizing dye III.

Samples 201, 202



Samples 203, 204



These samples were tested in the same manner as in Example 1. Good results, similar to those obtained with Samples 109 and 111, were obtained.

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

Claims

1. A silver halide color photographic material comprising at least one red-sensitive emulsion layer, at least one green-sensitive emulsion layer, at least one blue-sensitive emulsion layer and at least one yellow filter layer provided on a support, wherein the relationship between the sensitivity (S_G^{480}) of the green-sensitive emulsion layer to monochromic light of 480 nm and the sensitivity (S_B^{480}) of the blue-sensitive emulsion layer to monochromic light of 480 ranges from $-0.85 \leqq S_G^{480} - S_B^{480} \leqq 0.2$ when measured after the silver halide color photographic material having an ISO sensitivity of S is uniformly exposed to white light of 2/S lux•sec, and the optical density of the yellow filter layer at peak wavelength is 1.0.

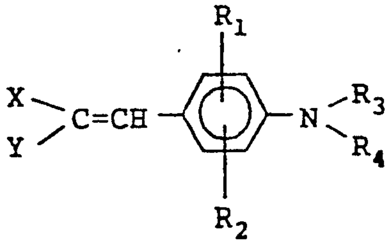
2. A silver halide color photographic material according to claim 1, wherein the relationship ranges from $-0.75 \leqq S_G^{480} \leqq 0$.

3. A silver halide color photographic material according to claim 1, wherein the relationship ranges from $-0.70 \leqq S_G^{480} - S_B^{480} \leqq -0.1$.

4. A silver halide color photographic material according to claim 1, wherein the optical density of the yellow filter layer is at least 1.2.

5. A silver halide color photographic material according to claim 4, wherein the optical density is at least 1.4.

6. A silver halide color photographic material according to claim 1, wherein the yellow filter layer contains a dye represented by formula:



(I)

wherein R_1 and R_2 may be the same or different and selected from a hydrogen atom, a halogen atom, an alkyl group, an alkoxy group, hydroxyl group, carboxyl group, a substituted amino group, a carbamoyl group, a sulfamoyl group, nitro group or an alkoxycarbamoyl group; R_3 and R_4 may be the same or different and selected from a hydrogen atom, an unsubstituted or substituted alkyl group, an unsubstituted or substituted alkenyl group, an unsubstituted or substituted aryl group, an acyl group or a sulfonyl group, and R_3 and R_4 may be combined together to form a 5-membered or 6-membered ring; and X and Y may be the same or different and are electron attractive groups.

7. A silver halide color photographic material according to claim 1, wherein the silver halide emulsion used for at least one of the blue-sensitive layers is monodispersed.

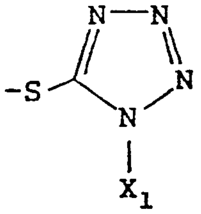
8. A silver halide color photographic material according to claim 1, wherein at least one emulsion layer contains an amount of ultra-tabular silver grains having a diameter of at least 5 times the thickness of the grain, which amount accounts for at least 50% of the total projected area of the total grains.

9. A silver halide color photographic material according to claim 1, wherein futher comprising a compound represented by formula:

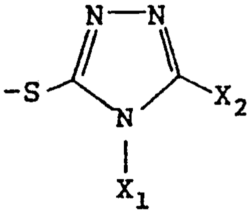
$A\text{-}(LINK)_n\text{-}B$ (I′)

wherein A represents a residue of a coupler which releases $(LINK)_n\text{-}B$ by the coupling reaction with the oxidant of an aromatic primary developing agent; LINK represents a group which is attached to the coupling active site of A and is capable of releasing B after it is released from A by the coupling reaction; B represents a group represented by the following general formulae (IIa), (IIb), (IIc), (IId),(IIe), (IIf), (IIg), (IIh), (IIi), (IIj), (IIk), (IIℓ), (IIm), (IIn), (IIo) or (IIp); and n represents an integer of 0 to 1 and when n = 0 B is directly attached to A.

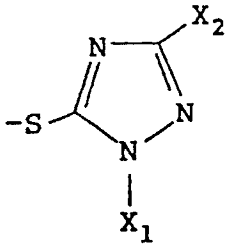
Formula (IIa)



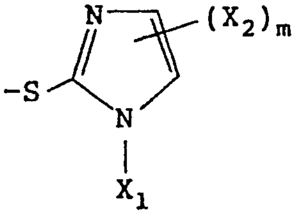
Formula (IIb)



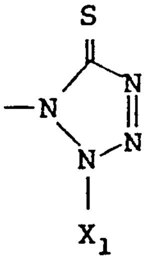
Formula (IIc)



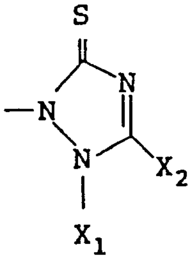
Formula (IId)



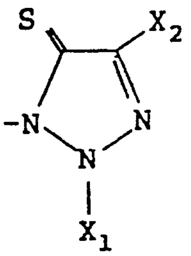
Formula (IIe)



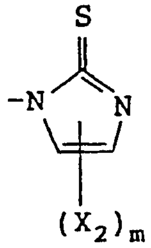
Formula (IIf)



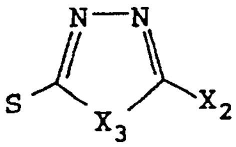
Formula (IIg)



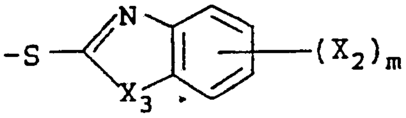
Formula (IIh)



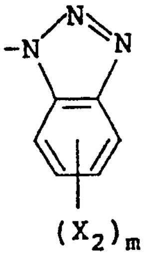
Formula (IIi)



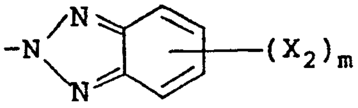
Formula (IIj)



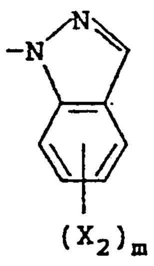
Formula (IIk)



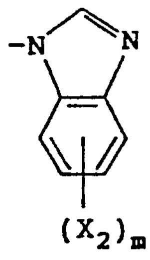
Formula (IIℓ)



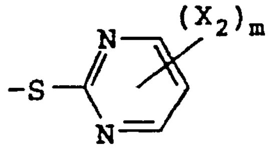
Formula (IIm)



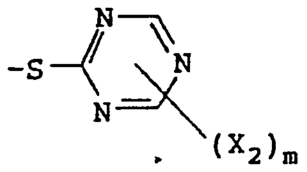
Formula (IIn)



Formula (IIo)



Formula (IIp)



wherein X_1 is a substituted or unsubstituted aliphatic group having from 1 to 4 carbon atoms wherein the substituent group has not more than 3 carbon atoms and is selected from the group consisting of an alkoxy group, an alkoxycarbonyl group, hydroxyl group, an acylamino group, a carbamoyl group, a sulfonyl group, a sulfonamido group, a sulfamoyl group, an amino group, an acylamino group, cyano group,a ureido group, an acyl group and an alkylthio group or X_1 is a substituted phenyl group wherein the substituent group has not more than 3 carbon atoms and is selected from the group consisting of 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, carboxyl group, cyano group, nitro group, an amino group and an acyl group; X_2 is hydrogen atom, an aliphatic group, halogen, 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, cyano group, nitro group, an amino group, an alkoxycarbonylamino group, an aryloxycarbonyl group or an acyl group; X_3 is oxygen atom, sulfur atom or an imino group having not more than 4 carbon atoms; m is an integer of 1 or 2; the sum total of carbon atoms of mX_2 is not more than 8; and when $m = 2$, two X_2 may be the same or different groups.

10. A silver halide color photographic material according to claim 1, wherein further comprising a compound of formula:

A'-P-Z [I'']

wherein A' represents a coupling component capable of reacting with the oxidants of color developing agents and a component capable of releasing the -P-Z group by reaction with the oxidants of the color developing agents; Z represents a development restrainer and -P-Z represents a group which forms a restrainer through the reaction with the oxidants of the developing agents after cleavage from the group A'.

FIG. 1