



12 **EUROPEAN PATENT SPECIFICATION**

45 Date of publication of patent specification :
13.09.95 Bulletin 95/37

51 Int. Cl.⁶ : **G03C 7/30**

21 Application number : **90100163.6**

22 Date of filing : **04.01.90**

54 **Silver halide color photographic material.**

30 Priority : **05.01.89 JP 746/89**

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

45 Publication of the grant of the patent :
13.09.95 Bulletin 95/37

84 Designated Contracting States :
DE FR GB NL

56 References cited :
EP-A- 0 115 304
EP-A- 0 251 042
GB-A- 2 165 058
US-A- 4 764 455
SMPTE JOURNAL, vol. 91, no. 12, December
1982, SCARSDALE, NEW YORK, US pages 1161
- 1170; K.J. Karl et al.: "Eastman color print
film 5384"
BRITISH JOURNAL OF PHOTOGRAPHY, vol.
313, no. 21, May 1984, LONDON GB pages 536-
538; G.ASHTON: "KONICA COLOR SR100"

56 References cited :
**BRITISH KINEMATOGRAPHY SOUND AND
TELEVISION SOCIETY JOURNAL**, vol. 64, no.
7, July 1982, LONDON GB pages 338 - 343;
B.DAVIES: "TWO NEW EASTMAN MOTION
PICTURE COLOUR CAMERA FILM"
PATENT ABSTRACTS OF JAPAN vol. 12, no.
23 (P-658)(2870) 23 January 1988, & JP-A-62
177547 (KONISHIROKU PHOTO INDUSTRY) 04
August 1987,
BRITISH JOURNAL OF PHOTOGRAPHY, vol.
131, no. 52, 28 December 1984, LONDON GB
PAGES 1389- 1393; G.ASHTON: "ISO 200 COL-
OUR NEGATIVE FILMS"

73 Proprietor : **FUJI PHOTO FILM CO., LTD.**
210 Nakanuma
Minami-Ashigara-shi
Kanagawa 250-01 (JP)

72 Inventor : **Nozawa, Yasushi Fuji Photo Film
Co., Ltd.**
No. 210 Nakanuma
Minami Ashigara-shi Kanagawa (JP)

74 Representative : **Grünecker, Kinkeldey,
Stockmair & Schwanhäusser Anwaltssozietät**
Maximilianstrasse 58
D-80538 München (DE)

EP 0 377 463 B1

Note : Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid (Art. 99(1) European patent convention).

Description

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.

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.

Many efforts have been made 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 US-A-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.

GB-A-2 165 058 provides a silver halide multilayer color photographic material capable of faithfully reproducing shades and purple forming red subjects during photography, and having a high saturation color reproducibility, which comprises a support having thereon at least a cyan-color-forming red-sensitive emulsion layer, a magenta-color-forming green-sensitive emulsion layer and a yellow-color-forming blue-sensitive emulsion layer having specifically defined characteristics of spectral sensitivity distribution, wavelengths and interlayer effects.

For 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, US-A-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 found 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 US-A-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.

It is therefore the object of the present invention to provide a novel multi-layer silver halide color photographic material providing excellent high-fidelity color reproducibility of primary colors and neutral tints, particularly those colors between blue and green with high color chroma.

According to the present invention this is achieved with 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 monochromatic light of 480 nm and the sensitivity (S_B^{480}) of the blue-sensitive emulsion layer to monochromatic light of 480 nm ranges from $-0.85 < S_G^{480} - S_B^{480} < 0.2$ 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 s, and the optical density of the yellow filter layer at the peak wavelength is 1.0 or more.

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

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 $2 \times 1/S$ lux-s 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 temper-

ature is $20\pm 5^\circ\text{C}$ and the relative humidity is $60\pm 10\%$. 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 480 nm within one hour after uniform exposure. As the exposure device, e.g., those of the non-intermittent exposure illuminance scale type 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 $20\pm 5^\circ\text{C}$ and a relative humidity of $60\pm 10\%$ until development. Development is completed after 30 min or longer from the completion of exposure, but within 6 h 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·s and H_B^{480} lux·s 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, e.g., US-A-3,672,898, and JP-A-50-2537, 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 $-0.85 \leq S_G^{480} - S_B^{480} \leq 0.2$ preferably $-0.75 \leq S_G^{480} - S_B^{480} \leq 0$, and more preferably $-0.70 \leq S_G^{480} - S_B^{480} \leq -0.1$.

In order to achieve the appropriate value of $S_G^{480} - S_B^{480}$ for the present invention, various techniques can be used. For example, emulsions containing sensitizing amounts of supersensitizing agents and cyanine dye forming J-associated material can be used (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, US-A-4,444,877, JP-A-57-182730, JP-A-58-49938, JP-A-58-37635, US-A-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 and JP-A-59-152438.

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

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

Silver halide emulsions used in the green-sensitive emulsion layer used in the present invention can be spectrally 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; nuclei formed by fusing an alicyclic hydrocarbon ring with any of the above-described heterocyclic nuclei; and nuclei formed by fusing an aromatic hydrocarbon ring with the above-described heterocyclic nuclei such as an indolenine nucleus, benzindolenine nucleus, indole nucleus, benzoxazole nucleus, naphthoxazole nucleus, benzthiazole nucleus, naphthothiazole nucleus, benzselenazole nucleus, benzimidazole nucleus and quinoline nucleus. These nuclei may

be substituted on carbon atoms.

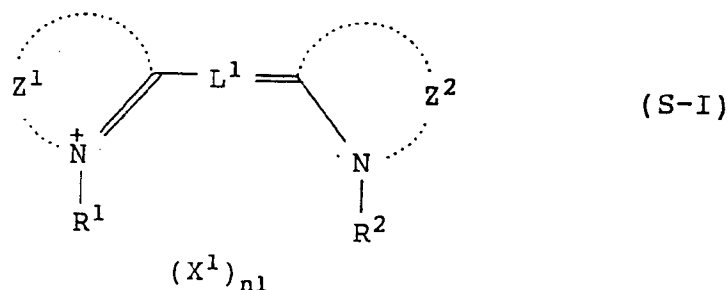
Merocyanine dyes or complex merocyanine dyes may have nuclei having a keto-methylene structure. Examples of such nuclei include five-membered to six-membered heterocyclic nuclei such as a pyrazoline-5-one nucleus, thiohydantoin nucleus, 2-thioxazolidine-2,4-dione nucleus, thiazolidine-2,4-dione nucleus,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

Specific examples of useful sensitizing dyes include those described in DE-A-929,080, US-A-2,231,658, US-A-2,493,748, US-A-2,503,776, US-A-2,519,001, US-A-2,912,323, US-A-3,656,959, US-A-3,672,897, US-A-3,694,217, US-A-4,025,349 and US-A-4,046,572, GB-A-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.

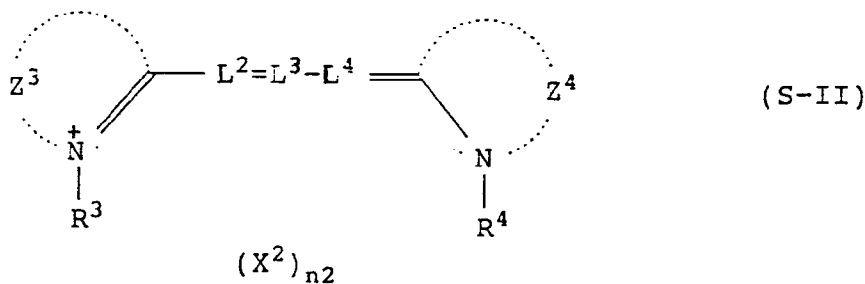
The sensitizing dyes may be used either alone or in combination. Combinations of sensitizing dyes are often used for the purpose of supersensitization. Typical examples of such combinations are described in US-A-2,688,545, US-A-2,977,229, US-A-3,397,060, US-A-3,522,052, US-A-3,527,641, US-A-3,617,293, US-A-3,628,964, US-A-3,666,480, US-A-3,672,898, US-A-3,679,428, US-A-3,703,377, US-A-3,769,301, US-A-3,814,609, US-A-3,837,862 and US-A-4,026,707, GB-A-1,344,281 and GB-A-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 US-A-2,933,390 and US-A-3,635,721), aromatic organic acid-formaldehyde condensates (see e.g., those described in US-A-3,743,510), cadmium salts and azaindene compounds. The combinations described in US-A-3,615,613, US-A-3,615,641, US-A-3,617,295 and US-A-3,635,721 are particularly preferred.

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

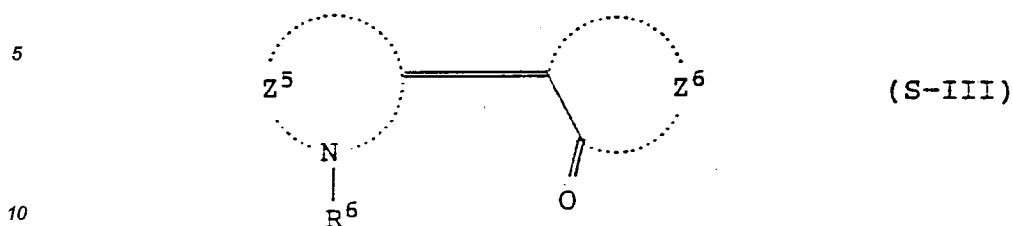


In formula (S-1), Z¹ and Z² each represent an appropriate atomic group for the formation of a nucleus originating from tellurazole nucleus, benzotellurazole nucleus, naphhotellurazole nucleus, quinoline nucleus, benzoxazole nucleus, naphthoxazole nucleus, benzthiazole nucleus, naphthothiazole nucleus, benzselenazole nucleus or naphthoselenazole nucleus; R¹ and R² each represent an alkyl group, preferably at least one of R¹ and R² is an alkyl group substituted by a sulfo group or a carboxyl group; L¹ represents a methine group; X¹ represents an anion; and n¹ represents 0 or 1 provided that when an inner salt is formed, n¹ is 0.



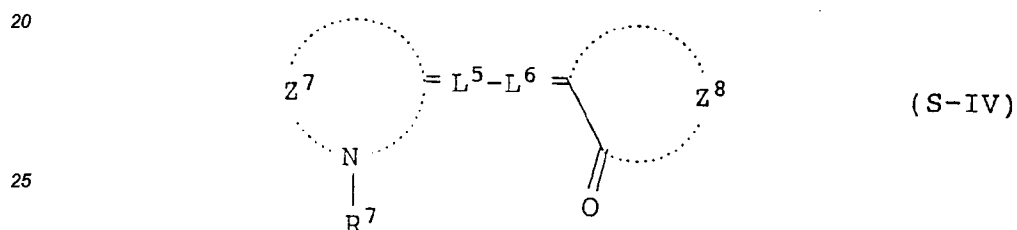
In formula (S-II), Z³ and Z⁴ each represent an appropriate atomic group for the formation of a nucleus originating from tellurazole nucleus, benzotellurazole nucleus, naphhotellurazole nucleus, benzoxazole nucleus, naphthoxazole nucleus, benzimidazole nucleus, naphthoimidazole nucleus, oxazolidine nucleus, oxazole nu-

cleus, 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 definition as L^1 ; X^2 has the same meaning as X^1 ; and n^2 has the same meaning as n^1 .



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.

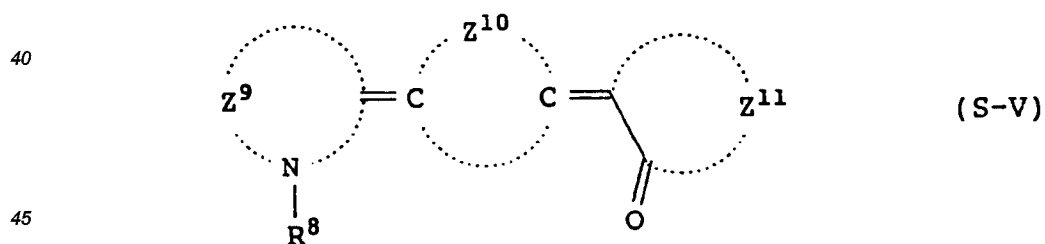
15



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 .

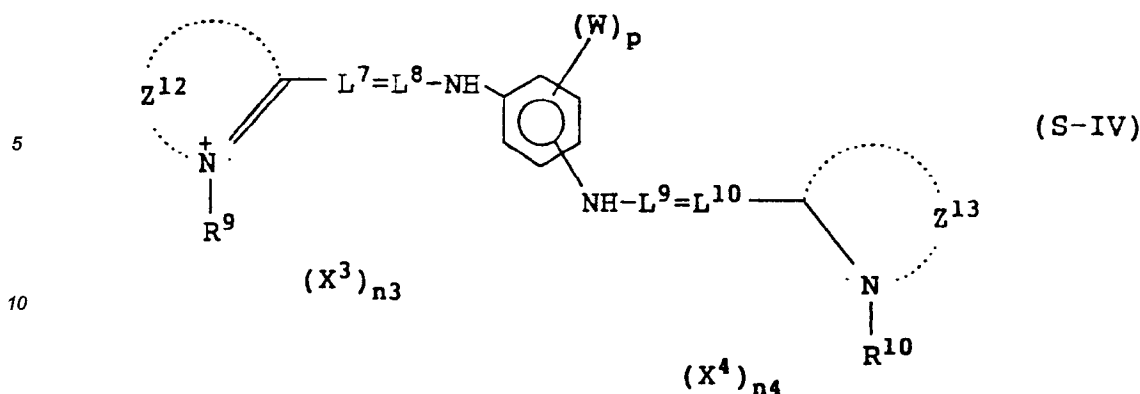
30

35



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 .

50



15 In formula (S-VI), Z¹² and Z¹³ 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; R⁹ and R¹⁰ have the same as R¹ and R²; L⁷, L⁸, L⁹ and L¹⁰ have the same meaning as L¹; X³ and X⁴ have the same meaning as X¹; n³ and n⁴ have the same meaning as n¹; W represents a hydrogen atom, a carboxyl group or a 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.

20 R¹, R², R³, R⁴, R⁵, R⁶, R⁷, R⁸, R⁹ and R¹⁰ are each preferably a 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 a carboxyl group, a sulfo group, a cyano group, a halogen (e.g., fluorine, chlorine, and bromine), a hydroxyl group, an 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 piperidinofulfonyl) 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).

25 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.

30 As metal atoms capable of forming a salt with R¹, R², R³, R⁴, R⁵, R⁶, R⁷, R⁸, R⁹ or R¹⁰, alkali metals are particularly preferred. As organic compounds, pyridines and amines are preferred.

35 Examples of nuclei formed by Z¹, Z², Z³, Z⁴, Z⁵, Z⁷, Z⁹, Z¹² and Z¹³ 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-methylloxazole, 4-nitroloxazole, 5-methylloxazole, 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 naphthox-

40

45

50

55

azole 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 Z⁶, Z⁸, Z¹⁰ and Z¹¹ 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-thioxazolidine-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 a 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).

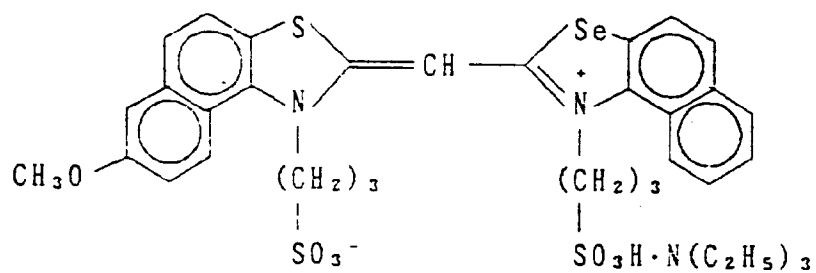
L¹, L², L³, L⁴, L⁵, L⁶, L⁷, L⁸, L⁹ and L¹⁰ each represent a methine group which may be optionally substituted by a substituted or unsubstituted alkyl group (e.g., methyl, and ethyl), a substituted or unsubstituted aryl group (e.g., phenyl) or halogen (e.g., chlorine, and bromine). The methine groups may combine to form a ring or may form a ring together with auxochrome.

The anion represented by X¹, X², X³ and X⁴ 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-benzenedisulfonate 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 .

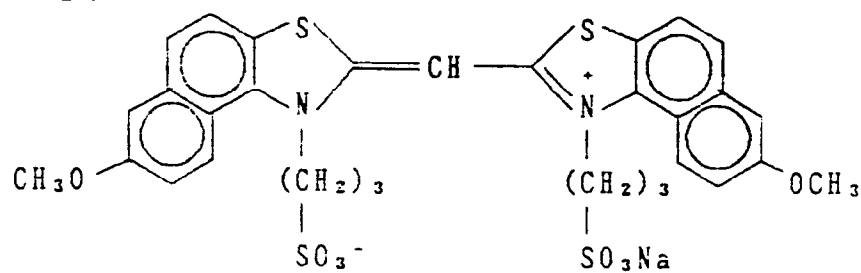
5



10

S - 2 .

15

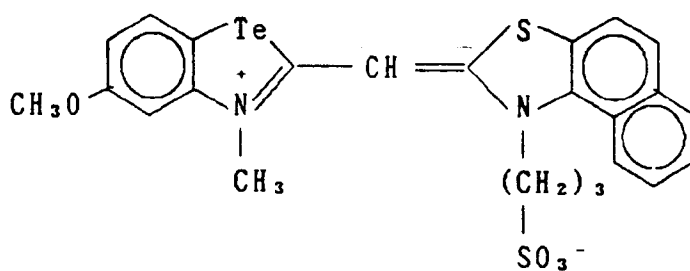


20

25

S - 3 .

30

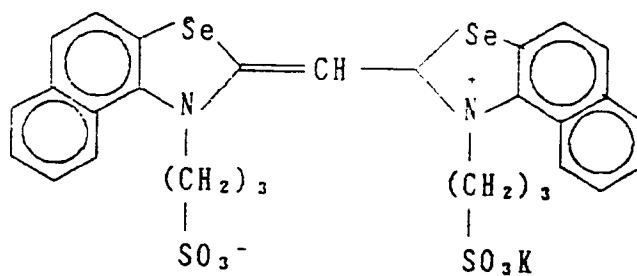


35

40

S - 4 .

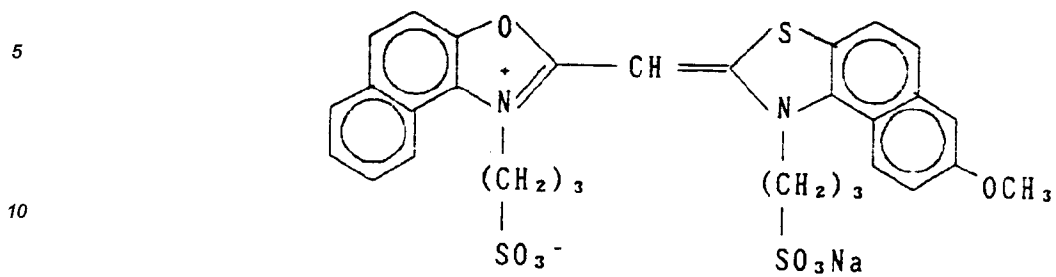
45



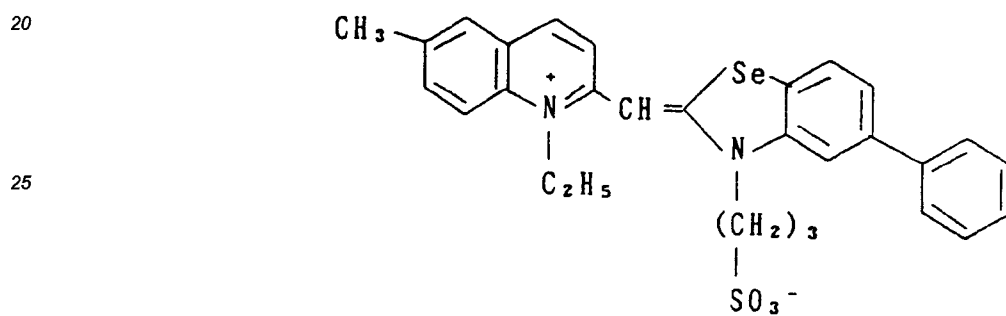
50

55

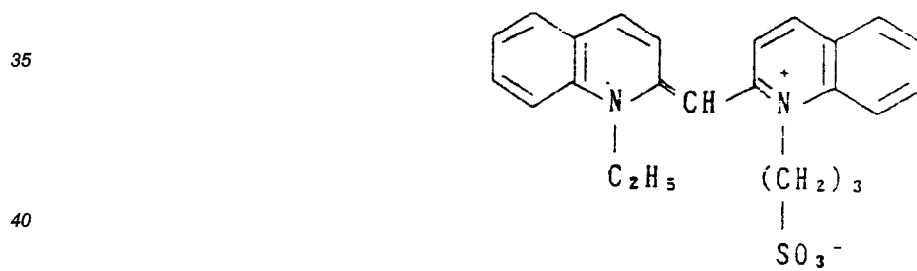
S - 5 .



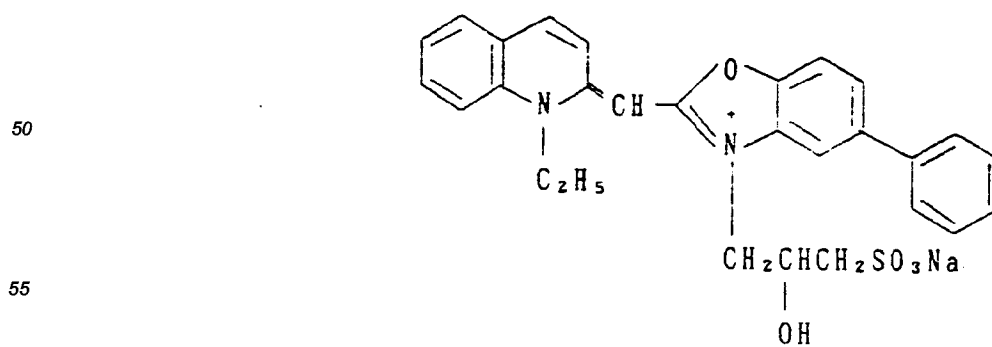
S - 6 .



S - 7



S - 8 .

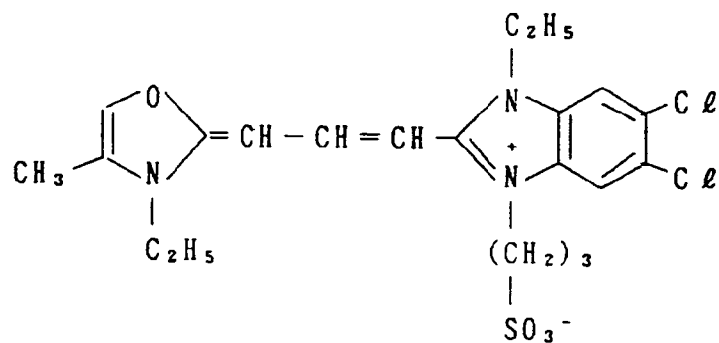


S - 9 .

5

10

15

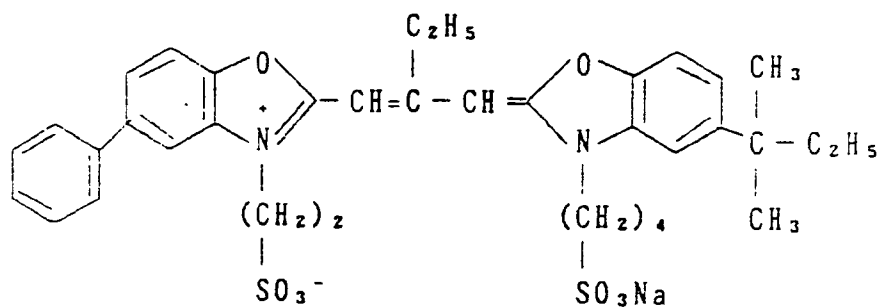


S - 1 0 .

20

25

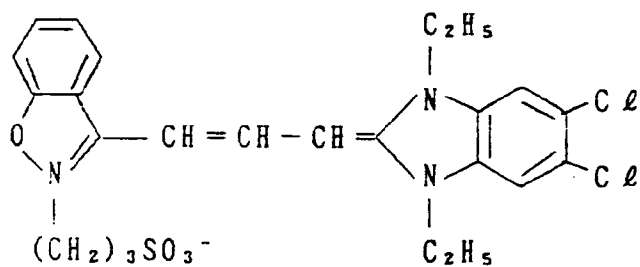
30



S - 1 1 .

35

40

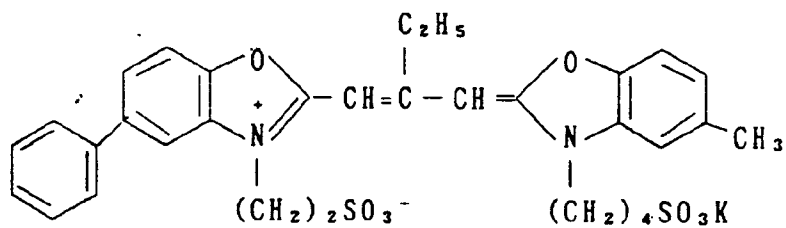


S - 1 2 .

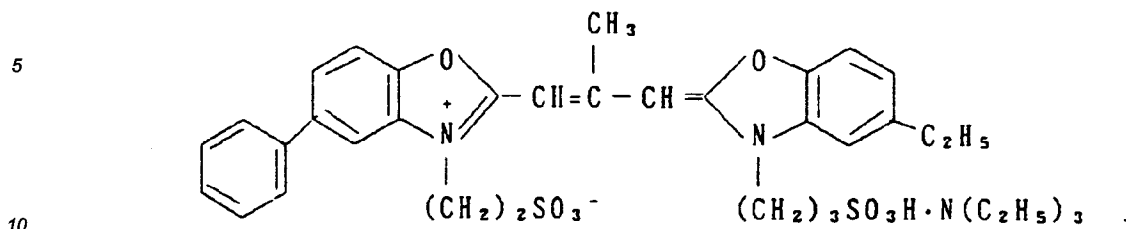
45

50

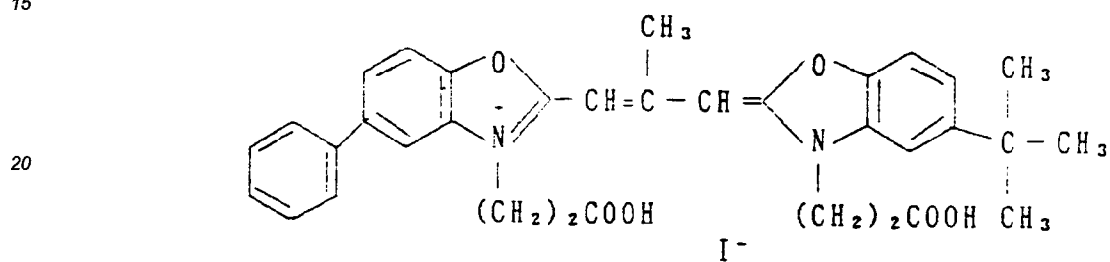
55



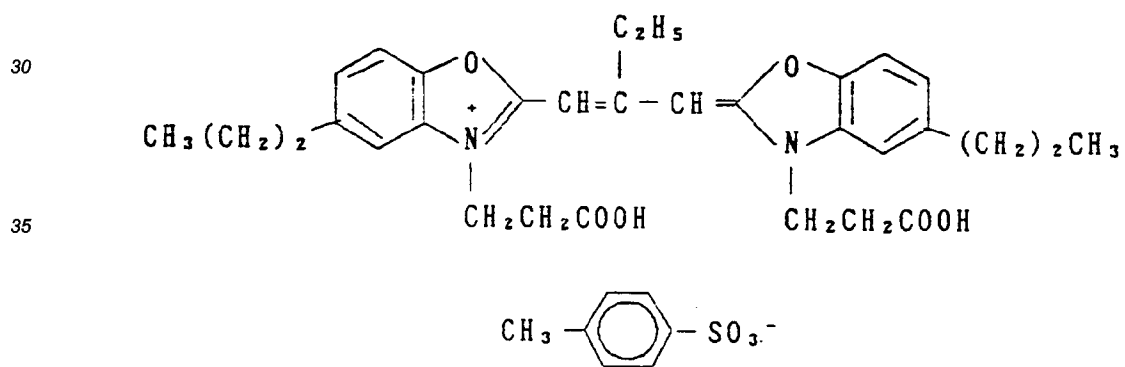
S - 1 3 .



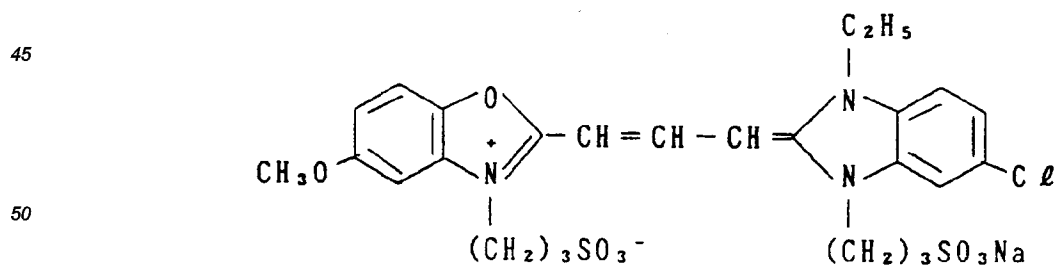
S - 1 4 .



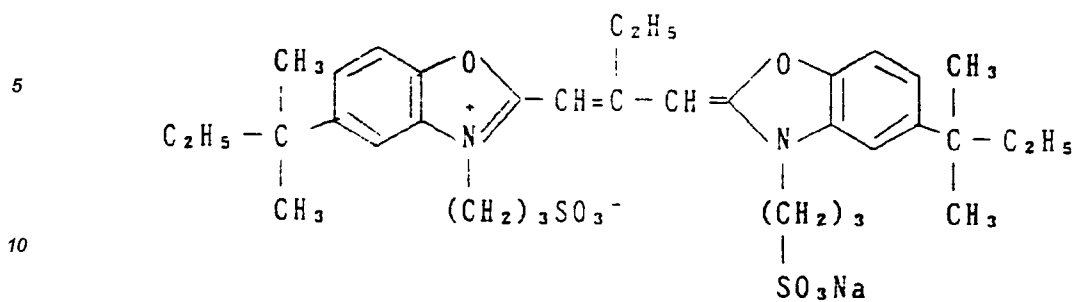
S - 1 5 .



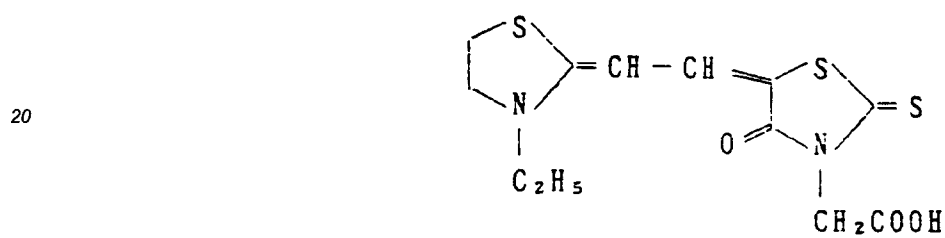
S - 1 6 .



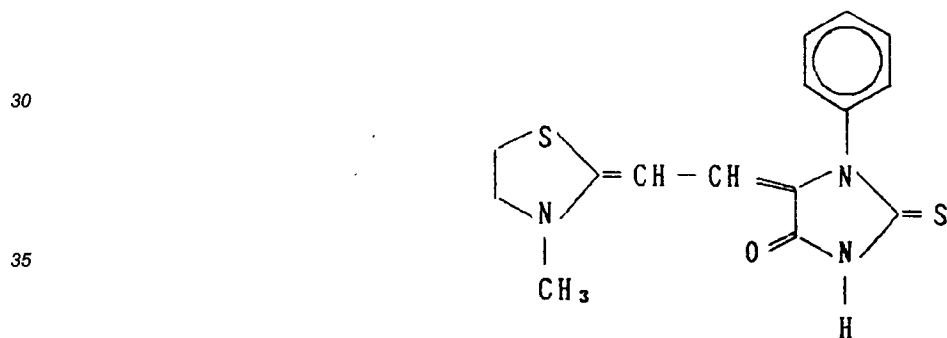
S - 2 2 .



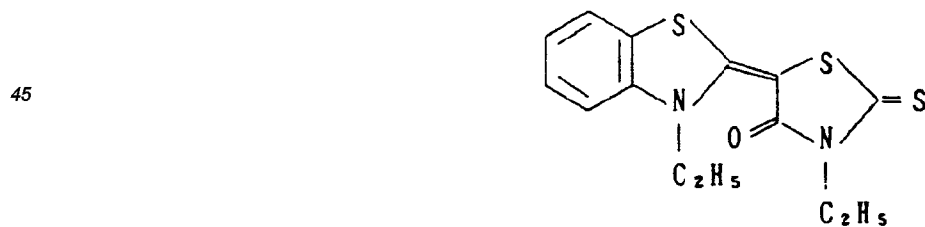
S - 2 3 .



S - 2 4 .

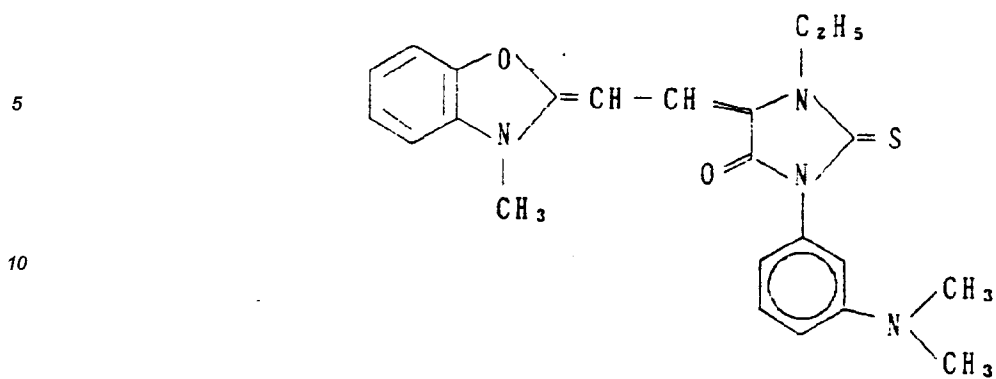


S - 2 5 .

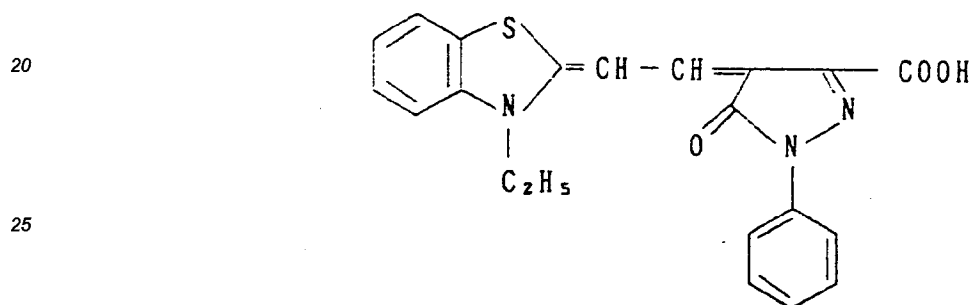


55

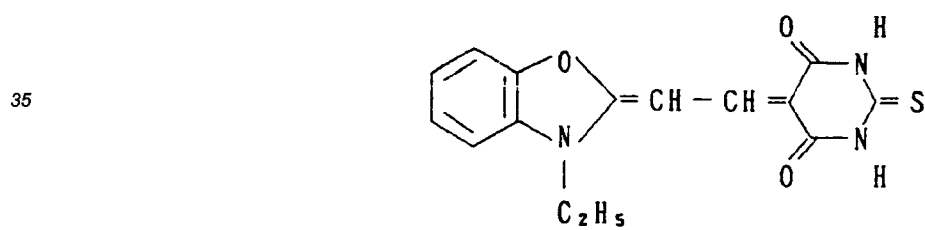
S - 2 6 .



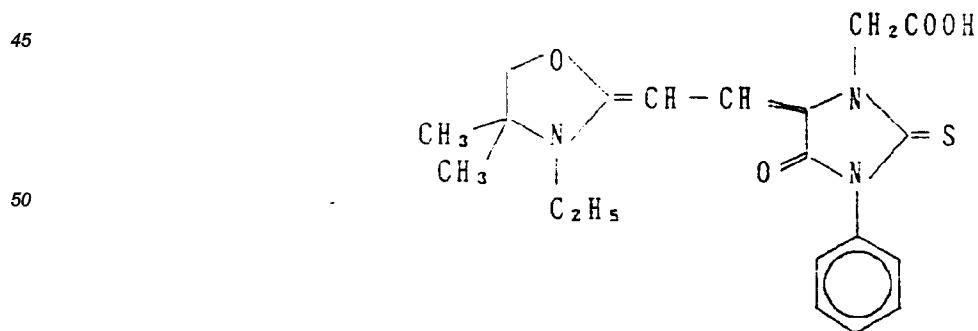
S - 2 7 .



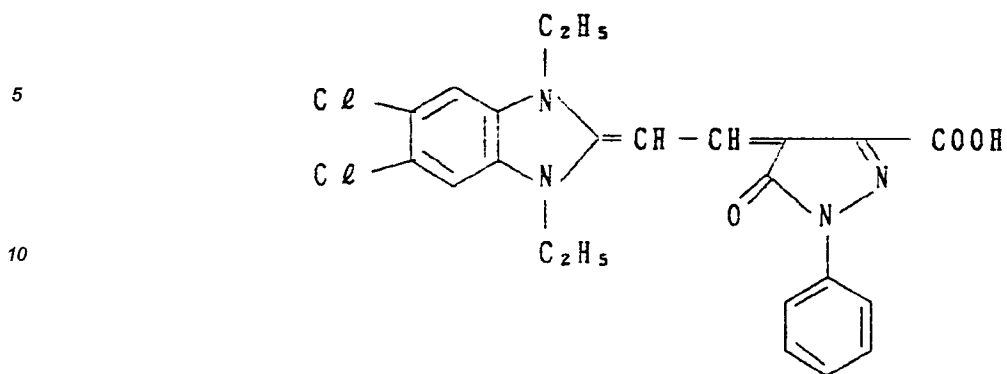
S - 2 8 .



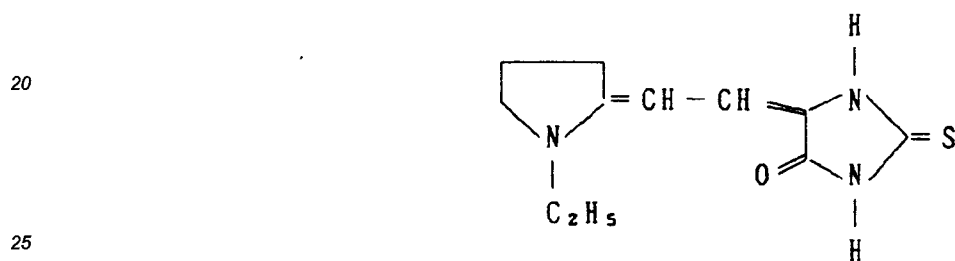
S - 2 9 .



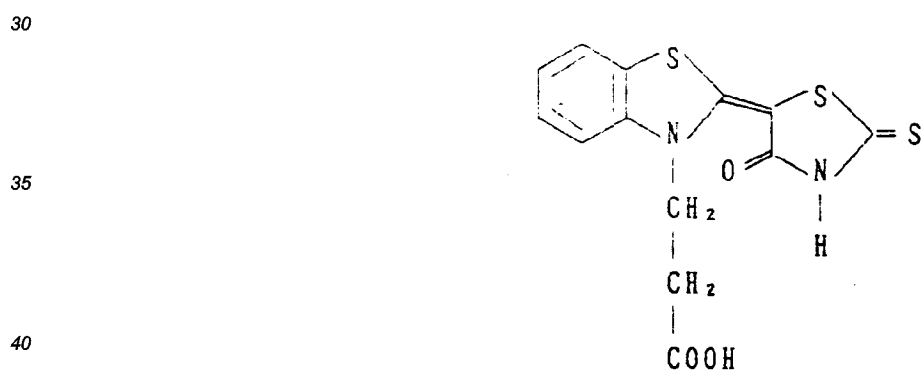
S - 3 0 .



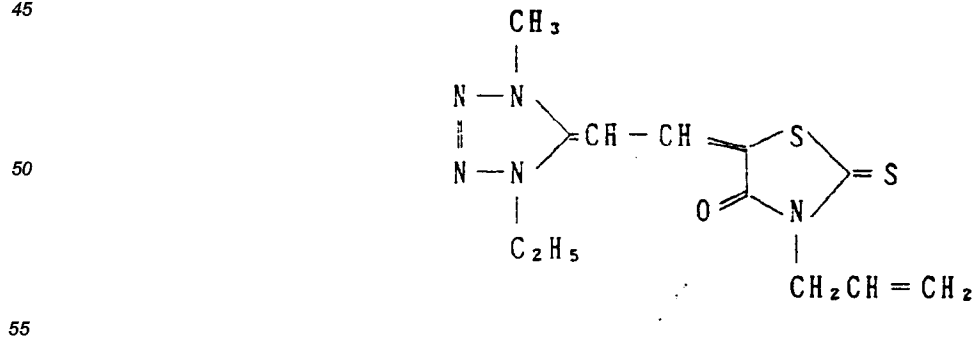
S - 3 1 .



S - 3 2 .



S - 3 3 .

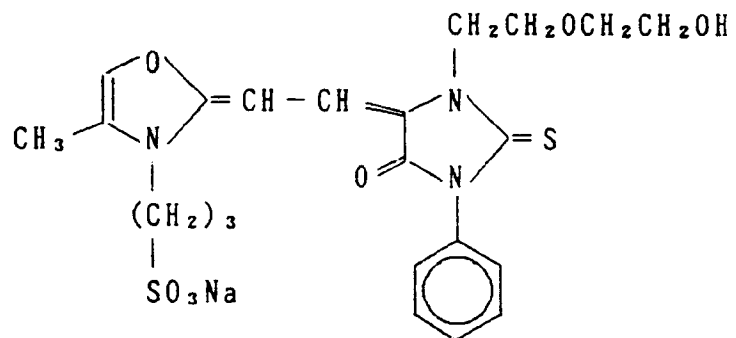


S - 3 4 .

5

10

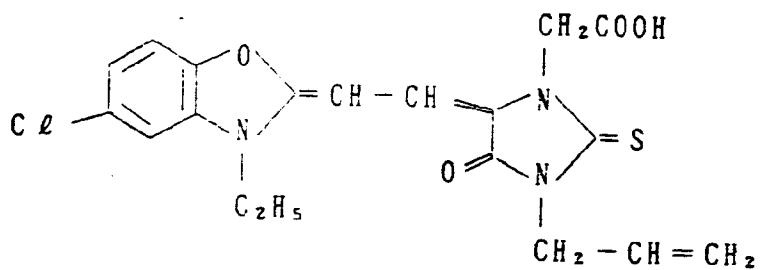
15



S - 3 5 .

20

25

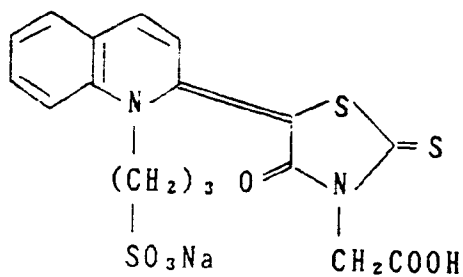


30

S - 3 6 .

35

40

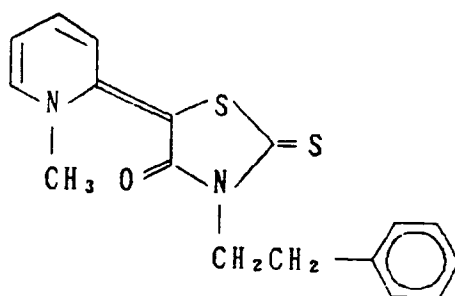


45

S - 3 7 .

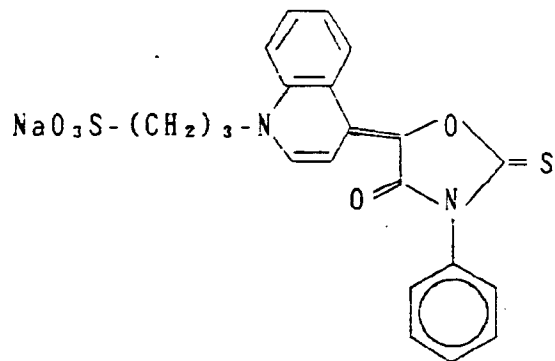
50

55



S - 3 8 .

5

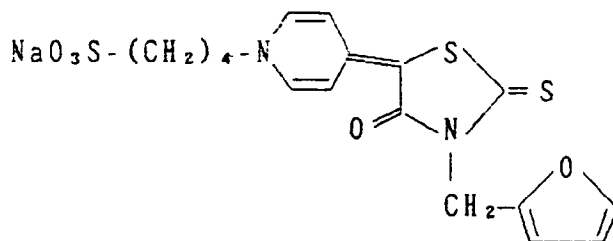


10

15

S - 3 9 .

20

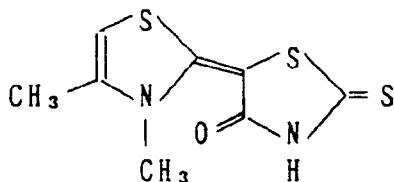


25

30

S - 4 0 .

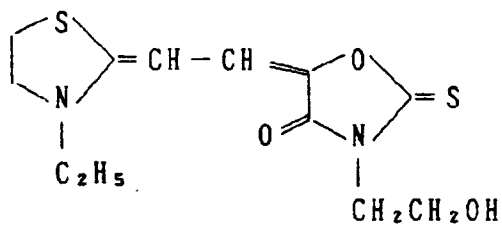
35



40

S - 4 1 .

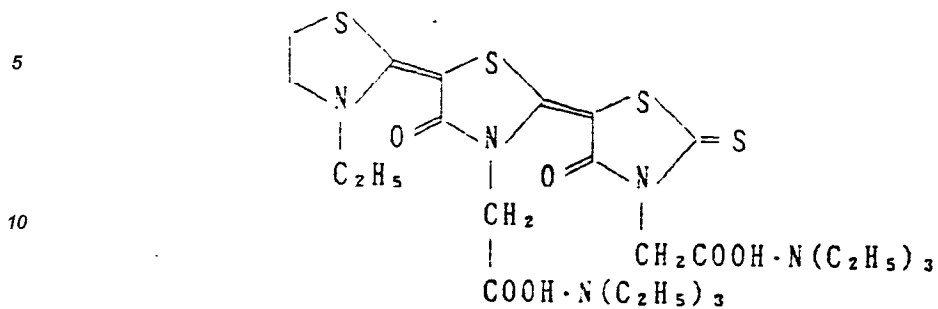
45



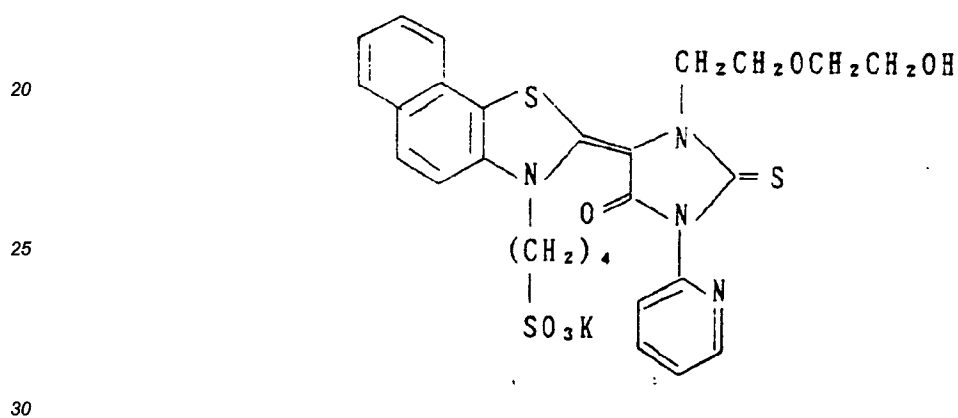
50

55

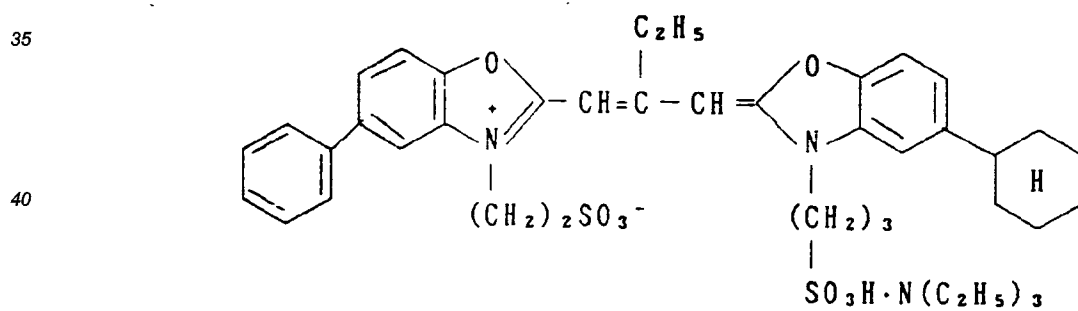
S - 4 2 .



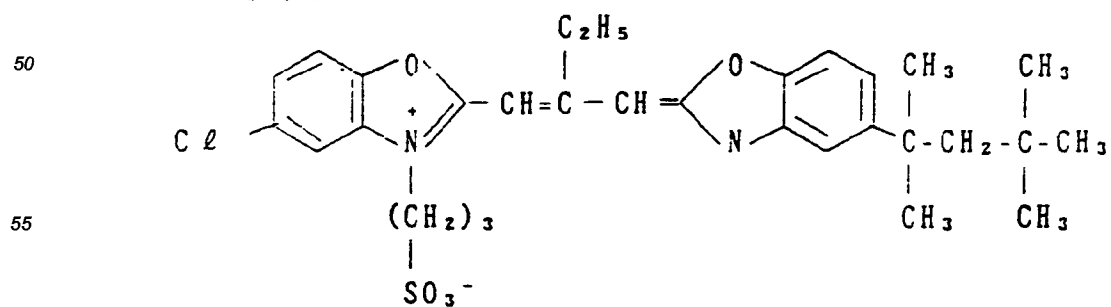
S - 4 3 .



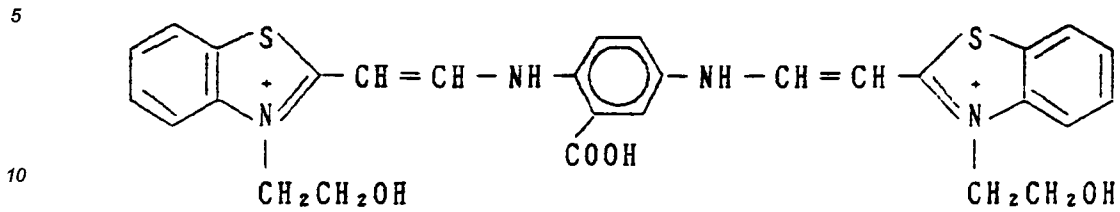
S - 4 4 .



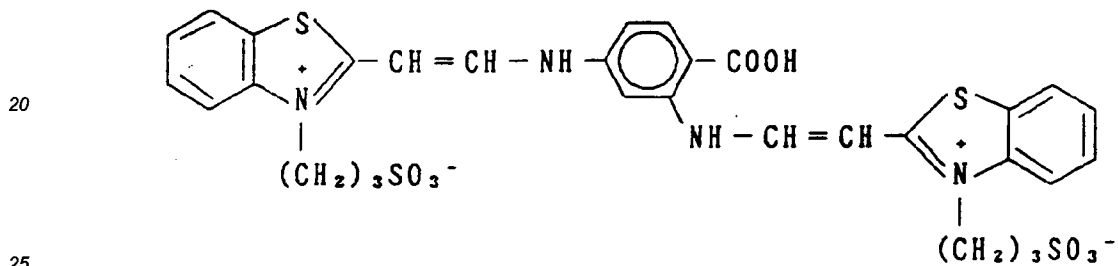
S - 4 5 .



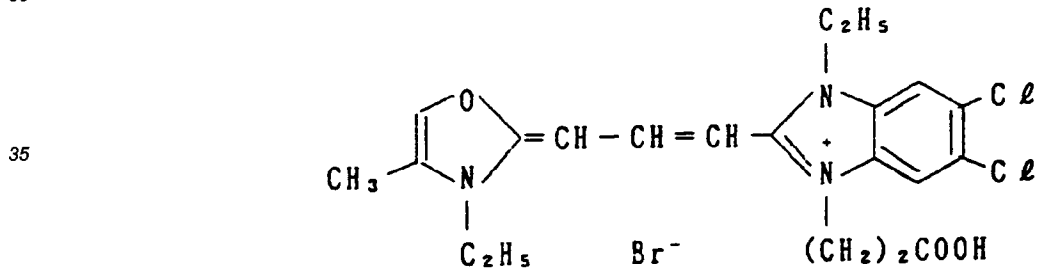
S - 4 6 .



S - 4 7 .



S - 4 8 .



45 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 a multi-layer effect as described in JP-A-54-118245 and JP-A-61-34541 which correspond to US-A-4,036,015 and US-A-4,705,744, respectively.

50 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.

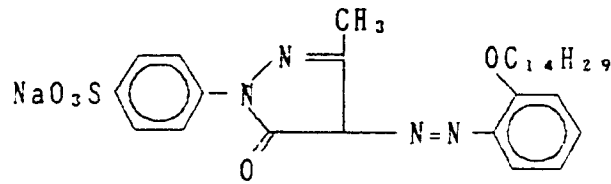
55 A density of the yellow filter is naturally depending on the colloidal silver halide grain, the yellow colored magenta coupler, the light absorption property and the used amount of nondiffusing yellow organic dyes. To determine the density of the yellow filter layer readily and accurately, a filter layer, which has the same composition and coated amount as 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.

5

Y D - 1

10



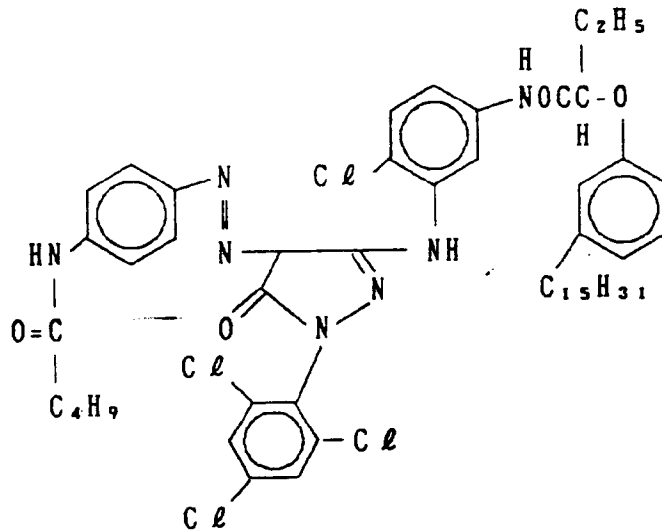
15

Y D - 2

20

25

30

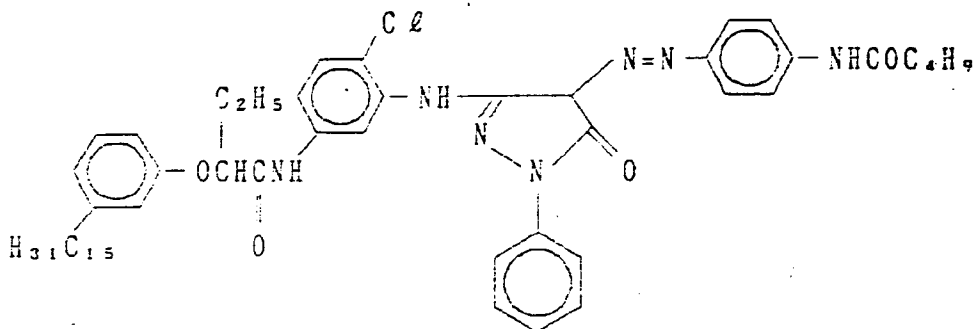


35

Y D - 3

40

45



50

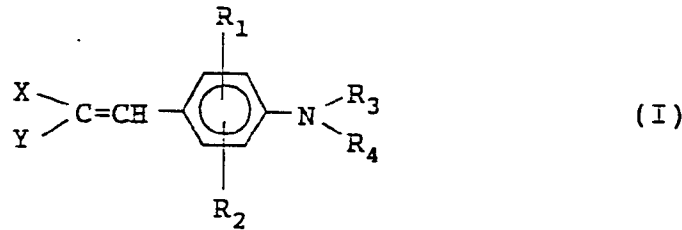
The yellow colored magenta couplers can be introduced into the yellow filter used in the present invention by conventional methods for introducing couplers into silver halide emulsion layers such as the method described in US-A-2,322,027. For example, they are dissolved in a solvent such as an alkyl 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 alkylamide (e.g., diethylaurylamide), 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

55

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.

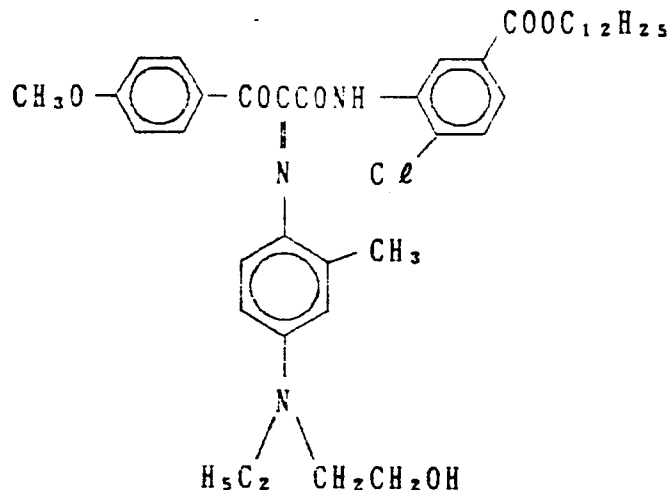
The nondiffusing yellow organic dyes which may be used in the present invention can be arbitrarily selected from among conventional dyes. Dyes represented by the following general formula (I) are particularly preferred.



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

Particularly preferred examples of the dyes include the following compounds.

Y D - 4



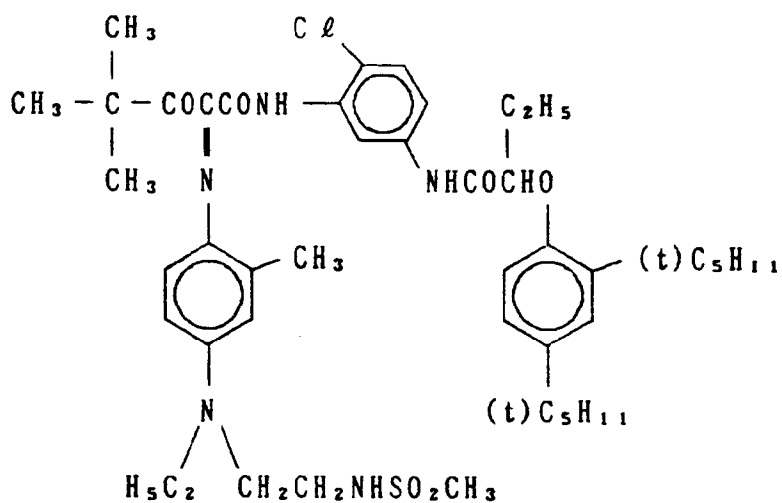
Y D - 5

5

10

15

20

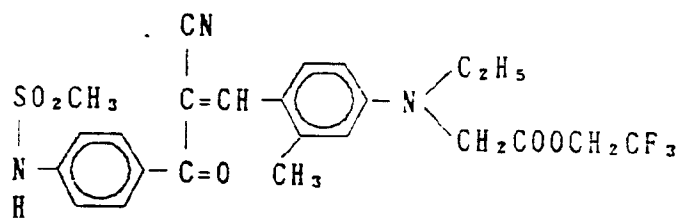


25

Y D - 6

30

35



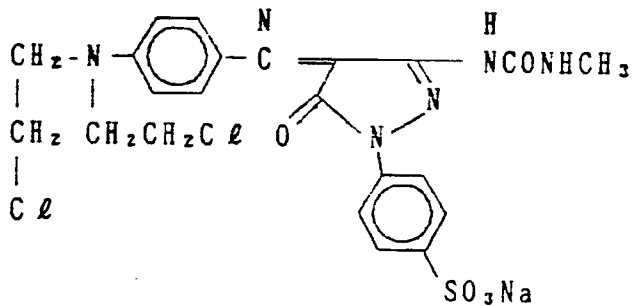
40

45

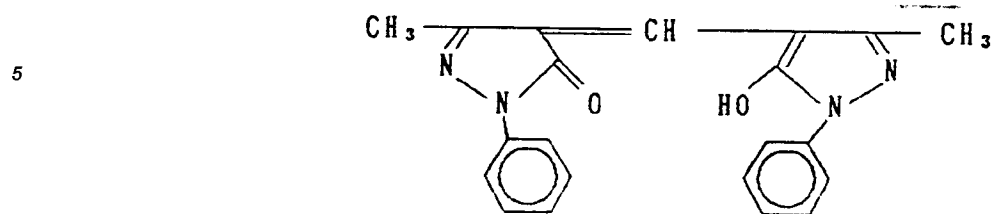
50

55

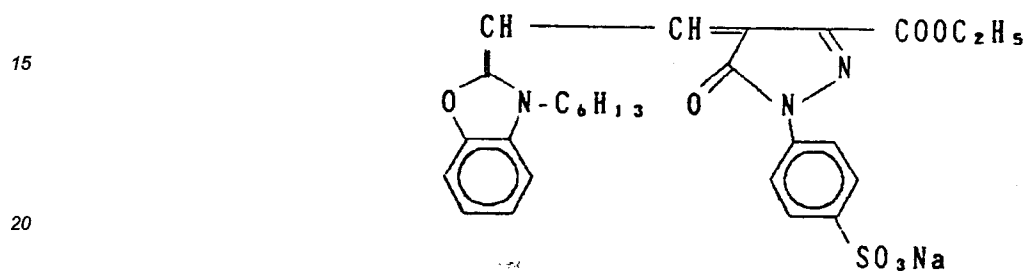
Y D - 7



Y D - 8



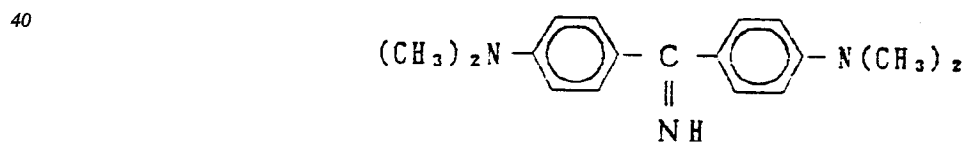
Y D - 9



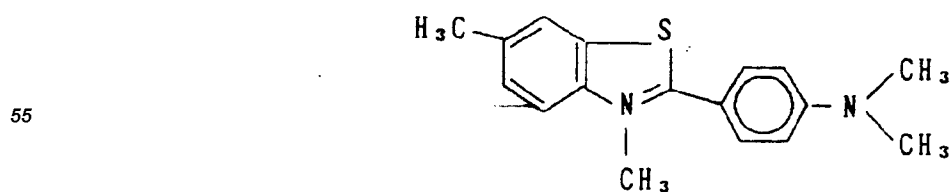
Y D - 1 0



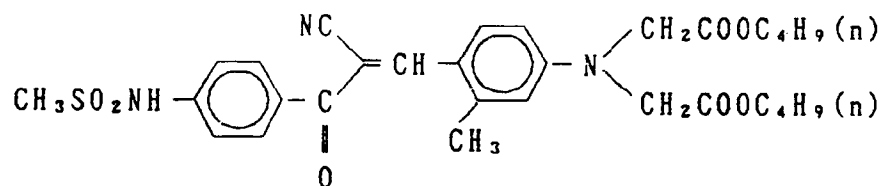
Y D - 1 1



Y D - 1 2



Y D - 1 3



The yellow filter layer containing the organic dye used in the present invention can be prepared by conventional methods. When the organic dyes are oil-soluble, the yellow filter layer 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 colloids. The yellow filter layer used in 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, the yellow 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 which has 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 $\pm 40\%$ of the mean grain size, preferably within $\pm 30\%$ 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, a controlled double jet process in which the pAg value in the liquid phase, in which silver halide is formed, is maintained constant can be used. As another embodiment, 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 can be used. Solvents for the silver halide such as ammonia, a Rhodan salt, thiourea, thioether and an amine may be used during the preparation of 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 in iodine content at the stage of a core.

Whether the halogen composition 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 the addition concentration is increased with time as disclosed in US-A-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 or 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 aqu-

eous inorganic salt solutions are simultaneously added in 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 of not higher than $Q=\alpha t^2+\beta t+\gamma$.

In the method described in US-A-4,242,445, the concentrations of aqueous solutions of inorganic salts to be reacted are increased in such a proportion that there is no significant formation of a new crystal nucleus during 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, pH, pAg and stirring conditions are important factors. In addition thereof, it is important to determine the amount of protective colloid 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 or 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 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 mixtures of grains having different crystal forms can be used.

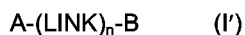
Usually, silver halide emulsions are subjected to physical ripening, chemical ripening and spectral sensitization and then used. Additives which are used in these stages are described in Research Disclosure (RD) No. 17643 and ibid. No. 18716 and listed in the following Table. Conventional photographic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

Table

| | <u>Type of Additive</u> | <u>RD 17643</u> | <u>RD 18716</u> |
|----|---|-----------------------------|--|
| 5 | 1. Chemical Sensitizer | Page 23 | Page 648, right column |
| | 2. Sensitivity 10 Increaser | | - ditto - |
| | 3. Spectral Sensitizing Agent, Supersensitizing Agent | Pages 23 to 24 | Page 648, right column to page 649, right column |
| 15 | 4. Brightener | Page 24 | |
| | 5. Antifogging Agent and Stabilizer | Pages 24 to 25 | Page 649, right column |
| 20 | 6. Light-Absorber, Filter Dye and UV Light Absorber | Pages 25 to 26 | Page 649, right column to page 650, left column |
| 25 | 7. Antistaining Agent | Page 25, right column | Page 650, left column to right column |
| | 8. Dye Image Stabilizer | Page 25 | |
| 30 | 9. Hardening Agent | Page 26 | Page 651, left column |
| | 10. Binder | Page 26 | - ditto - |
| 35 | 11. Plasticizer, Lubricant | Page 27 | Page 650, right column |
| | 12. Coating Aid, Surfactant | Pages 26 to 27 | - ditto - |
| 40 | 13. Antistatic Agent | Page 27 | - ditto - |

45 It is preferred that the emulsion layers according to the present invention contain two equivalent type couplers.

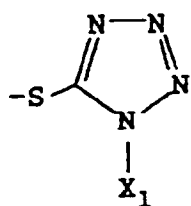
It is particularly preferred to use compounds which release a diffusing restrainer or a precursor thereof by a coupling reaction with the oxidant of a developing agent. As such compounds, compounds represented by the following formula (I'):



50 are preferred. In the above formula, A represents a residue of a coupler which releases $(\text{LINK})_n-B$ 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 or 1 and when n=0, B is
55 directly attached to A.

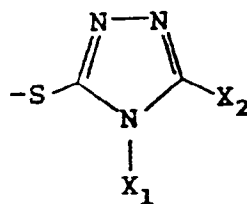
Formula (IIa)

5



10

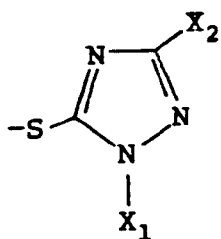
Formula (IIb)



15

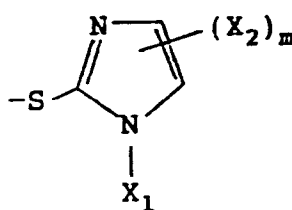
Formula (IIc)

20



25

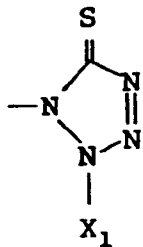
Formula (IIId)



30

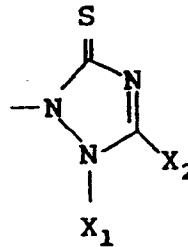
Formula (IIe)

35



40

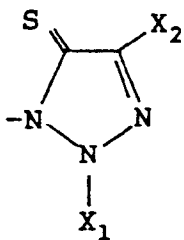
Formula (IIf)



45

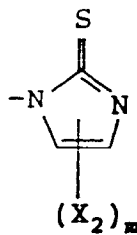
Formula (IIg)

50

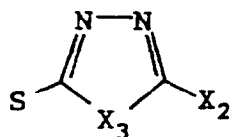


55

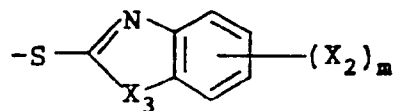
Formula (IIh)



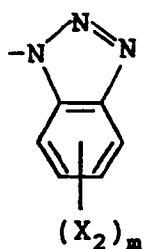
Formula (IIIi)



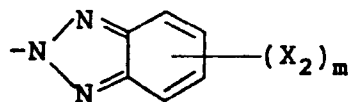
Formula (IIj)



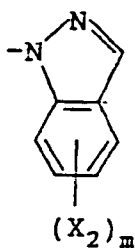
Formula (IIk)



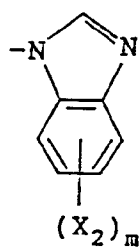
Formula (IIl)



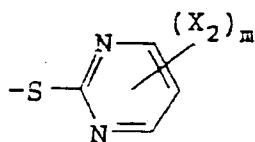
Formula (IIm)



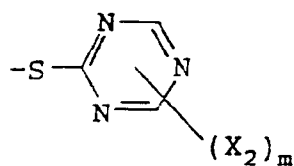
Formula (IIn)



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 alkoxy carbonyl group, a hydroxyl group, an acylamino group, a carbamoyl group, a sulfonyl

group, a sulfonamido group, a sulfamoyl group, an amino group, an acylamino group, a 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 a hydroxyl group, an alkoxy-carbonyl group, an acylamino group, a carbamoyl group, a sulfonyl group, a sulfonamido group, a sulfamoyl group, an acyloxy group, a ureido group, a carboxyl group, a cyano group, a nitro group, an amino group and an acyl group; X_2 is a hydrogen atom, an aliphatic group, a halogen, a hydroxyl group, an alkoxy group, an alkylthio group, an alkoxy-carbonyl group, an acylamino group, a carbamoyl group, a sulfonyl group, a sulfonamido group, a sulfamoyl group, an acyloxy group, a ureido group, a cyano group, a nitro group, an amino group, an alkoxy-carbonylamino group, an aryloxy-carbonyl group or an acyl group; X_3 is an oxygen atom, a sulfur atom or an imino group having not more than 4 carbon atoms; m is an integer of 1 or 2; the total number 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 and cyan dyes 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, malonic ester monoamide type, benzthiazolyl acetate type, benzoxazolylacetamide type, benzoxazolyl acetate type, malonic diester type, benzimidazolylacetamide type and benzimidazolyl acetate type residues; coupler residues derived from heterocyclic ring-substituted acetamides or heterocyclic ring-substituted acetates such as those described in US-A-3,841,880; coupler residues derived from cyclacetamides such as those described in US-A-3,770,446, GB-A-1,459,171, DE-A-2,503,099, JP-A-50-139738 and Research Disclosure No. 15737; and heterocyclic ring type coupler residues such as those described in US-A-4,046,574.

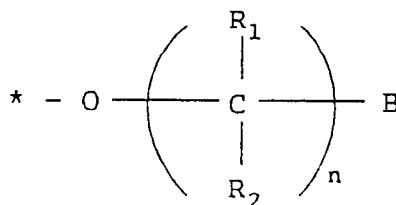
Preferred examples of magenta dye image forming coupler residues represented by A include residues having 5-oxo-2-pyrazoline nucleus, pyrazolo[1,5-a]benzimidazole nucleus, pyrazoloimidazole nucleus, pyrazolotriazole nucleus or pyrazolotetrazole nucleus and cyanoacetophenone type residues.

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 US-A-4,052,213, US-A-4,088,491, US-A-3,632,345, US-A-3,958,993 and US-A-3,961,959. The group A may also be residues of polymer couplers such as those described in US-A-3,451,820, US-A-4,080,211 and US-A-4,367,282 and GB-A-2,102,173.

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

(1) Groups which utilize the cleavage reaction of a hemi-acetal. An example thereof is a group represented by the following formula and described in US-A-4,146,396, and Japanese Patent Application Nos. 59-106223, 59-106224 and 59-75475.



In the formula, the mark * represents 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 combine 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 US-A-4,248,962.

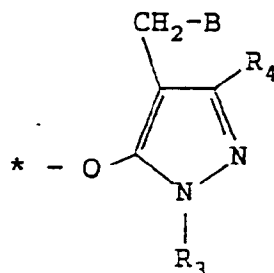
(3) Groups which allow a cleavage reaction to take place by utilizing an electron transfer reaction along conjugated system. Examples thereof include a group such as that described in US-A-4,409,323 and a

group such as that represented by the following formula (see GB-A-2,096,783A).

In the formula, the mark * represents a position at which the group is attached to the coupling position of A; R₃ and R₄ 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 R₃ include an alkyl group having from 1 to 24 carbon atoms

5

10



15

(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 R₄ 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), a 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), a 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).

20

25

Substituent groups represented by X₁, X₂ and X₃ in formulae (IIa) to (IIp) are illustrated below.

Examples of the group X₁ include methyl, ethyl, propyl, butyl, methoxyethyl, ethoxyethyl, isobutyl, allyl, dimethylaminoethyl, propargyl, chloroethyl, methoxycarbonylmethyl, methylthioethyl, 4-hydroxyphenyl, 3-hydroxyphenyl, 4-sulfamoylphenyl, 3-sulfamoylphenyl, 4-carbamoylphenyl, 3-carbamoylphenyl, 4-dimethylaminophenyl, 3-acetamidophenyl, 4-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 X₂ include a hydrogen atom, methyl, ethyl, benzyl, n-propyl, i-propyl, n-butyl, i-butyl, cyclohexyl, a fluorine atom, a chlorine atom, a bromine atom, an iodine atom, hydroxymethyl, hydroxyethyl, hydroxyl, methoxy, ethoxy, butoxy, allyloxy, benzyloxy, methylthio, ethylthio, methoxycarbonyl, ethoxycarbonyl, acetamido, propaneamido, butaneamido, octaneamido, benzamido, dimethylcarbamoyl, methylsulfonyl, methylsulfonamido, phenylsulfonamido, dimethylsulfamoyl, acetoxyl, ureido, 3-methylureido, cyano, nitro, amino, 1-methyl-2-benzthiazolyldeneamino, dimethylamino, methoxycarbonylamino, ethoxycarbonylamino, phenoxy carbonyl, methoxyethyl and acetyl. Examples of the group X₃ include an oxygen atom, a sulfur atom, imino, methylimino, ethylimino, propylimino and allylimino.

30

35

40

Among the groups represented by formulae (IIa) to (IIp), the groups represented by the formulae (IIa), (IIb), (III), (IIj), (IIIk) and (II^l) are preferred. Among these, the groups represented by formulae (IIa), (III), (IIj) and (IIIk) are particularly preferred.

45

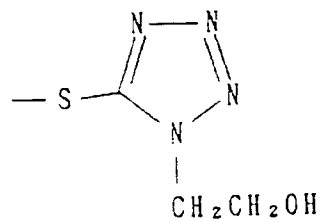
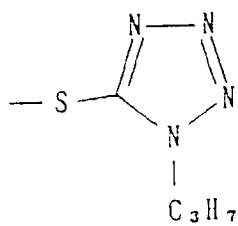
Examples of the group represented by B in the formula (I') include the following groups.

50

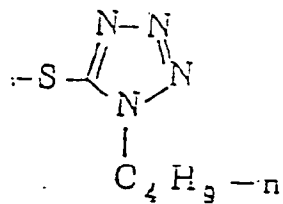
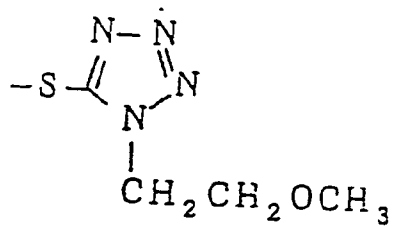


55

5



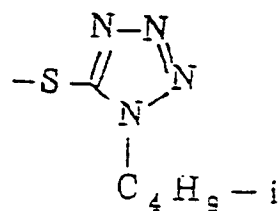
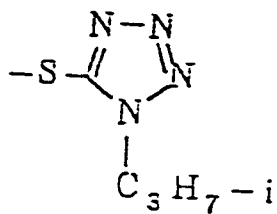
10



15

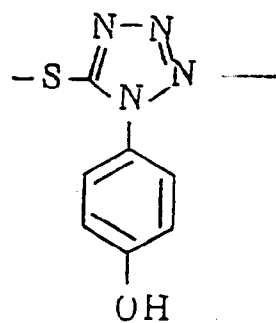
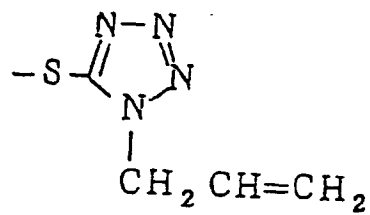
20

25



30

35



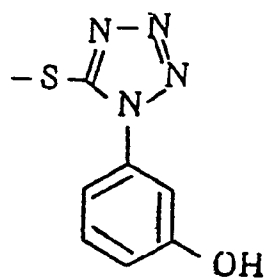
40

45

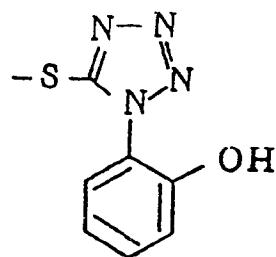
50

55

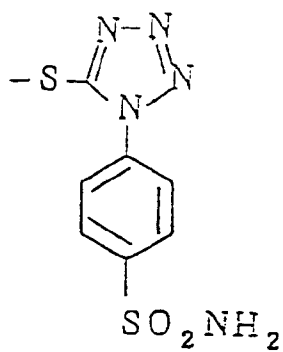
5



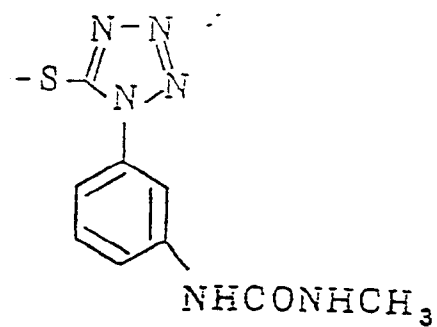
10



15

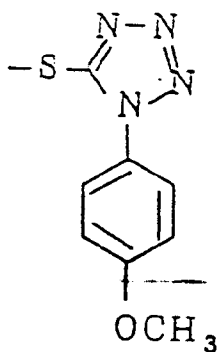


20

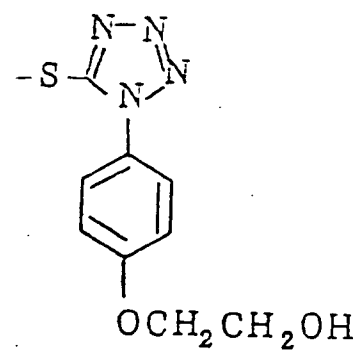


25

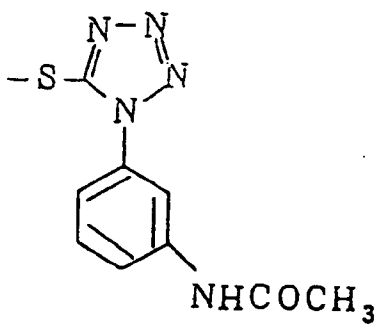
30



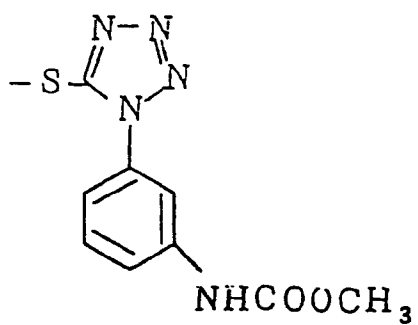
35



40



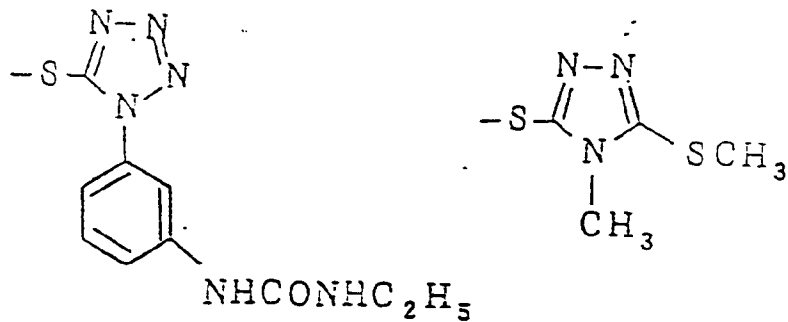
45



50

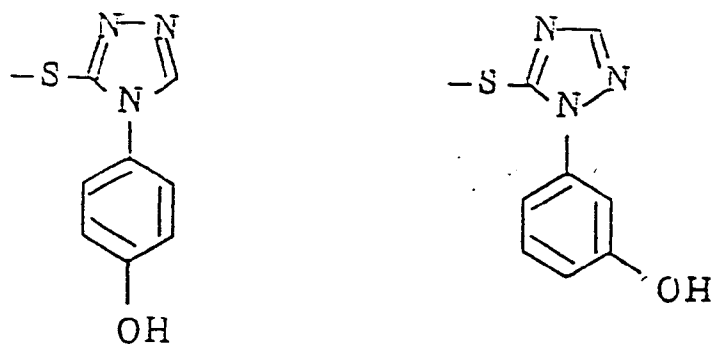
55

5



10

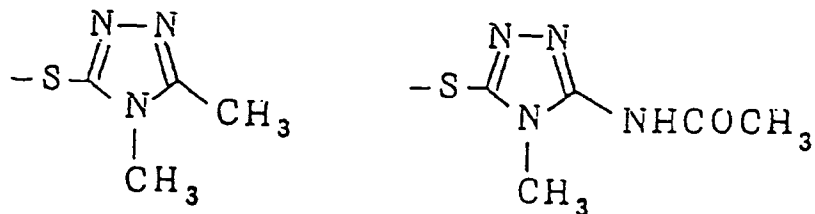
15



20

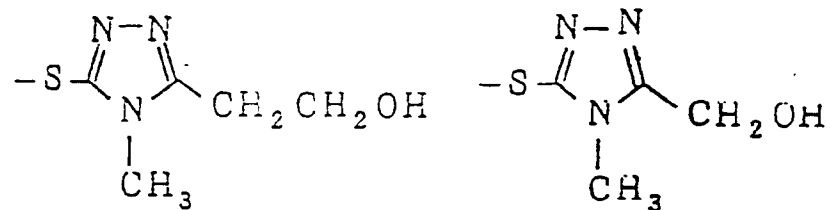
25

30



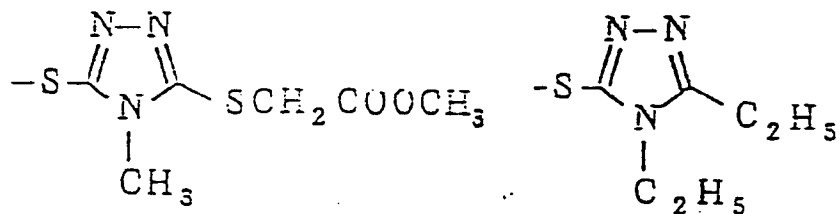
35

40



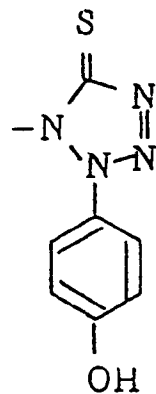
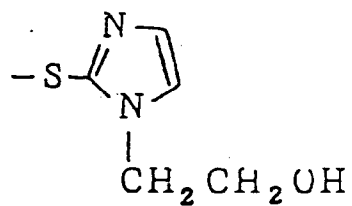
45

50



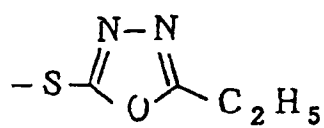
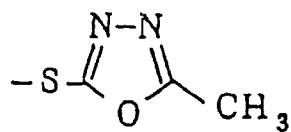
55

5



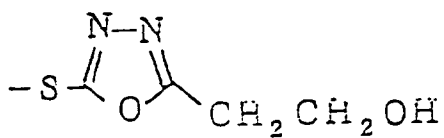
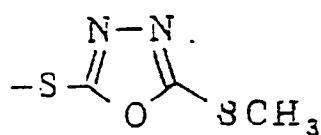
10

15

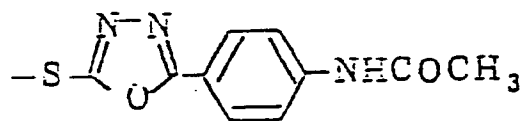


20

25

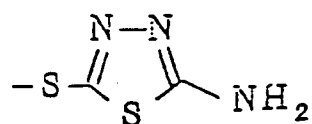
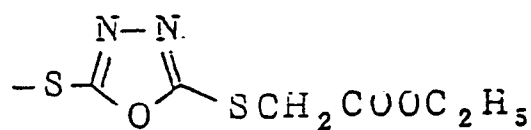


30

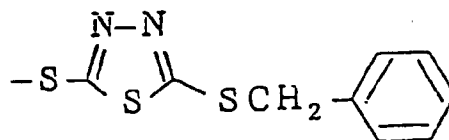
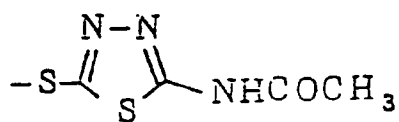


35

40

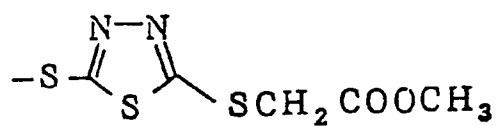


45

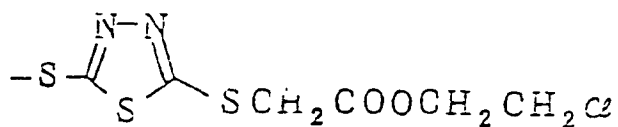


50

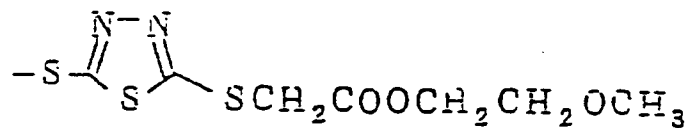
55



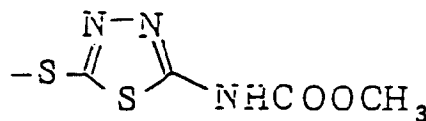
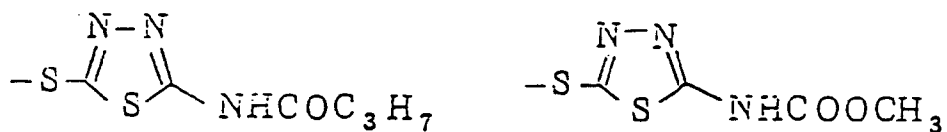
5



10

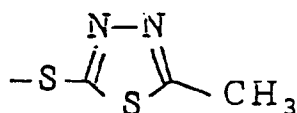


15

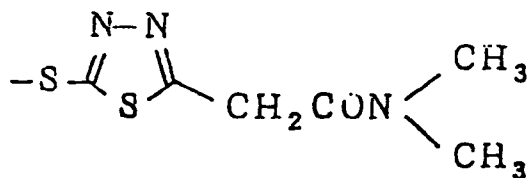


20

25

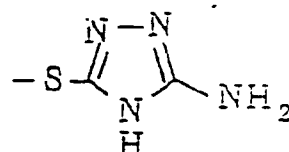
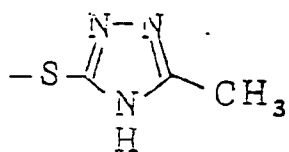


30

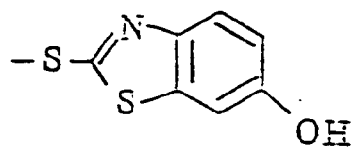
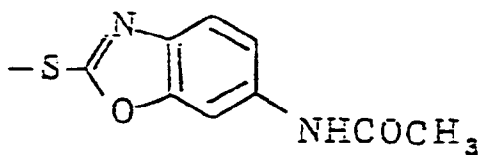


35

40

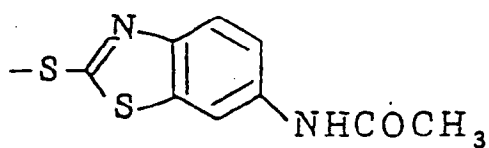
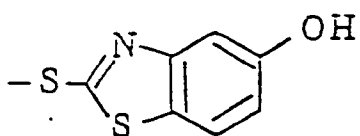


45

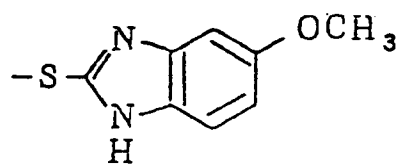
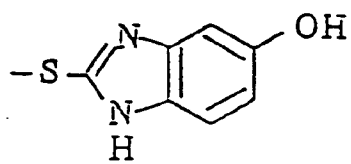


50

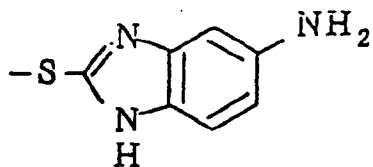
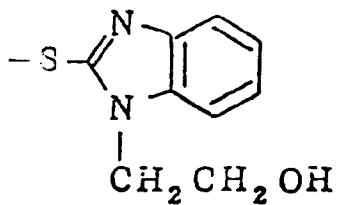
55



5

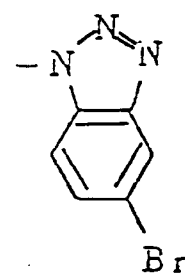
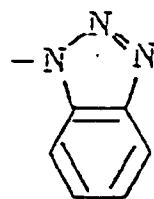


10



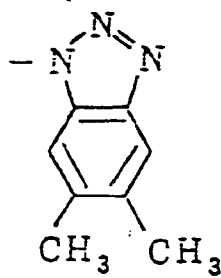
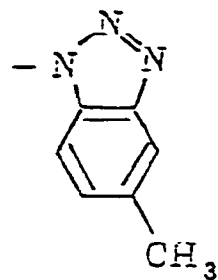
15

20



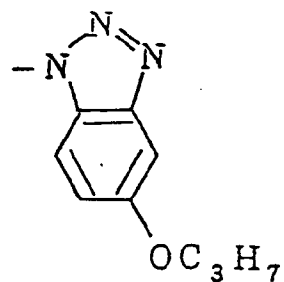
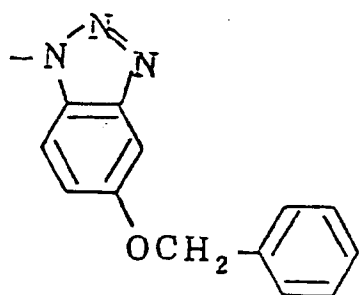
25

30



35

40

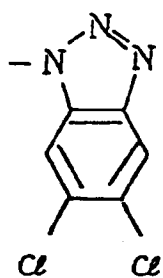


45

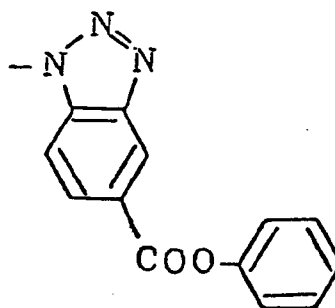
50

55

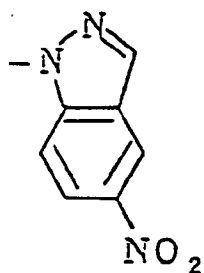
5



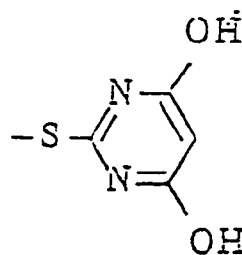
10



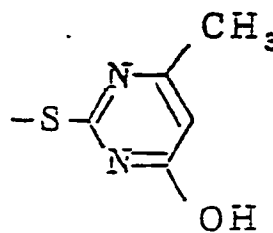
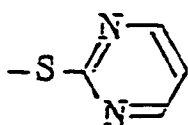
15



20

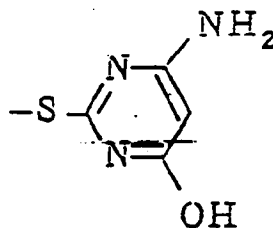
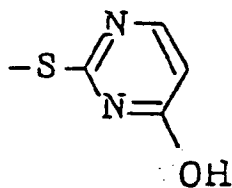


25



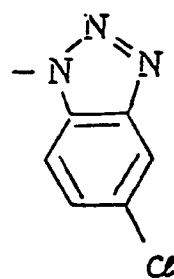
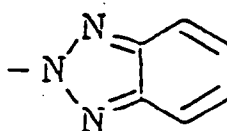
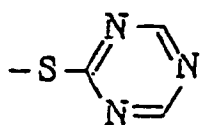
30

35



40

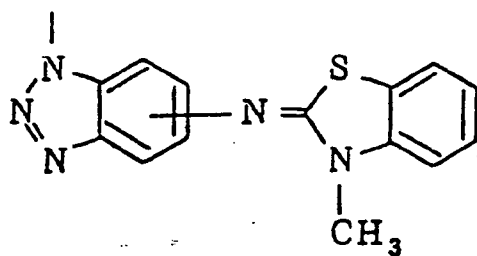
45



50

55

5



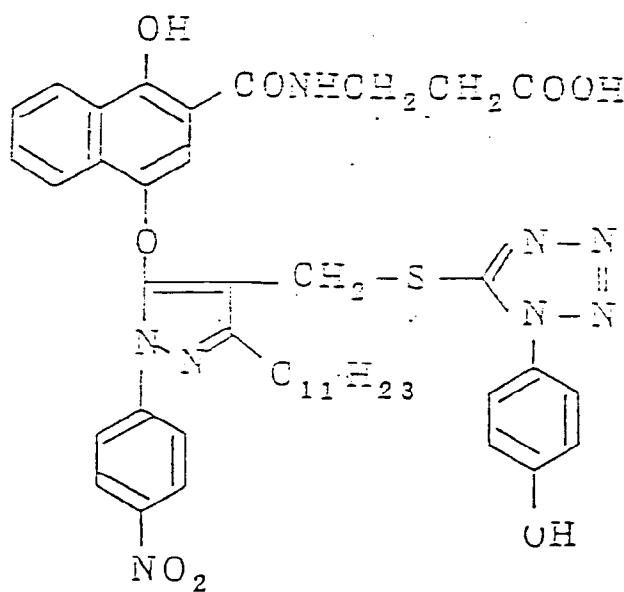
10

Examples of the couplers which are used in the present invention include the following compounds.

15

(D - 1)

20



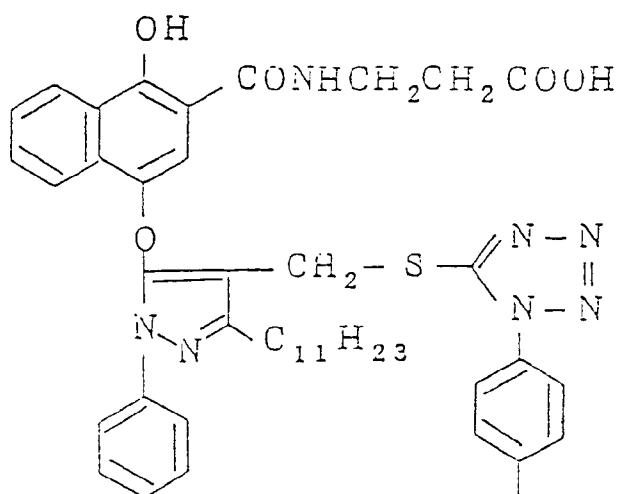
25

30

35

(D - 2)

40

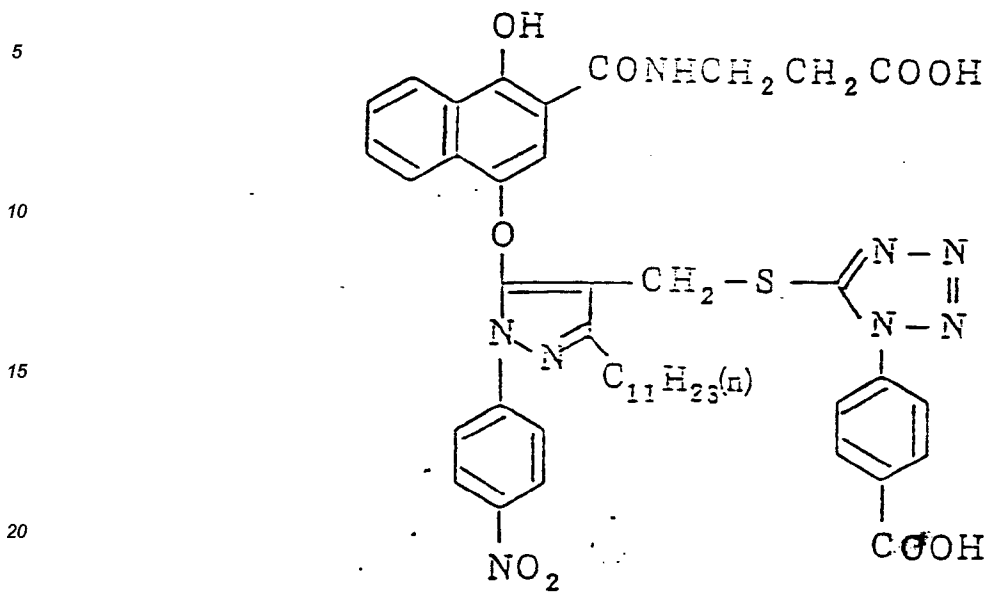


45

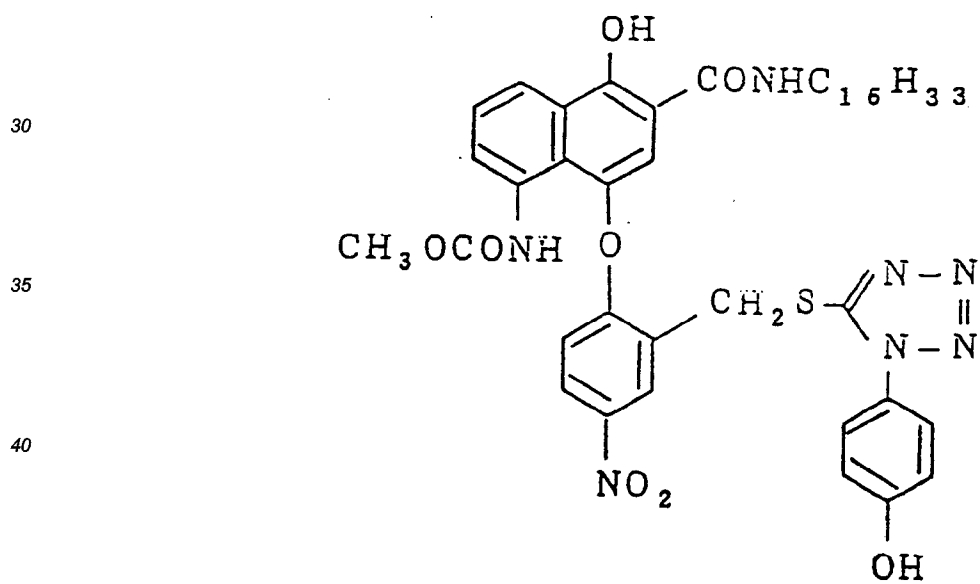
50

55

(D - 3)



(D - 4)



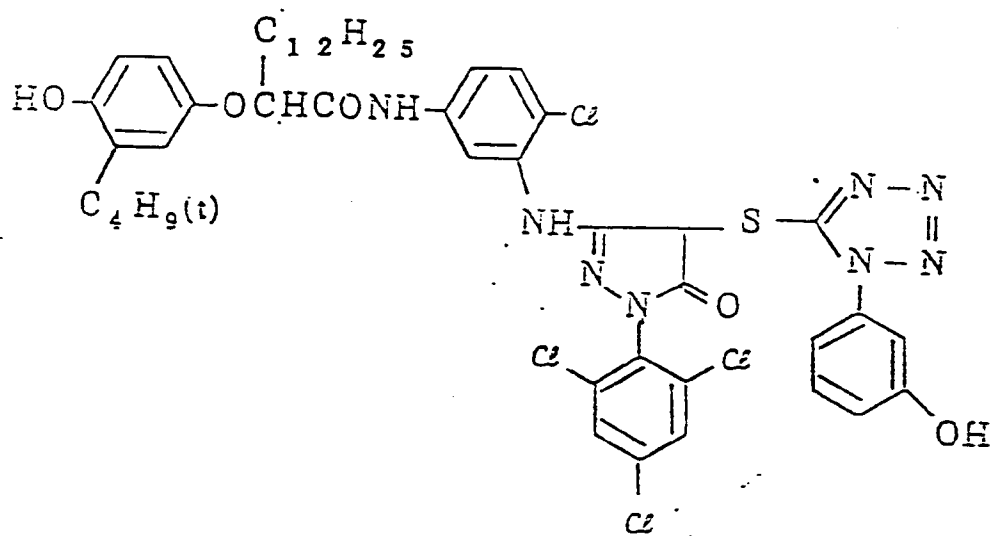
(D - 5)

5

10

15

20



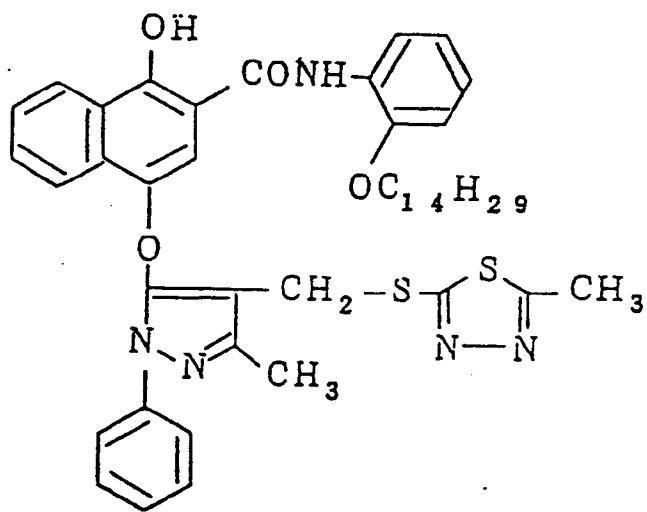
(D - 6)

25

30

35

40



45

50

55

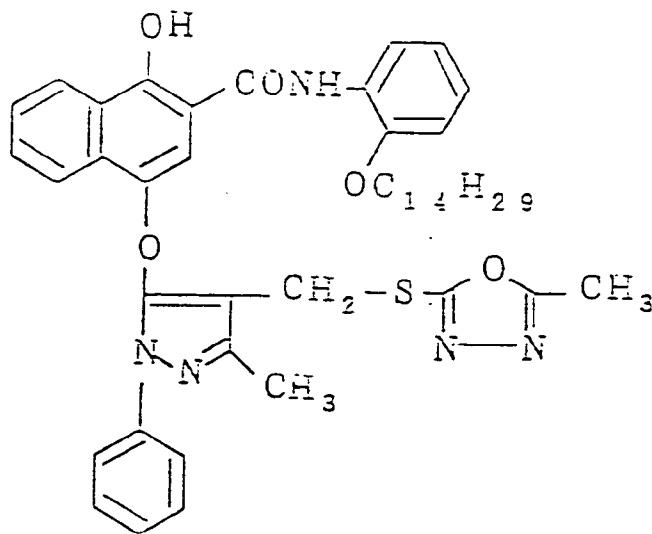
(D - 7)

5

10

15

20



25

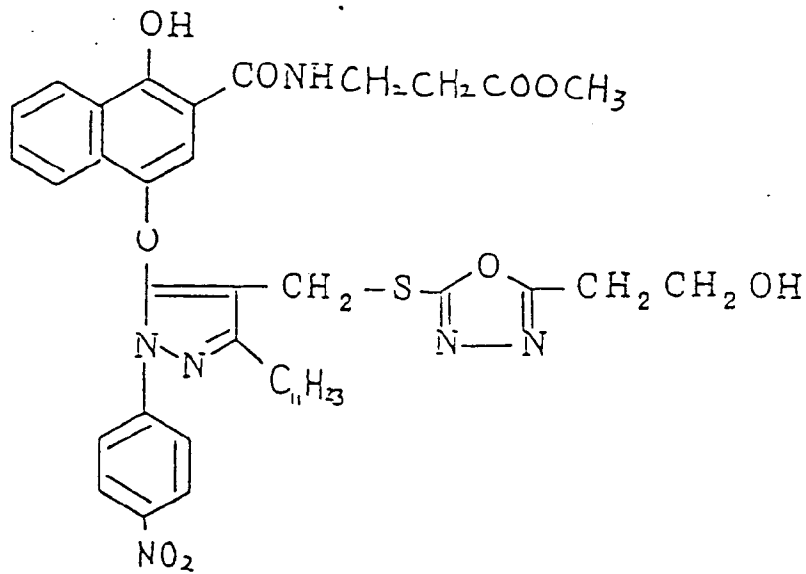
(D - 8)

30

35

40

45



50

55

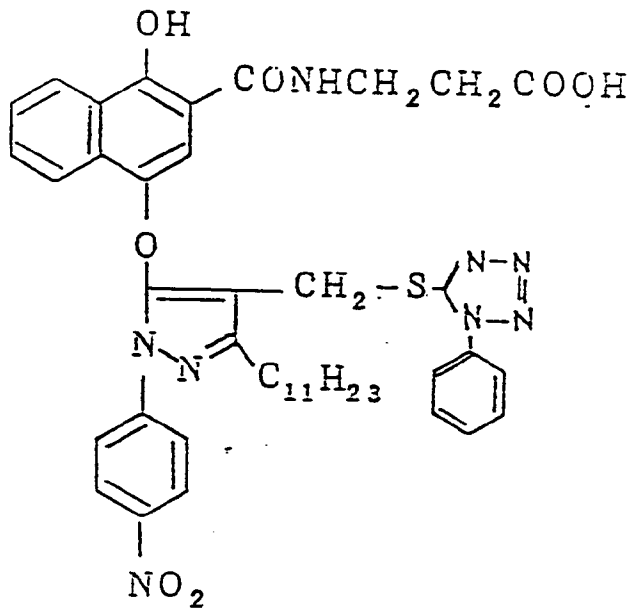
(D - 9)

5

10

15

20



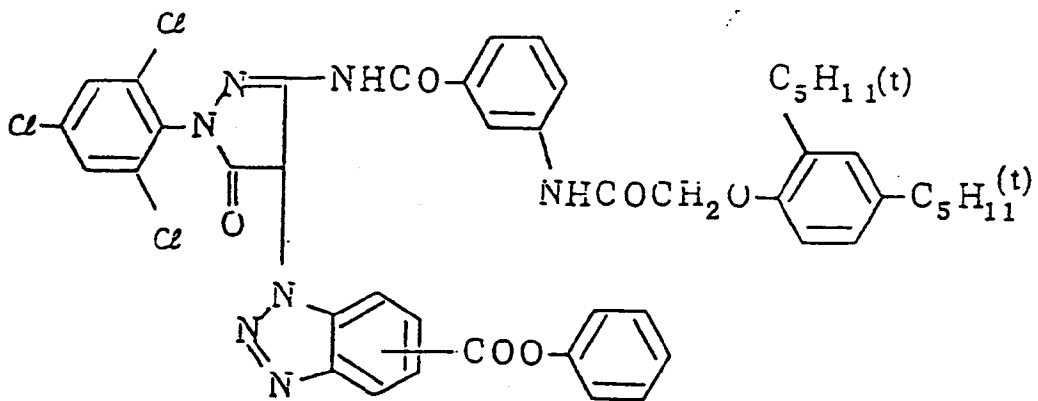
25

(D - 10)

30

35

40

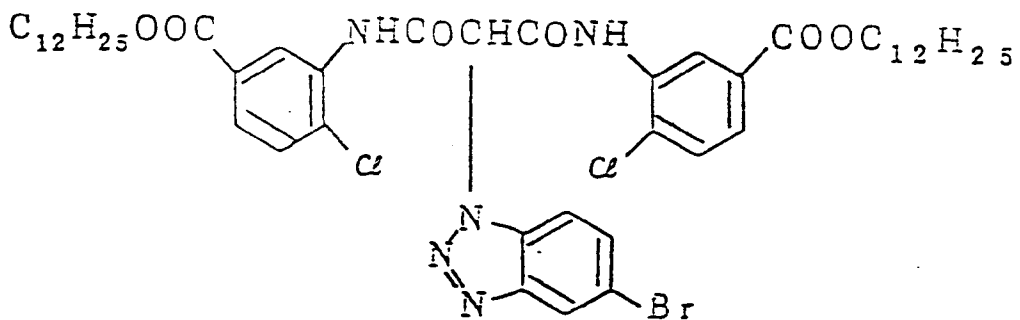


45

(D - 11)

50

55



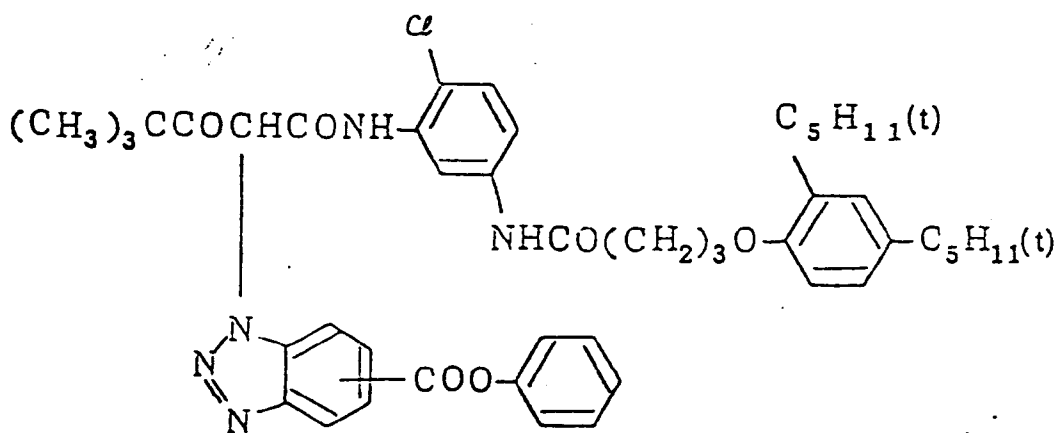
(D - / 2)

5

10

15

20

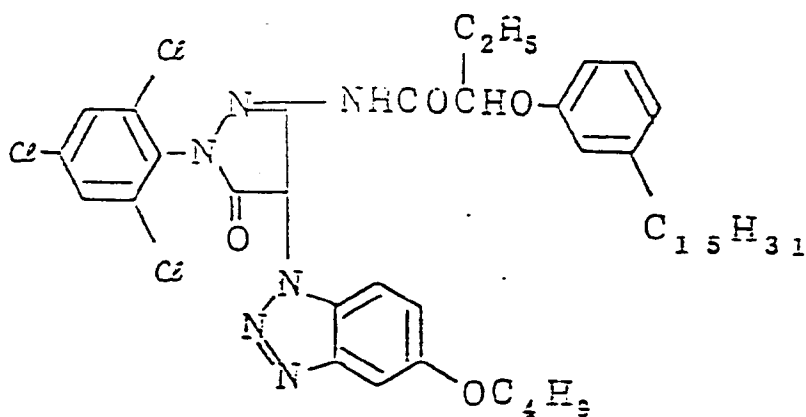


(D - / 3)

25

30

35



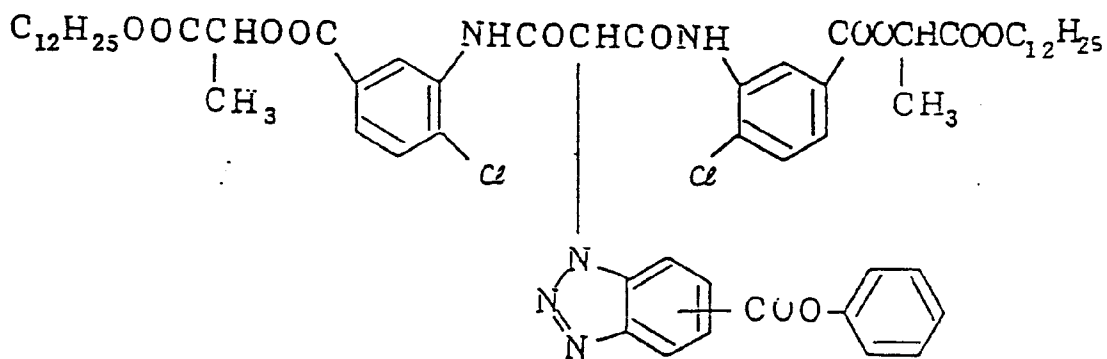
40

(D - / 4)

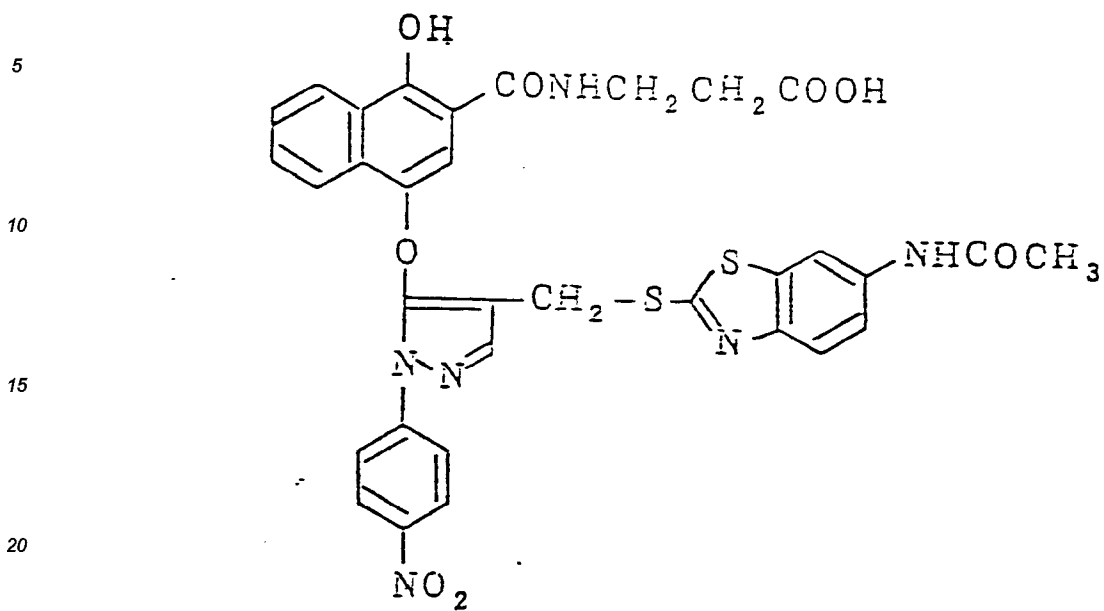
45

50

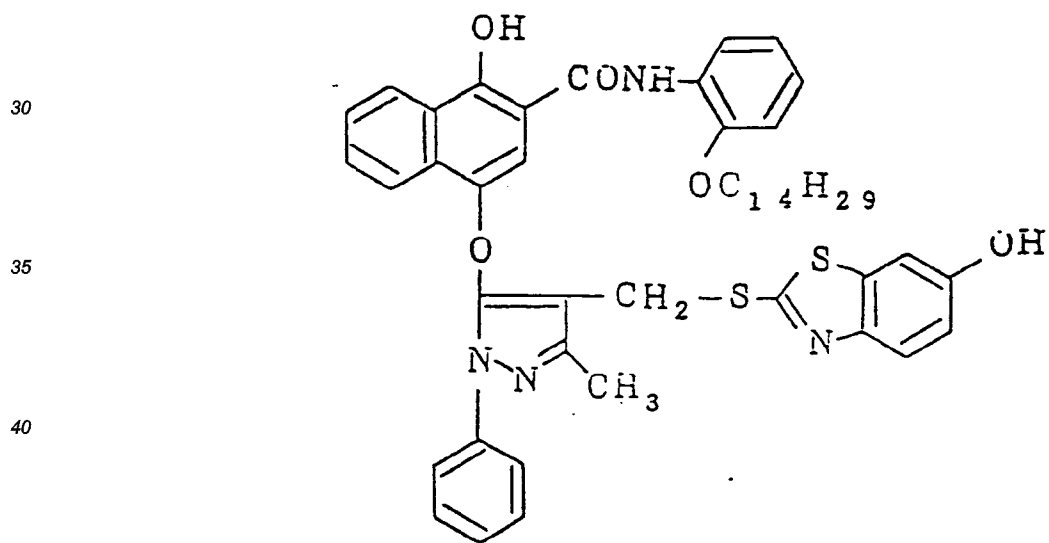
55



(D - 1 5)



(D - 1 6)



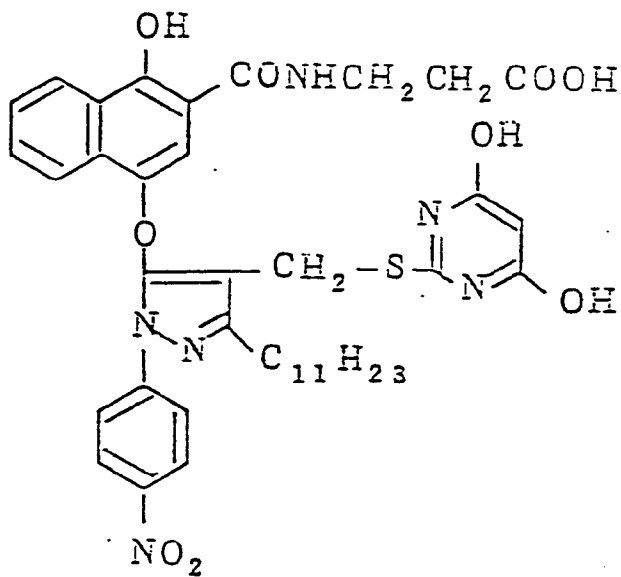
(D - / 7) .

5

10

15

20



25

(D - / 8)

30

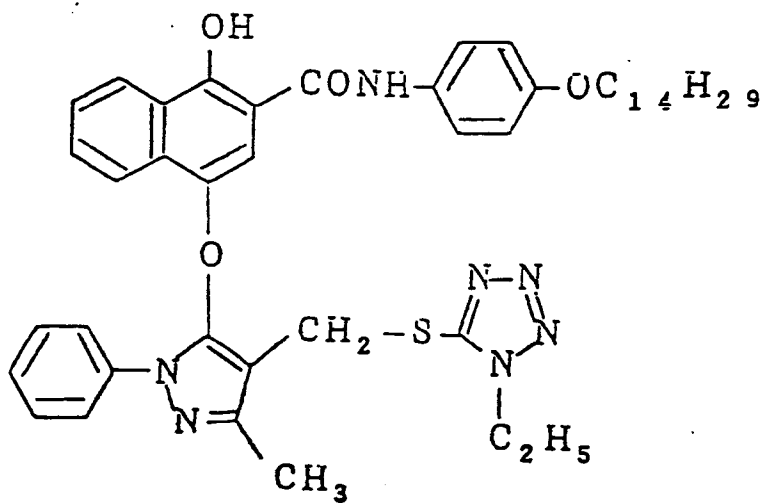
35

40

45

50

55



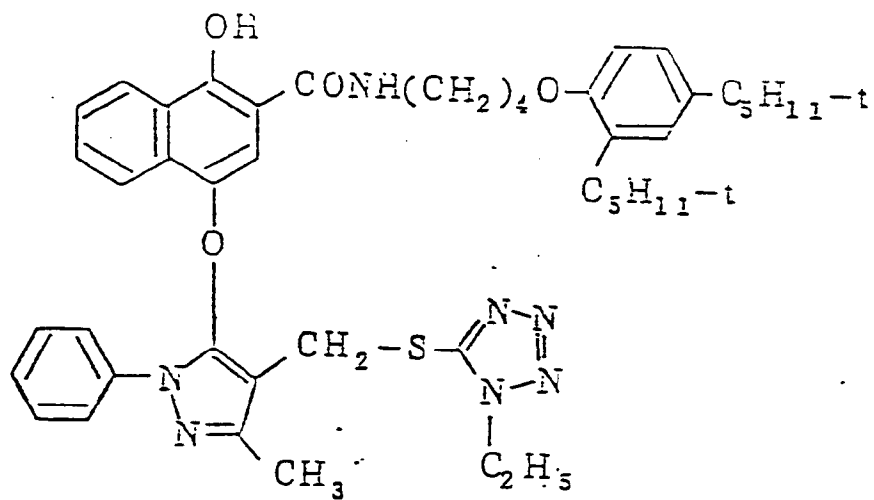
(D - 1 9)

5

10

15

20



25

(D - 2 0)

30

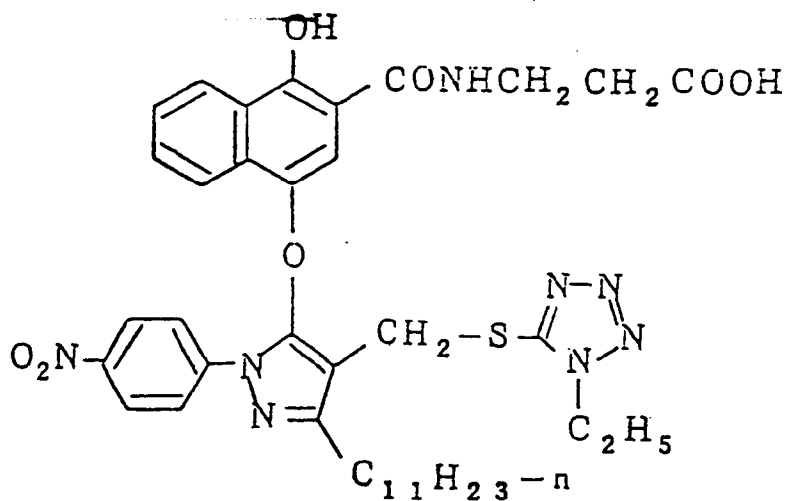
35

40

45

50

55



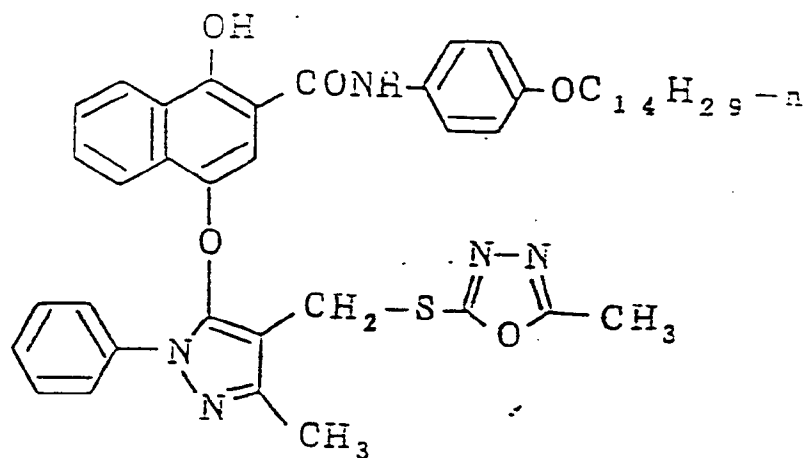
(D - 2 /)

5

10

15

20



(D - 2 /)

25

30

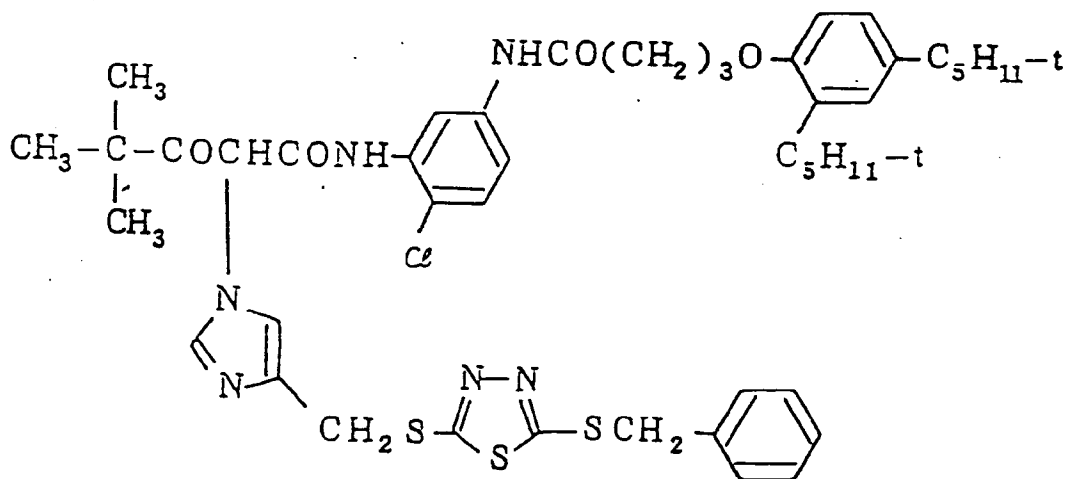
35

40

45

50

55



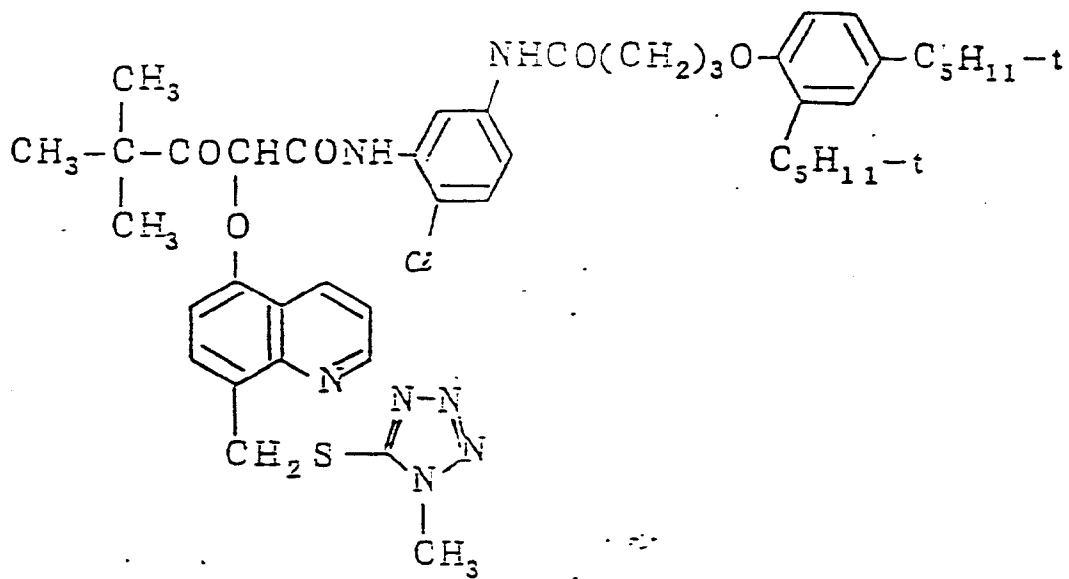
(D - 2 2)

5

10

15

20



25

(D - 2 3)

30

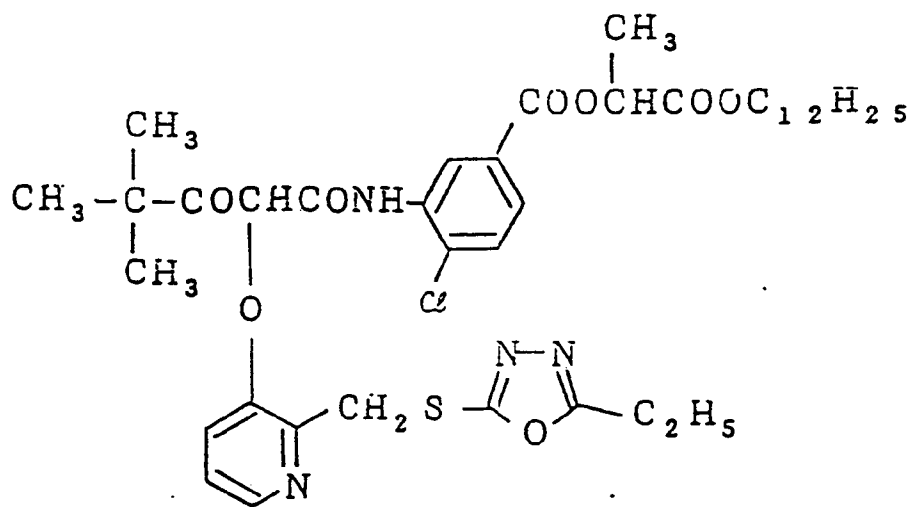
35

40

45

50

55



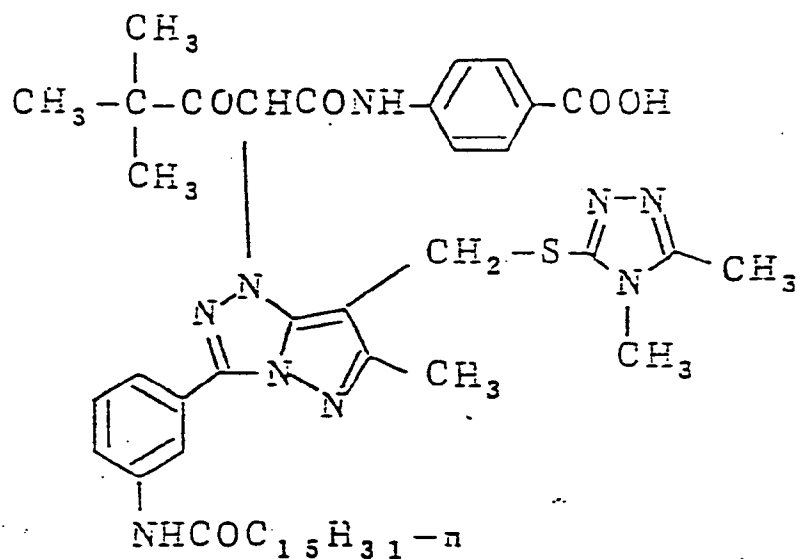
(D - 2 4)

5

10

15

20



25

(D - 2 5)

30

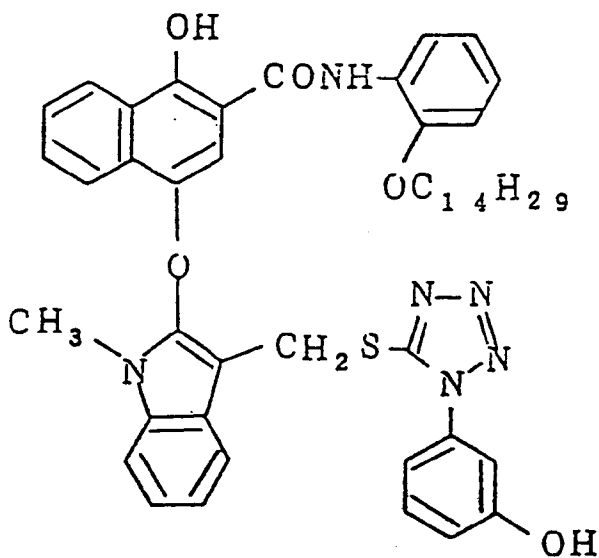
35

40

45

50

55

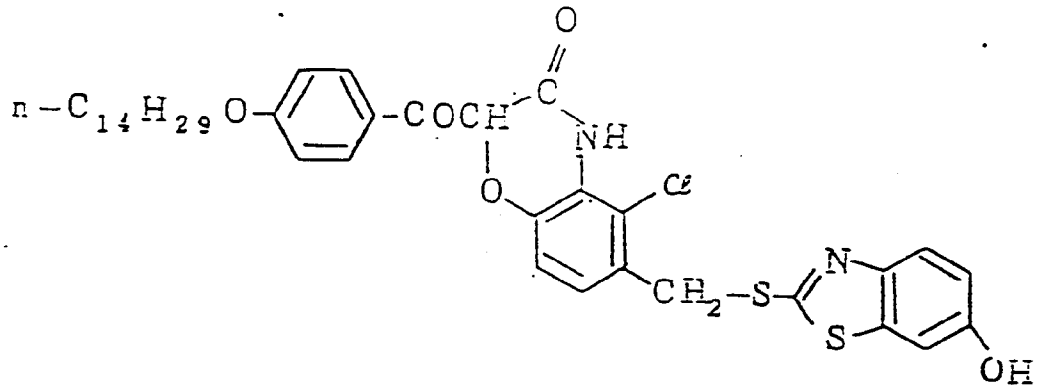


(D - 2 6)

5

10

15



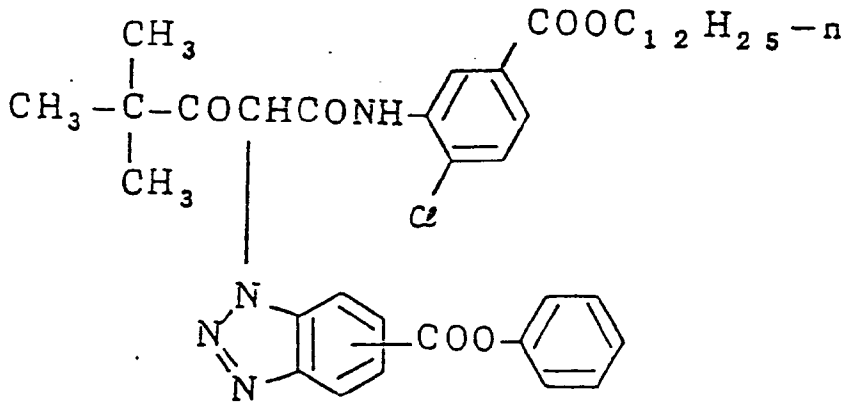
(D - 2 7)

20

25

30

35



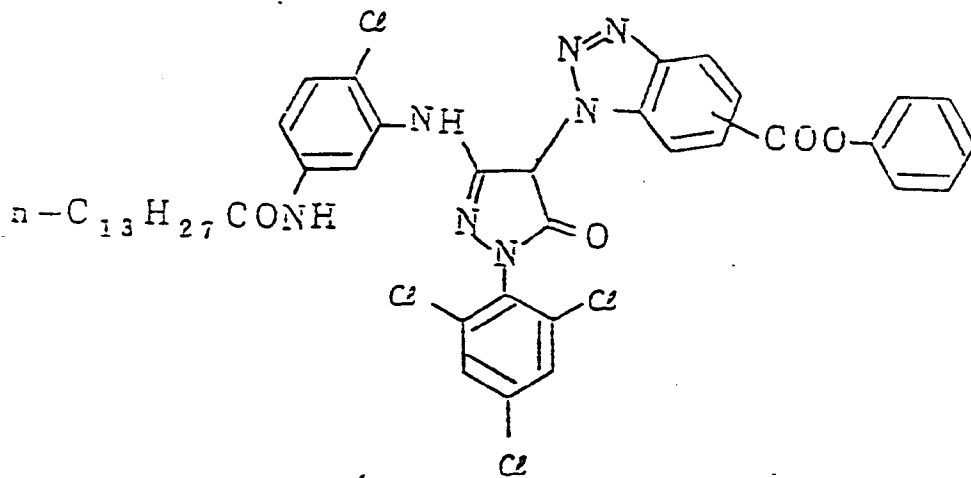
(D - 2 8)

40

45

50

55



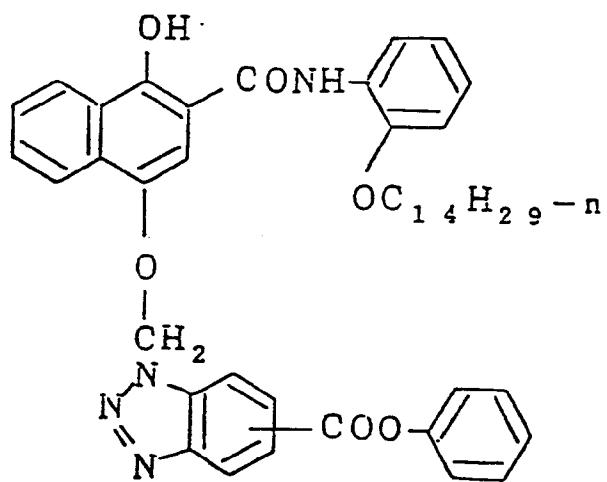
(D - 2 9)

5

10

15

20



(D - 3 0)

25

30

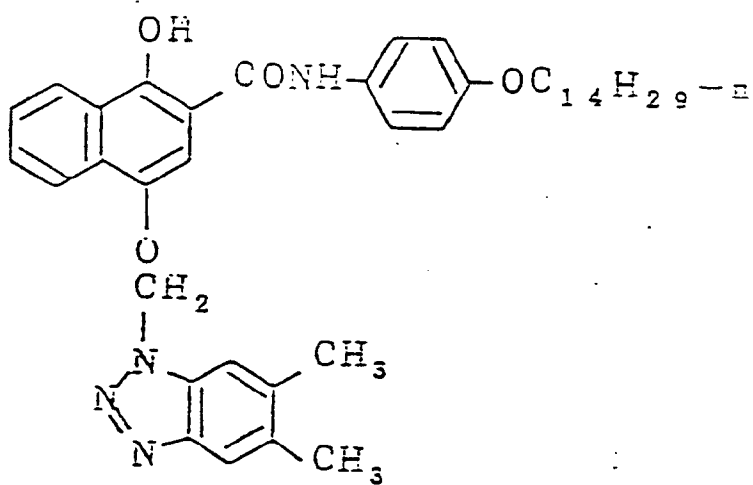
35

40

45

50

55



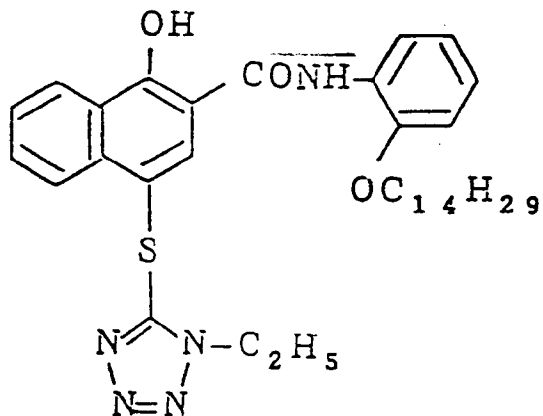
(D - 3 1)

5

10

15

20



(D - 3 2)

25

30

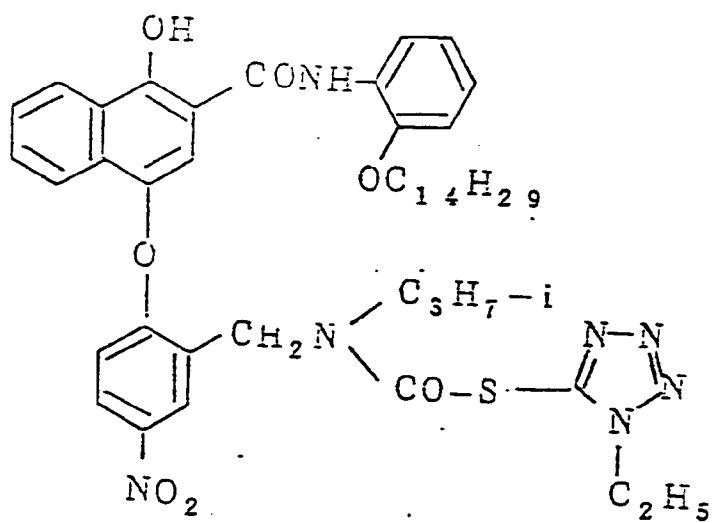
35

40

45

50

55



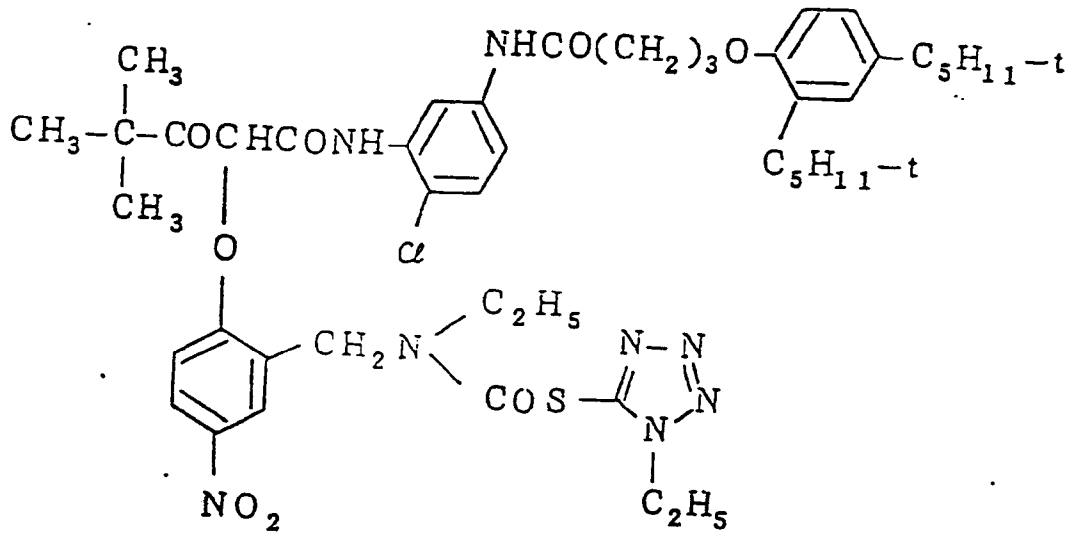
(D - 3 3)

5

10

15

20

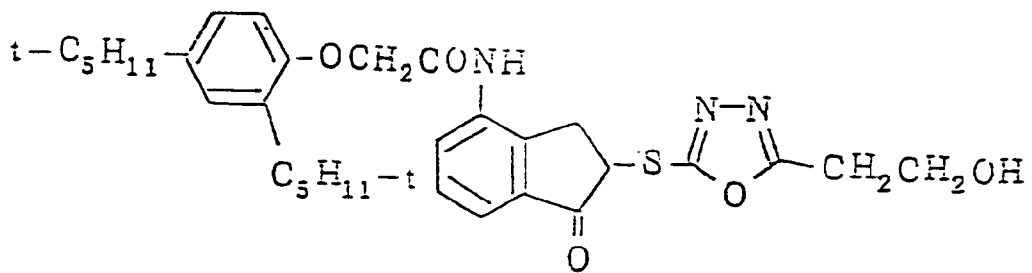


25

(D - 3 4)

30

35



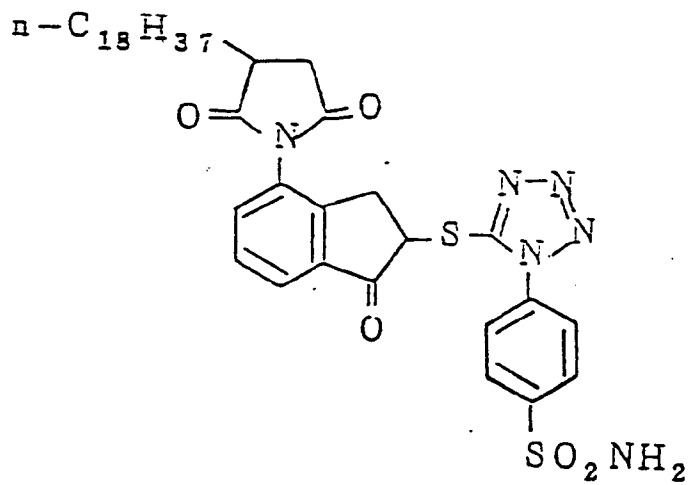
40

(D - 3 5)

45

50

55

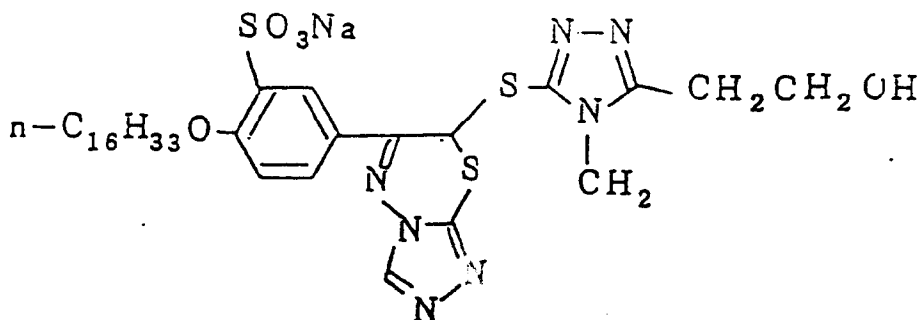


(D - 3 6)

5

10

15

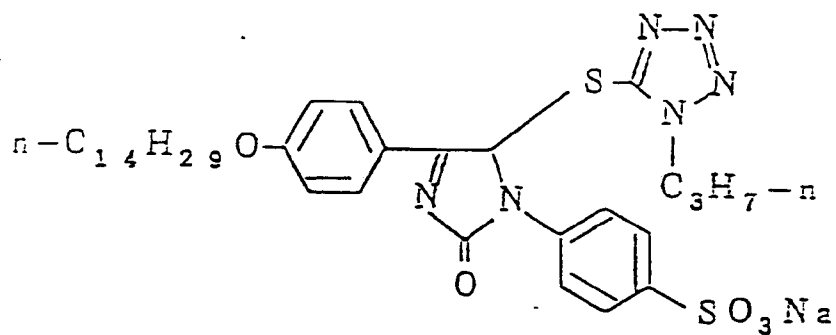


(D - 3 7)

20

25

30



(D - 3 8)

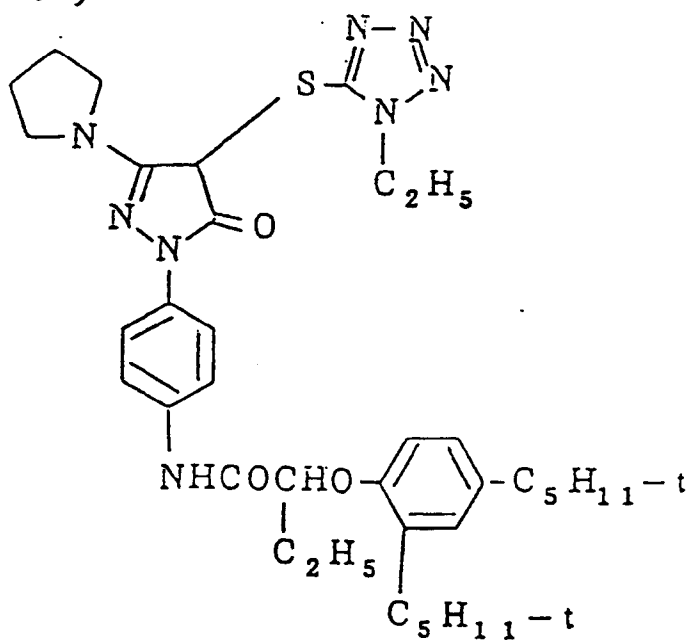
35

40

45

50

55



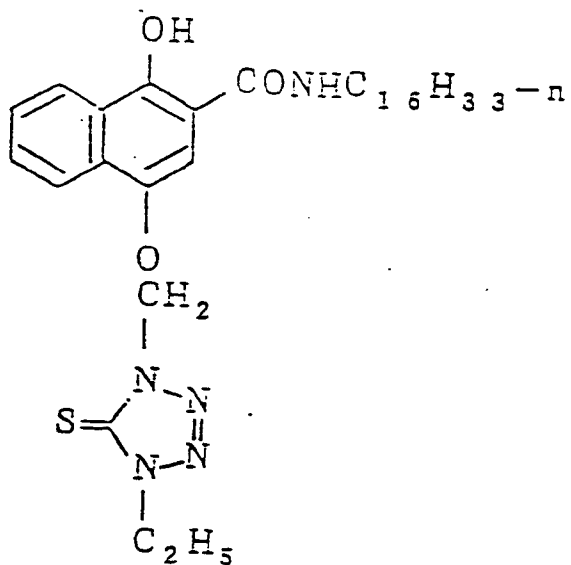
(D - 3 9)

5

10

15

20



25

(D - 4 0)

30

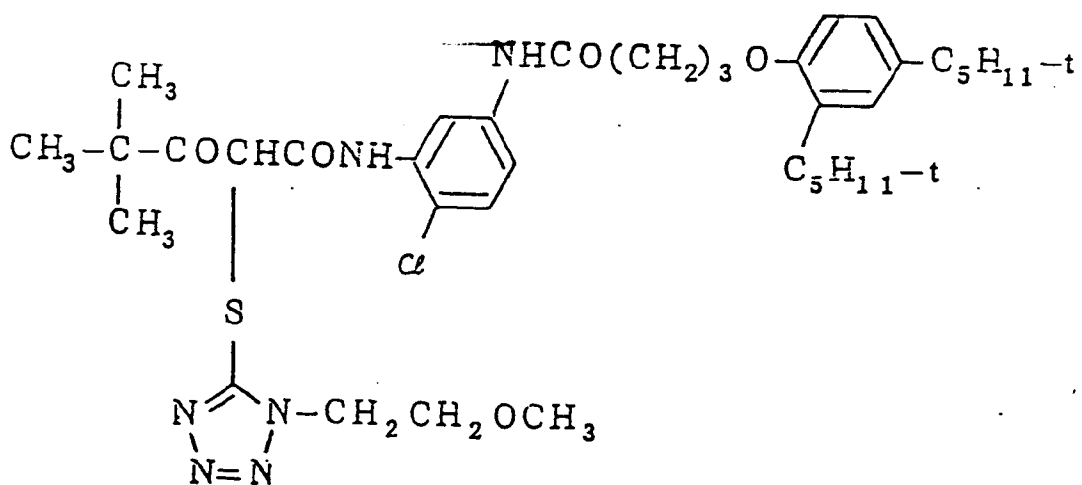
35

40

45

50

55



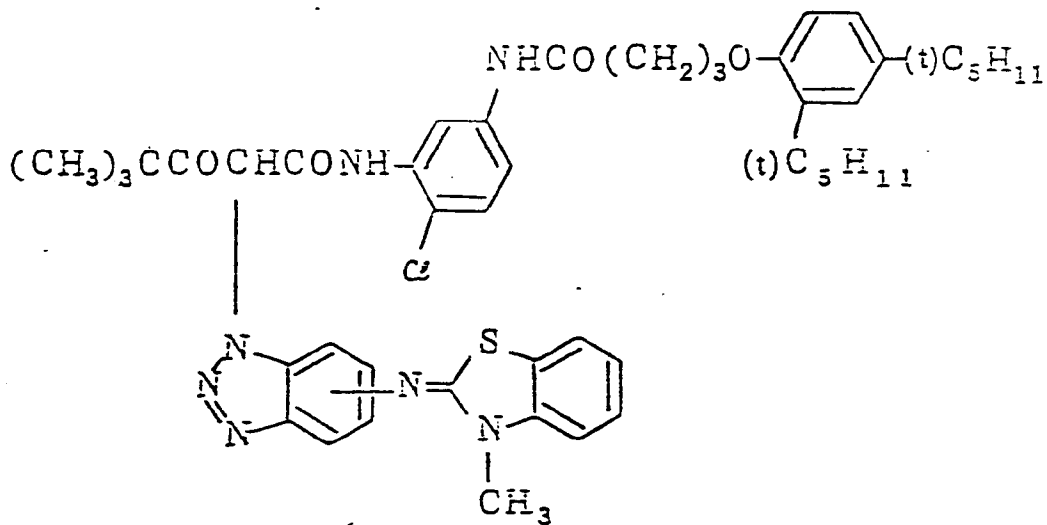
(D - 4 1)

5

10

15

20



(D - 4 2)

25

30

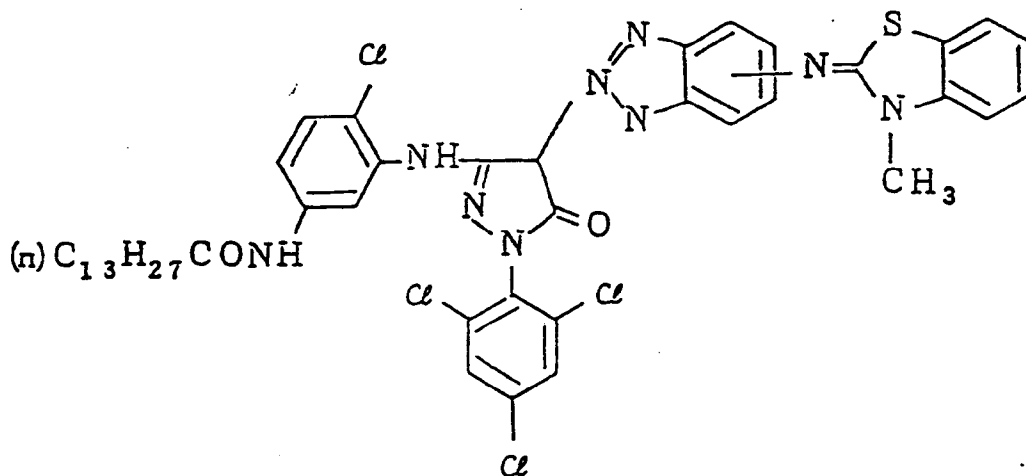
35

40

45

50

55



(D - 4 3)

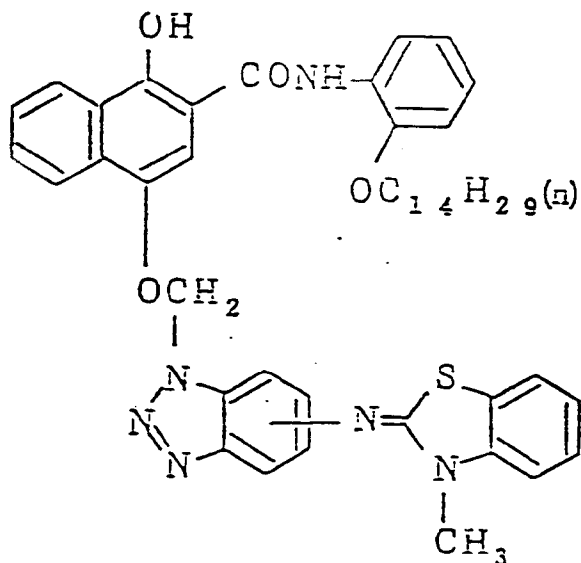
5

10

15

20

25

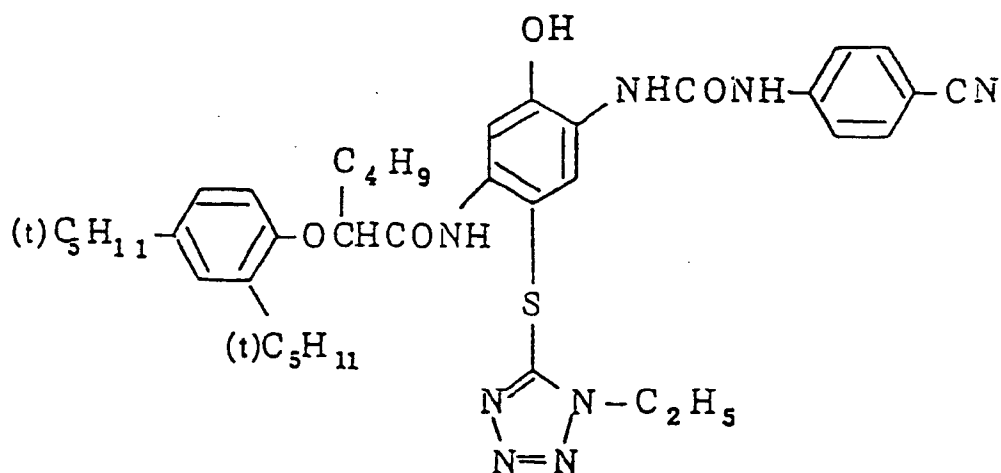


(D - 4 4)

30

35

40



45

The compounds represented by the formula (I) can be prepared according to the methods described in US-A-4,174,966, US-A-4,183,752, US-A-4,421,845 and US-A-4,477,563, 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.

50

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 according to the present invention or a layer sensitive to the same color as the layers and adjacent to the layers.

55

The compounds having the formula (I') can be added to the photographic material in the same manner as in coupler dispersion method described hereinafter. The compounds are used in an amount of 10^{-6} to 10^{-3} mol/m², preferably 3×10^{-6} to 5×10^{-4} mol/m² and more preferably 5×10^{-6} to 2×10^{-4} mol/m².

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 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 molecule of the oxidant of the developing agent, can be represented by the following general formula [I']



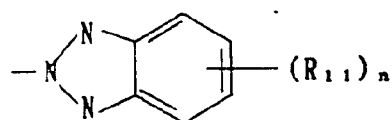
In the above formula, A' represents a coupling component capable of reacting with the oxidants of color developing agents and a component capable of releasing the -P-Z group by reaction with the oxidants of the color developing agents; Z represents a development restrainer whose diffusion can be freely 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.

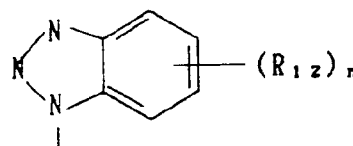
20

(Z - 1)



25

(Z - 2)



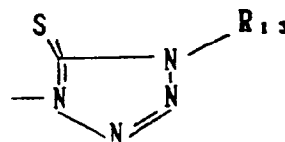
30

(Z - 3)



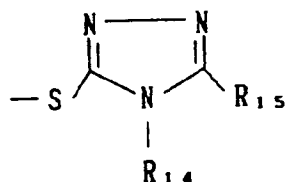
35

or



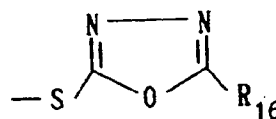
40

(Z - 4)



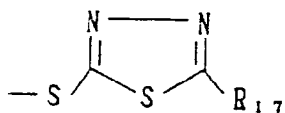
45

(Z - 5)



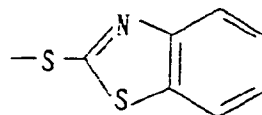
50

(Z - 6)

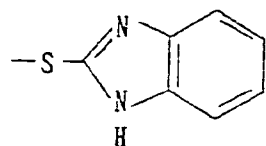


55

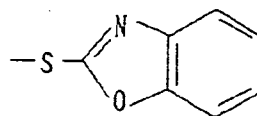
(Z - 7)



(Z - 8)



(Z - 9)



5

10 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 alkoxy carbonyl group, a thiazolideneamino group, an aryloxy carbonyl group, an acyloxy group, a carbamoyl group, an N-alkylcarbamoyl group, an N,N-dialkylcarbamoyl group, a nitro group, an amino group, an N-arylcarbamoyloxy group, a sulfamoyl group, a sulfonamido group, an N-alkylcarbamoyloxy group, a ureido group, hydroxyl group, an alkoxy carbonylamino group, an aryloxy group, an alkylthio group, an arylthio group, an anilino group, an aryl group, an imido group, a heterocyclic group, a cyano group, an alkylsulfonyl group or an aryloxy carbamoylamino 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 total number of carbon atoms of n R_{11} or n R_{12} is 0 to 20.

15 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.

20 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 a halogen, a nitro group, a cyano group, an aryl group, an alkoxy group, an aryloxy group, an alkoxy carbonyl group, an aryloxy carbonyl group, a sulfamoyl group, a carbamoyl group, a hydroxyl group, an alkanesulfonyl group, an arylsulfonyl group, an alkylthio group and an arylthio group.

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

30 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, an oxygen atom or a sulfur atom as the hetero-atom. Examples of the heterocyclic group include a pyridyl group, a quinolyl group, a furyl group, a benzthiazolyl group, an oxazolyl group, an imidazolyl group, a thiazolyl group, a triazolyl group, a benztriazolyl group, an imido group and an oxazine group. These groups may optionally be substituted by one or more substituent groups already described above for the aryl group.

35 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 total number of carbon atoms of each of R_{13} to R_{17} is 1 to 20, more preferably 4 to 20.

40 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 the compounds having the following formulas.

45

50

55

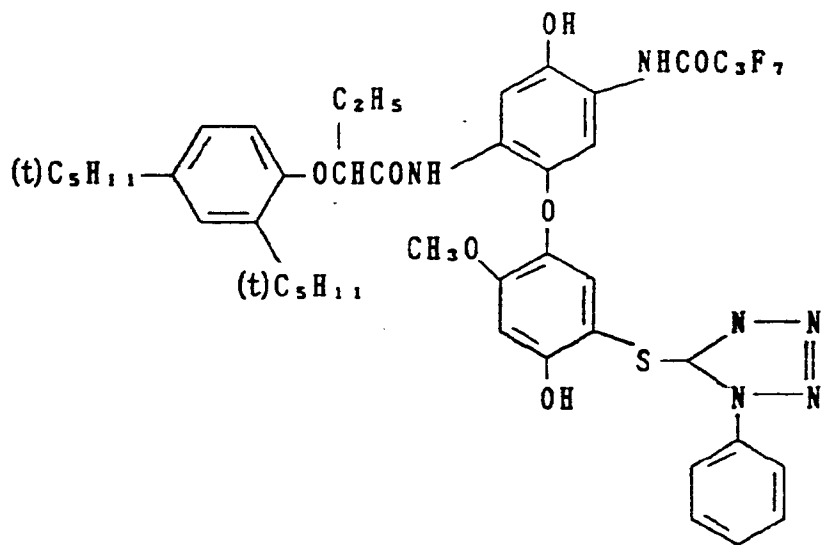
T - 1

5

10

15

20



25

T - 2

30

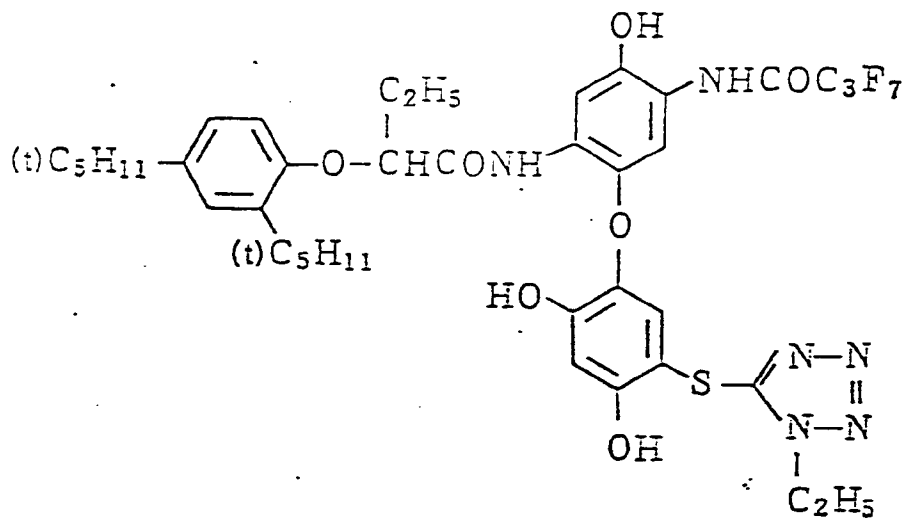
35

40

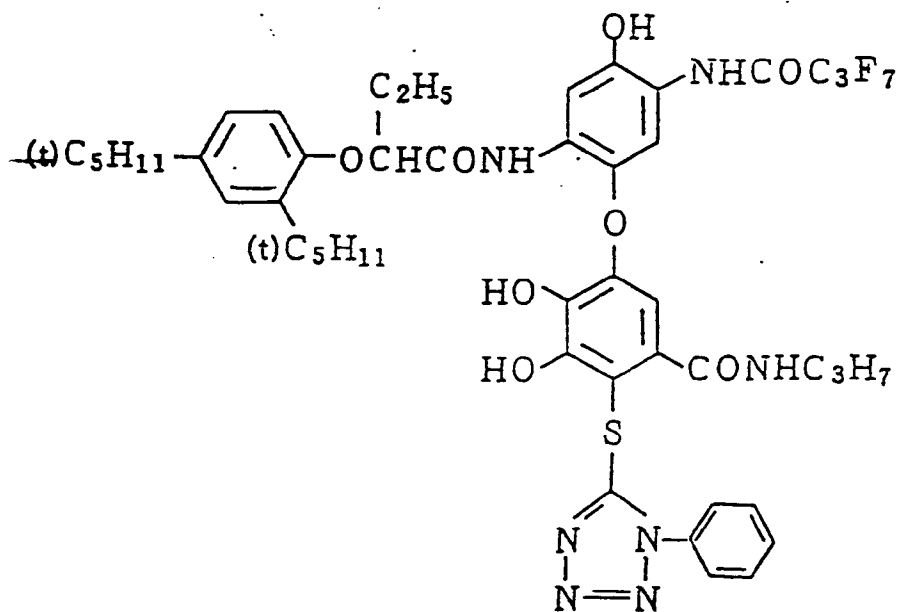
45

50

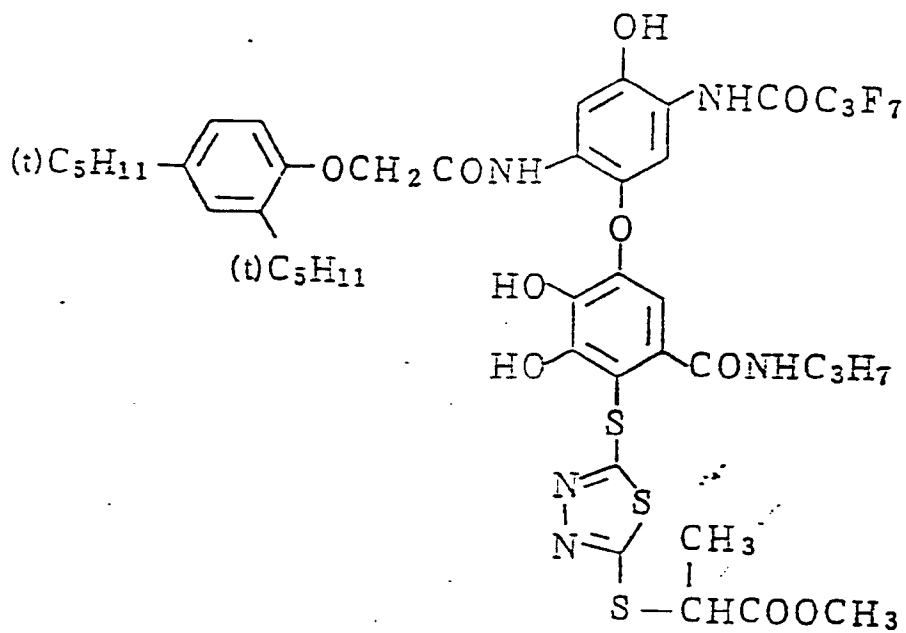
55



T - 3



T - 4



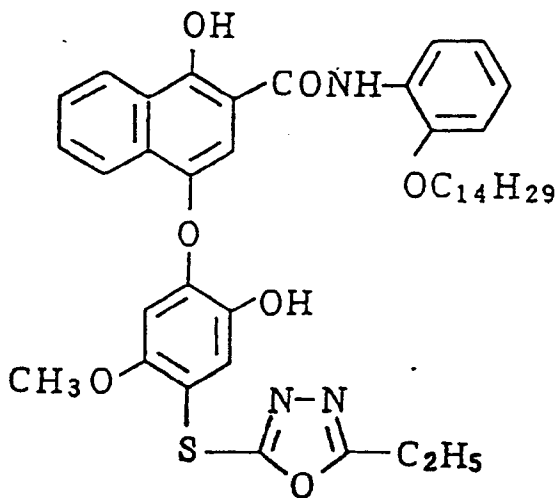
T - 5

5

10

15

20



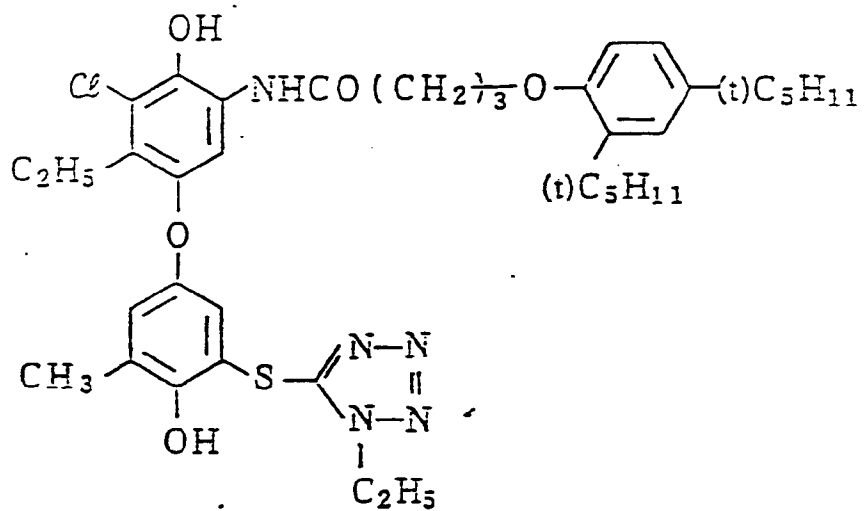
T - 6

25

30

35

40



45

50

55

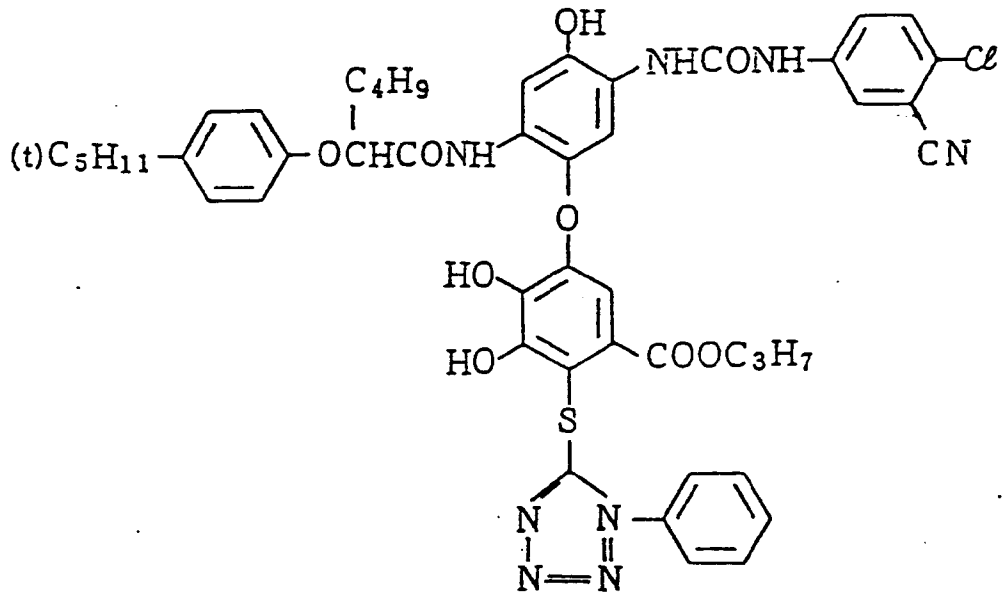
T - 7

5

10

15

20



25

T - 8

30

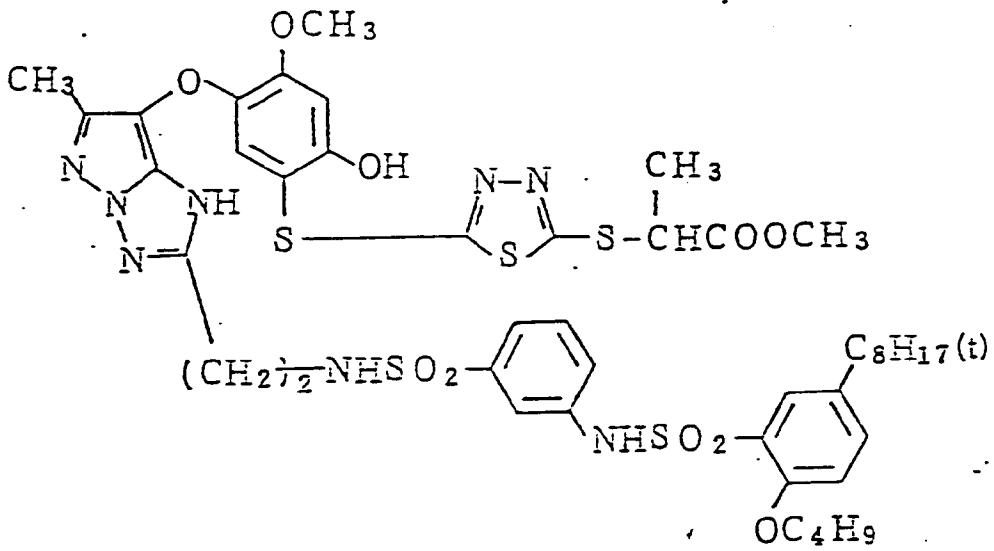
35

40

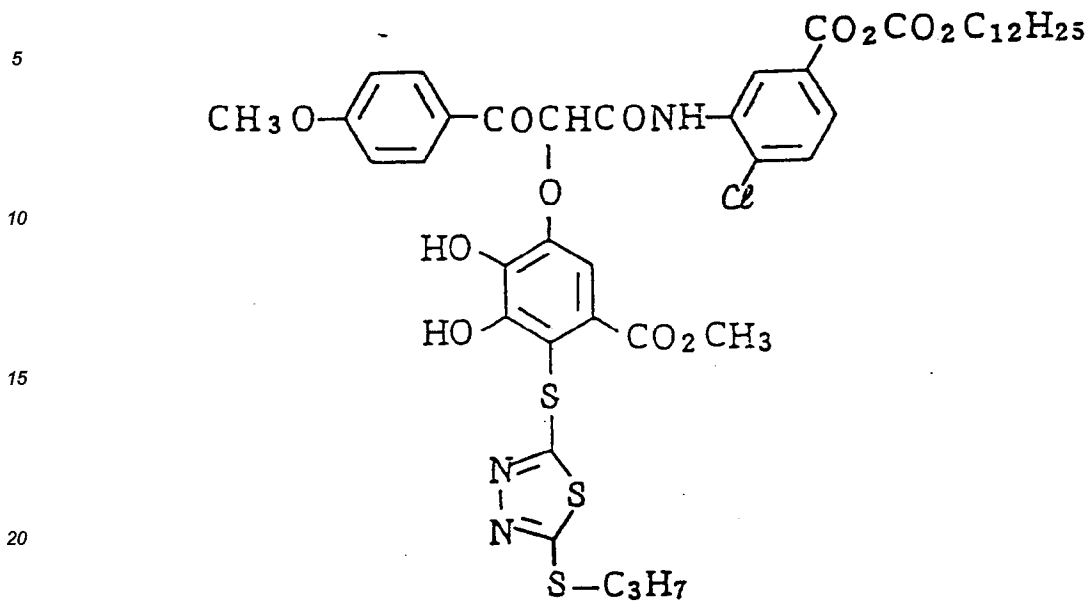
45

50

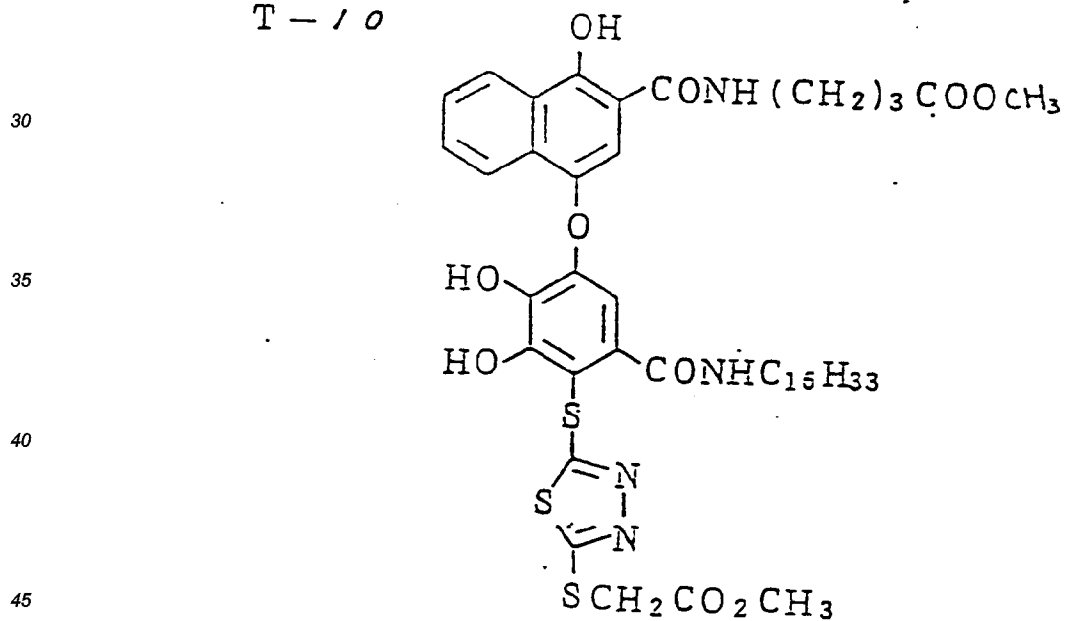
55



T - 9



T - 10



T - / /

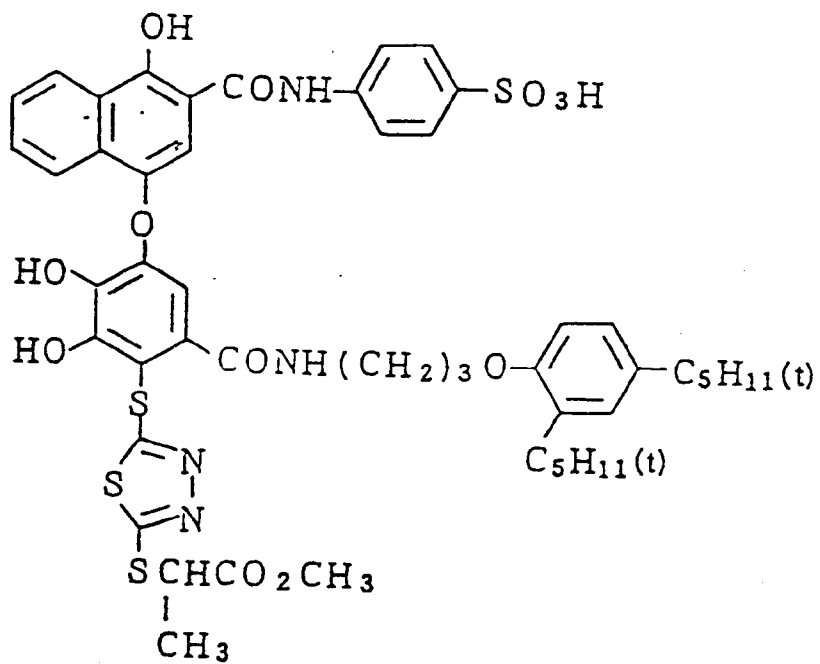
5

10

15

20

25



T - / 2

30

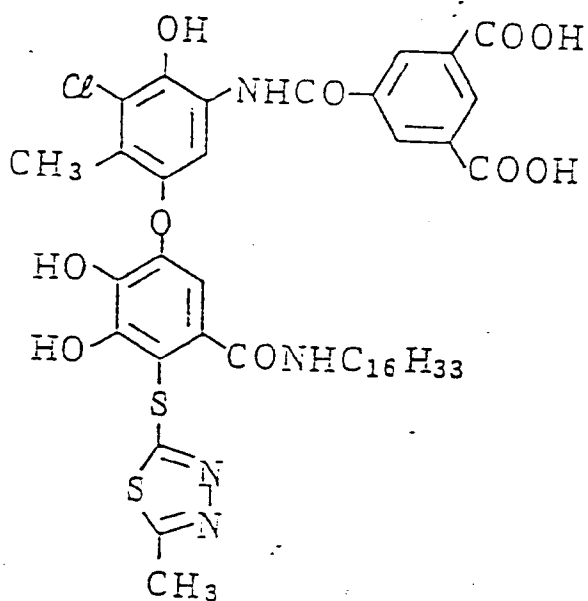
35

40

45

50

55



T - 1 3

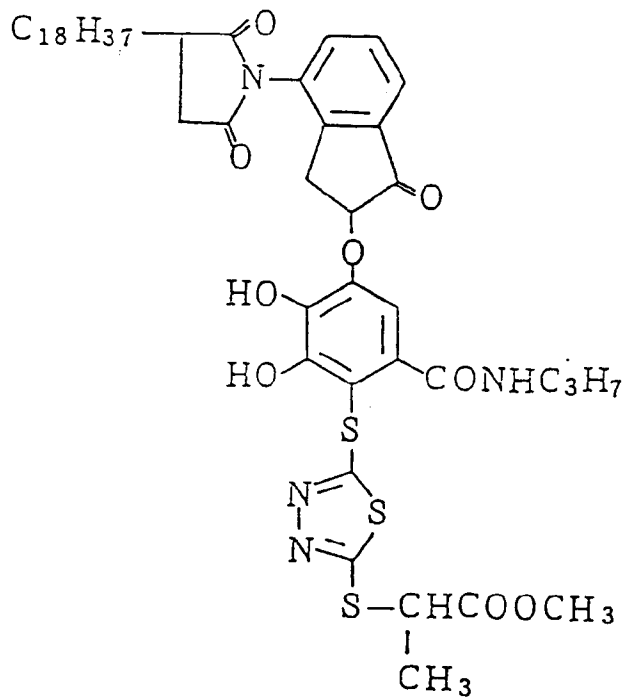
5

10

15

20

25



30

T - 1 4

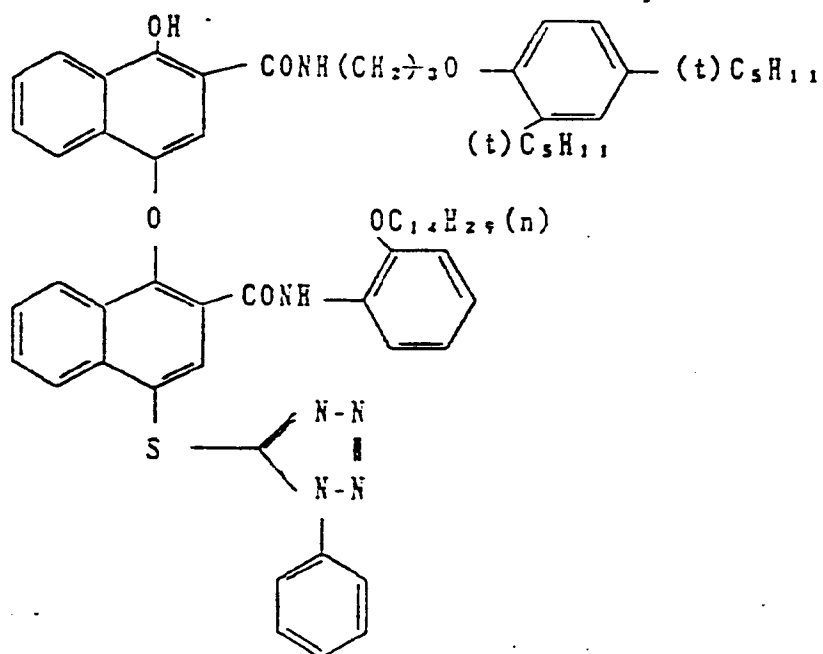
35

40

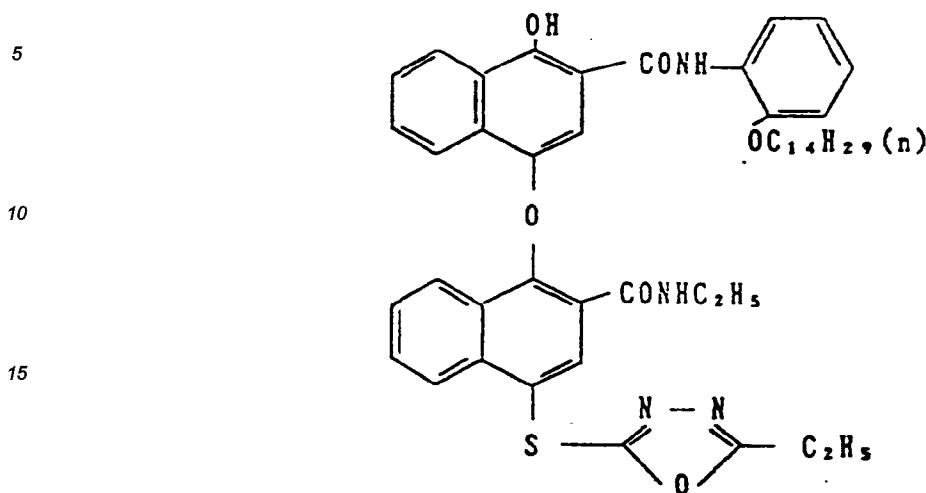
45

50

55



T - 1 5



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/m², preferably 5×10^{-6} to 3×10^{-4} mol/m².

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 tabular (platform) 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 are used.

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.

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 may be used.

In the present invention, it is preferred that compounds capable of reacting with formaldehyde for fixing (see e.g., US-A-4,411,987 and US-A-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 the 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 US-A-3,933,501, US-A-4,022,620, US-A-4,326,024 and 4,401,752, JP-B-58-10739, GB-A-1,425,020 and GB-A-1,476,760, US-A-3,973,968, US-A-4,314,023 and US-A-4,511,649, and EP-A-249,473.

5-Pyrazolone compounds and pyrazoloazole compounds are preferred as magenta couplers. Particularly preferred compounds are described in US-A-4,310,619 and US-A-4,351,897, EP-B-73,636, US-A-3,061,432 and US-A-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, US-A-4,500,630, US-A-4,540,654 and US-A-4,556,630.

Cyan couplers include phenol couplers and naphthol couplers. Preferred examples of cyan couplers include those compounds described in US-A-4,052,212, US-A-4,146,396, US-A-4,228,238, US-A-4,296,200, US-A-2,369,929, US-A-2,801,171, US-A-2,772,162, US-A-2,895,826, US-A-3,772,002, US-A-3,758,308, US-A-4,334,011 and US-A-4,327,173, DE-A-3,329,729, EP-A-121,365 and EP-A-249,453, US-A-3,446,622, US-A-4,333,999, US-A-4,753,871, US-A-4,451,559, US-A-4,427,767, US-A-4,690,889, US-A-4,254,212 and US-A-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, US-A-4,163,670, JP-B-57-39413, US-A-4,004,929 and US-A-4,138,258 and GB-A-1,146,368. It is preferred that couplers for correcting the unnecessary absorption of color forming dyes by fluorescent dye released during coupling, described in US-A-4,774,181, or couplers having, as an eliminable group, a dye precursor group capable of forming a dye by the reaction with developing agents

such as those described in US-A-4,777,120, are used.

As couplers whose color forming dyes are properly diffusing, the couplers described in US-A-4,366,237, GB-A-2,125,670, EP-B-96,570 and DE-A-3,234,533 are preferred.

5 Typical examples of dye forming polymer couplers are described in US-A-3,451,820, US-A-4,080,211, US-A-4,367,282, US-A-4,409,320 and US-A-4,576,910, and GB-A-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 described 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 US-A-4,782,012 in addition to the compounds represented by the general formula (I).

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

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
15 are described in EP-A-173,302. Other useful couplers include releasing bleaching accelerators such as those described in JP-A-61-201247; couplers releasing ligands such as those described in US-A-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 US-A-4,744,181.

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

Examples of high-boiling solvents for use in oil-in-water dispersion methods are described in US-A-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
25 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-diethylaurylamide 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 tributryrate, isostearyl lactate and trioctyl citrate; aniline derivatives such as N,N-dibutyl-2-butoxy-5-t-octylaniline; and hydrocarbons
30 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 US-A-4,199,363, and DE-A-2,541,274 and DE-A-2,541,230.

40 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 total of the layer
45 thicknesses of the entire hydrophilic colloid layers on the side having the emulsion layers is not more than 28 µm and the layer swelling rate $T_{1/2}$ is not larger than 30 s. 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 $T_{1/2}$ can be measured by conventional methods, for example, by using a swellometer described in A. Green, et al., Photographic Science and Engineering, Vol. 19, No. 2, pages 124-129. $T_{1/2}$ 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 s.

The layer swelling rate $T_{1/2}$ can be controlled by adding a hardening agent to gelatin as a binder, or by changing conditions with time after coating. 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
50 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 primarily 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 polyaminocarboxylic 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 min. 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 carried out separately. 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 diaminetetraacetic acid) citric acid, tartaric acid, and malic acid; persulfates; bromates; permanganates; and nitrobenzenes. Among these, iron(III) complex salts of polyaminocarboxylic acids such as (ethylenediaminetetraacetato)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 US-A-3,893,858, DE-B-1,290,812 and DE-B-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 US-A-3,706,561; iodides such as those described in DE-B-1,127,715 and JP-A-58-16235; polyxyethylene compounds such as those described in DE-B-996,410 and DE-B-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 a mercapto group or a disulfide group are preferred from the viewpoint of a high accelerating effect. Particularly, the compounds described in US-A-3,893,858, DE-B-1,290,812 and JP-A-53-95630 are preferred. Furthermore, compounds such as those described in US-A-4,552,834 are preferred. These bleaching accelerators 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 the 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, it is a problem that the residence time of water in the tanks is prolonged. As a result, bacteria grow 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 Antibacterial 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, e.g., the characteristics of the photographic materials and use, but the temperature and time of washing are generally 15 to 45°C for 20 to 10 min, preferably 25 to 40°C for 30 to 5 min. 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 includes a stabilizing bath containing formalin and a surfactant. The stabilizing bath may contain various chelating agents and antifungal agents.

The 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 US-A-3,342,597; Schiff base-type compounds such as those described in US-A-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 US-A-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 be used to accelerate

processing and to shorten the processing time, while lower temperatures can be used to improve the 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 DE-B-2,226,770 and US-A-3,674,499 may be carried out to save silver.

5 The silver halide photographic materials of the present invention can be applied to heat-developing photosensitive materials such as those described in US-A-4,500,626, JP-A-60-133449, JP-A-59-218443, JP-A-61-238056, and EP-A-210,660.

The present invention will now be illustrated in greater detail by reference to the following examples.

10 EXAMPLE 1

Comparative sample 101 was prepared. This sample was a photographic material which has a spectral sensitive distribution similar to that disclosed in US-A-3,672,898 and had a low multi-layer effect.

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

Compositions of Sensitive Layers

20 The coating weights of silver halide and colloidal silver are given in g/m² in terms of silver. The amounts of couplers, additives and gelation are given in g/m². The amounts of sensitizing dyes are given in moles per one mole of silver halide in the same layer.

First Layer: Antihalation Layer

| | | |
|----|---------------------------------|------|
| 25 | Black colloidal silver | 0.2 |
| | Gelatin | 1.3 |
| 30 | Colored coupler C-1 | 0.06 |
| | Ultraviolet light absorber UV-1 | 0.1 |
| | Ultraviolet light absorber UV-2 | 0.2 |
| 35 | Dispersion oil Oil-1 | 0.01 |
| | Dispersion oil Oil-2 | 0.01 |

40 Second Layer: Interlayer

| | | |
|----|--|------|
| | Fine silver bromide grains (mean grain size: 0.07 μm) | 0.15 |
| 45 | Gelatin | 1.0 |
| | Colored coupler C-2 | 0.02 |
| 50 | Dispersion oil Oil-1 | 0.1 |

55

Third Layer: First Red-sensitive Emulsion Layer

| | | |
|----|--|----------------------|
| 5 | Silver iodobromide emulsion (silver iodide: 2 mol%, mean grain size: 0.3 μm) | 0.3 |
| | Gelatin | 0.6 |
| 10 | Sensitizing dye I | 3.0×10^{-4} |
| | Sensitizing dye II | 1.0×10^{-4} |
| 15 | Coupler C-3 | 0.06 |
| | Coupler C-4 | 0.06 |
| 20 | Coupler C-5 | 0.01 |
| | Coupler C-8 | 0.04 |
| | Coupler C-2 | 0.03 |
| 25 | Dispersion oil Oil-1 | 0.03 |
| | Dispersion oil Oil-3 | 0.012 |

30 Fourth Layer: Second Red-sensitive Emulsion Layer

| | | |
|----|--|----------------------|
| 35 | Silver iodobromide emulsion (silver iodide: 5 mol%, mean grain size: 0.5 μm) | 0.5 |
| | Sensitizing dye I | 2.0×10^{-4} |
| | Sensitizing dye | 0.6×10^{-4} |
| 40 | Coupler C-3 | 0.24 |
| | Coupler C-5 | 0.02 |
| 45 | Coupler C-4 | 0.24 |
| | Coupler C-8 | 0.04 |
| | Coupler C-2 | 0.04 |
| 50 | Dispersion oil Oil-1 | 0.15 |
| | Dispersion oil Oil-3 | 0.02 |

55

Fifth Layer: Third Red-sensitive Emulsion Layer

| | | |
|----|---|----------------------|
| 5 | Silver iodobromide emulsion (silver iodide: 10 mol%, mean grain size: 0.7 μm) | 1.0 |
| | Gelatin | 1.0 |
| 10 | | |
| | Sensitizing dye I | 1.5×10^{-4} |
| 15 | Sensitizing dye II | 0.5×10^{-4} |
| | Coupler C-6 | 0.05 |
| | Coupler C-7 | 0.1 |
| 20 | Dispersion oil Oil-1 | 0.01 |
| | Dispersion oil Oil-2 | 0.05 |

25 Sixth Layer: Interlayer

| | | |
|----|----------------------|------|
| | Gelatin | 1.0 |
| 30 | Compound Cpd-A | 0.03 |
| | Dispersion oil Oil-1 | 0.05 |

35 Seventh Layer: First Green-sensitive Emulsion Layer

| | | |
|----|--|--------------------|
| 35 | Silver iodobromide emulsion (silver iodide: 4 mol%, mean grain size: 0.3 μm) | 0.10 |
| 40 | Sensitizing dye III | 2×10^{-4} |
| | Sensitizing dye IV | 4×10^{-4} |
| 45 | Sensitizing dye V | 1×10^{-4} |
| | Gelatin | 1.0 |
| | Coupler C-9 | 0.2 |
| 50 | Coupler C-1 | 0.03 |
| | Dispersion oil Oil-1 | 0.5 |

55

Eighth Layer: Second Green-sensitive Emulsion Layer

| | | |
|----|--|----------------------|
| 5 | Silver iodobromide emulsion (silver iodide: 5 mol%, mean grain size: 0.5 μm) | 0.10 |
| | Sensitizing dye III | 1.2×10^{-4} |
| 10 | Sensitizing dye IV | 2.8×10^{-4} |
| 15 | Sensitizing dye V | 0.6×10^{-4} |
| | Coupler C-9 | 0.25 |
| | Coupler C-1 | 0.03 |
| 20 | Coupler C-10 | 0.015 |
| | Dispersion oil Oil-1 | 0.2 |

25 Ninth Layer: Third Green-sensitive Emulsion Layer

| | | |
|----|--|----------------------|
| 30 | Silver iodobromide emulsion (silver iodide: 6 mol%, mean grain size: 0.7 μm) | 0.3 silver |
| | Gelatin | 1.0 |
| 35 | Sensitizing dye III | 1.0×10^{-4} |
| | Sensitizing dye IV | 2.0×10^{-4} |
| | Sensitizing dye V | 0.5×10^{-4} |
| 40 | Coupler C-11 | 0.01 |
| | Coupler C-12 | 0.03 |
| | Coupler C-13 | 0.20 |
| 45 | Coupler C-1 | 0.02 |
| | Coupler C-15 | 0.02 |
| 50 | Dispersion oil Oil-1 | 0.20 |
| | Dispersion oil Oil-2 | 0.0.5 |

55

Tenth Layer: Yellow Filter Layer

| | | |
|----|-------------------------|------|
| 5 | Gelatin | 1.2 |
| | Yellow colloidal silver | 0.04 |
| | Compound Cpd-B | 0.1 |
| 10 | Dispersion oil Oil-1 | 0.3 |

Eleventh Layer: First Blue-sensitive Emulsion Layer

| | | |
|----|---|--------------------|
| 15 | Monodisperse silver iodobromide emulsion (silver iodide: 4 mol%, mean grain size: 0.3 μm) | 0.2 silver |
| 20 | Gelatin | 1.0 |
| | Sensitizing dye VI | 2×10^{-4} |
| | Coupler C-3 | 0.01 |
| 25 | Coupler C-14 | 0.9 |
| | Dispersion oil Oil-1 | 0.2 |

30 Twelfth Layer: Second Blue-sensitive Emulsion Layer

| | | |
|----|---|--------------------|
| 35 | Silver iodobromide emulsion (silver iodide: 10 mol%, mean grain size: 1.5 μm) | 0.4 silver |
| | Gelatin | 0.6 |
| 40 | Sensitizing dye VI | 1×10^{-4} |
| | Coupler C-14 | 0.25 |
| | Dispersion oil Oil-1 | 0.07 |

45

Thirteenth Layer: First Protective Layer

| | | |
|----|---------------------------------|------|
| 50 | Gelatin | 0.8 |
| | Ultraviolet light absorber UV-1 | 0.1 |
| | Ultraviolet light absorber UV-2 | 0.2 |
| 55 | Dispersion oil Oil-1 | 0.01 |
| | Dispersion oil Oil-2 | 0.02 |

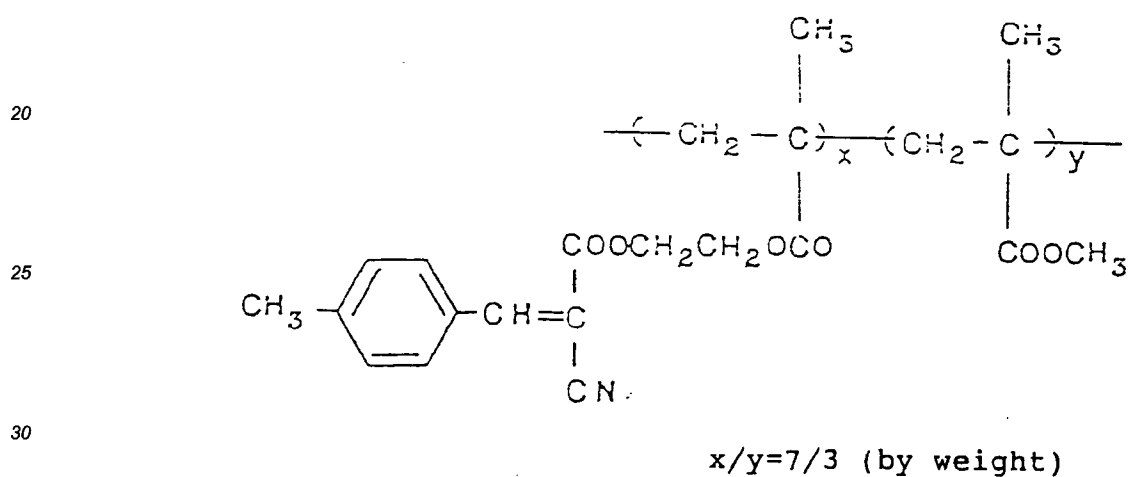
Fourteenth Layer: Second Protective Layer

| | | |
|---|--|------|
| 5 | Fine silver bromide grains (mean grain size: 0.07 μm) | 0.5 |
| | Gelatin | 0.45 |

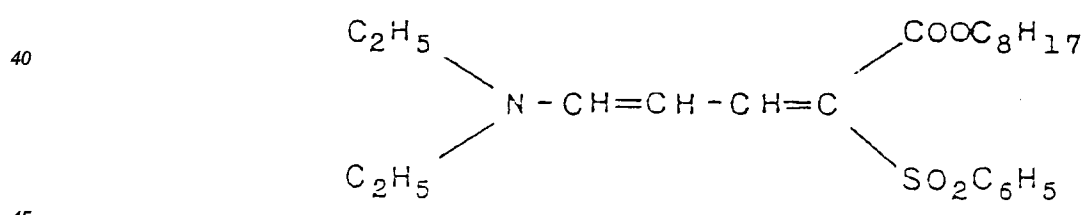
10 In addition to the above-described ingredients, a surfactant component was added to each layer. The thus prepared sample was referred to as Sample 101.

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

15 UV-1



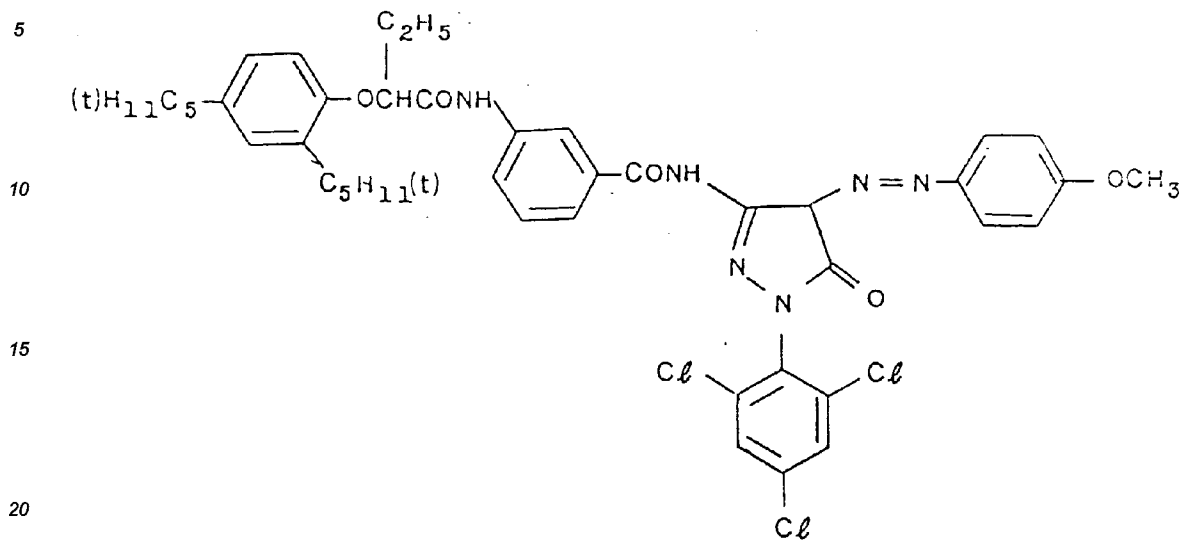
35 UV-2



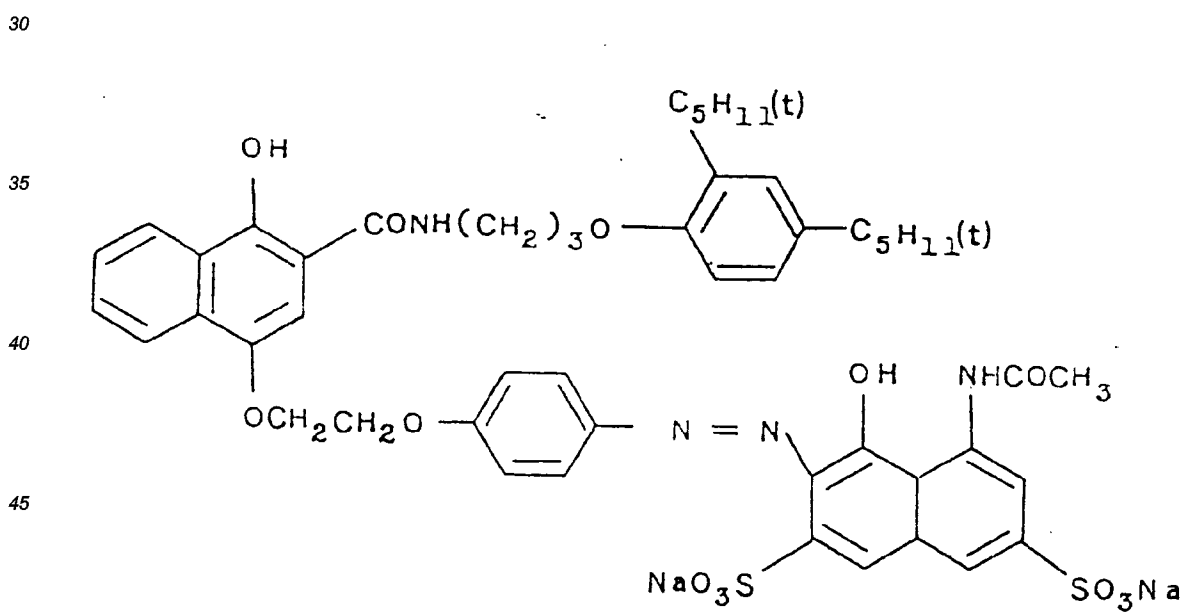
- 50
- Oil-1 Tricresyl phosphate
 - Oil-2 Dibutyl phthalate
 - Oil-3 Bis(2-ethylhexyl) phthalate

55

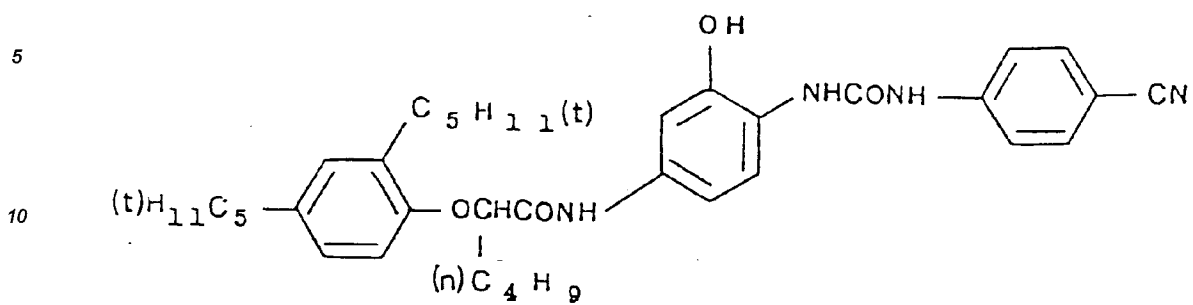
C - 1



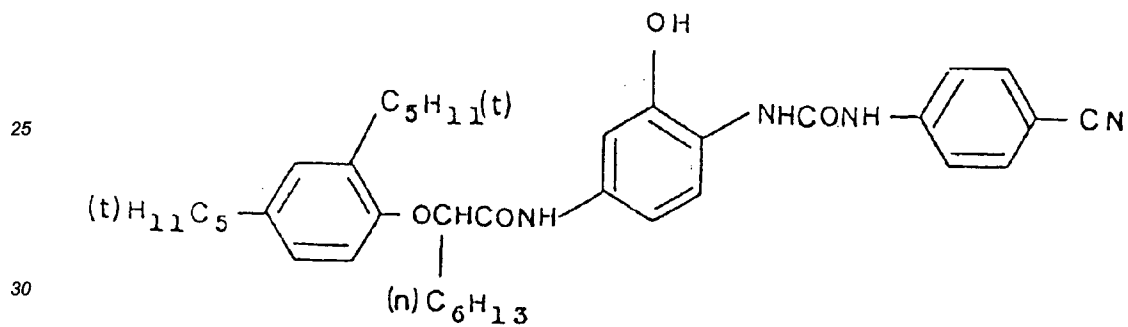
C - 2



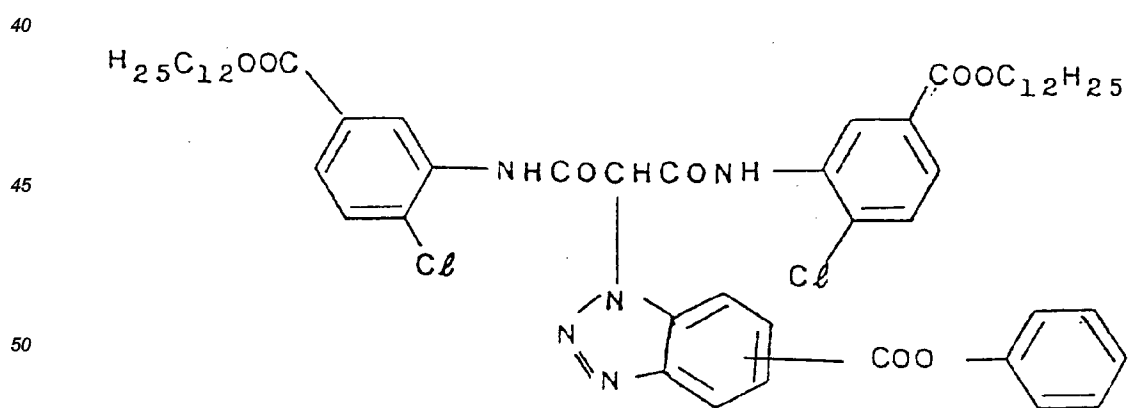
C - 3



C - 4



C - 5



C - 6

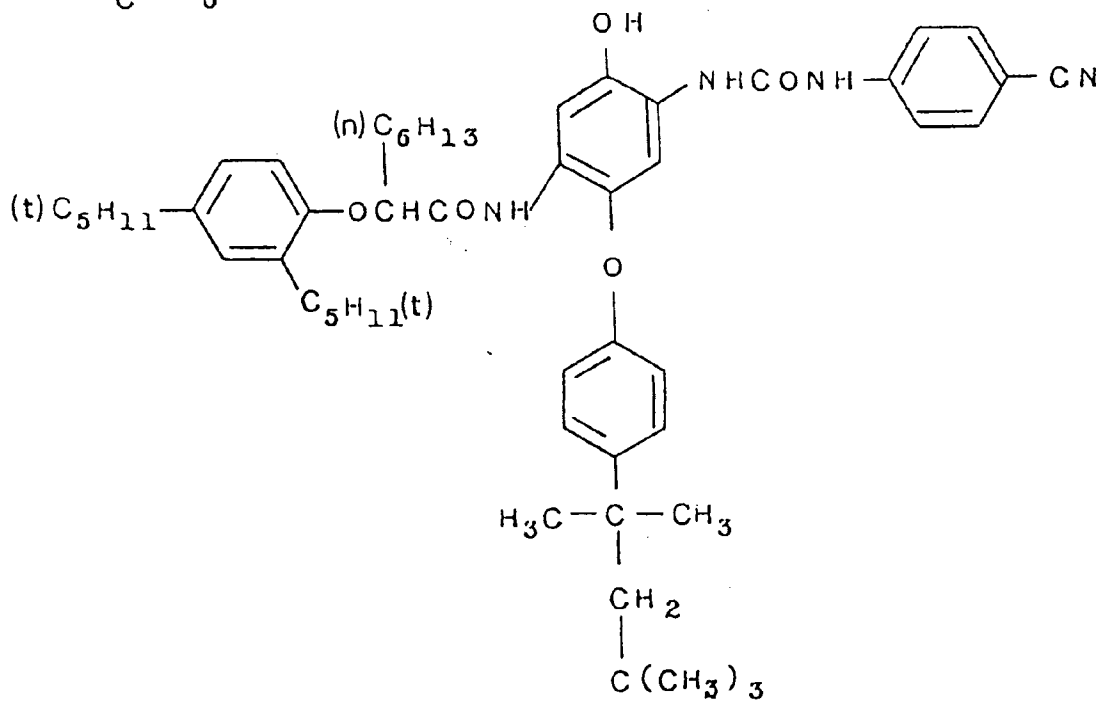
5

10

15

20

25



C - 7

30

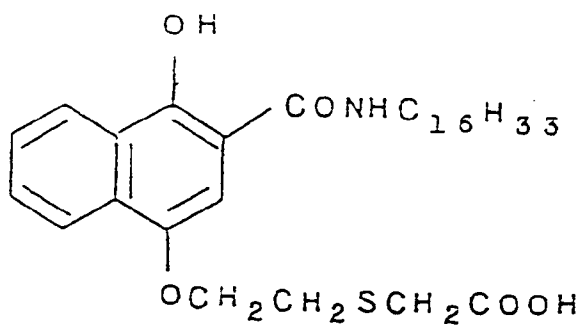
35

40

45

50

55

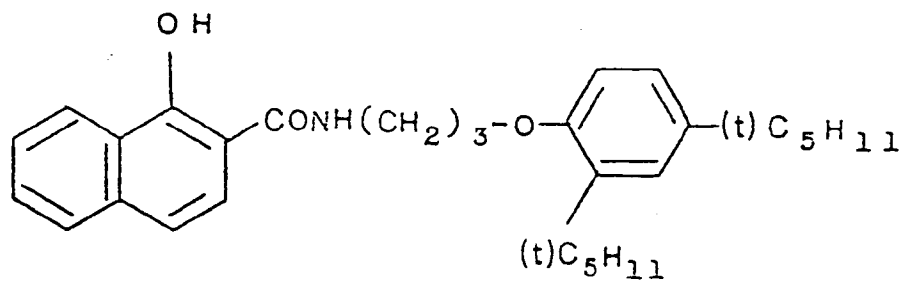


C - 8

5

10

15



20

C - 9

25

30

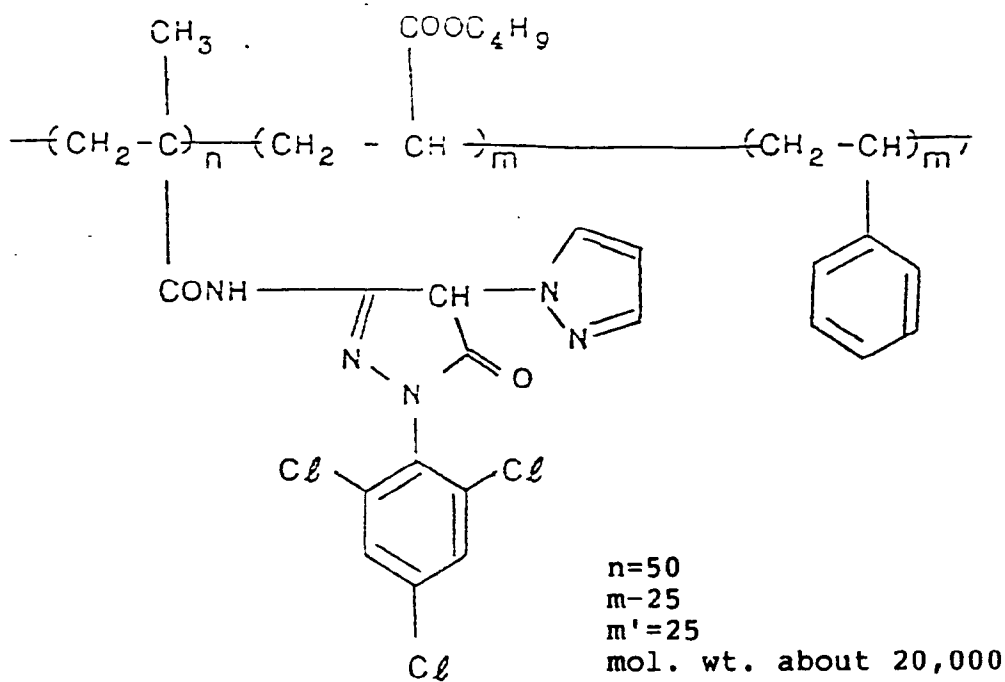
35

40

45

50

55



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

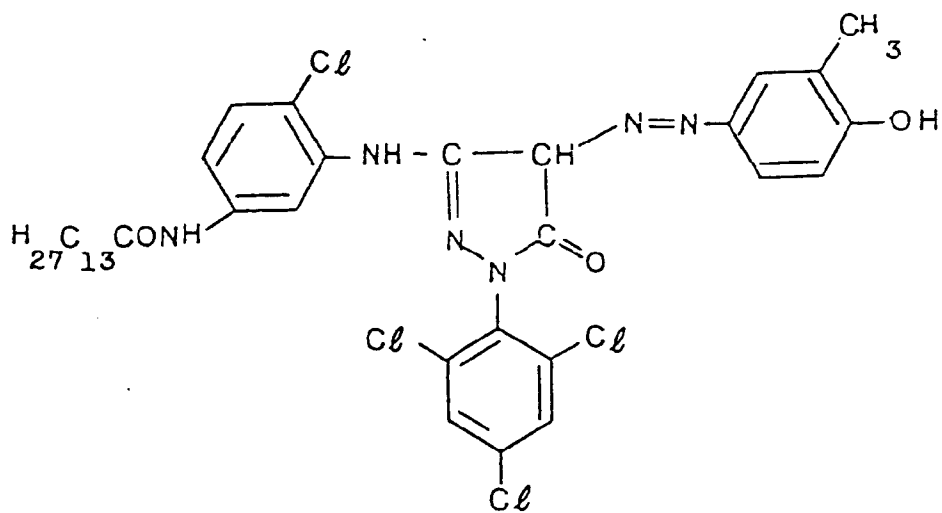
C - 1 0

5

10

15

20



C - 1 1

25

30

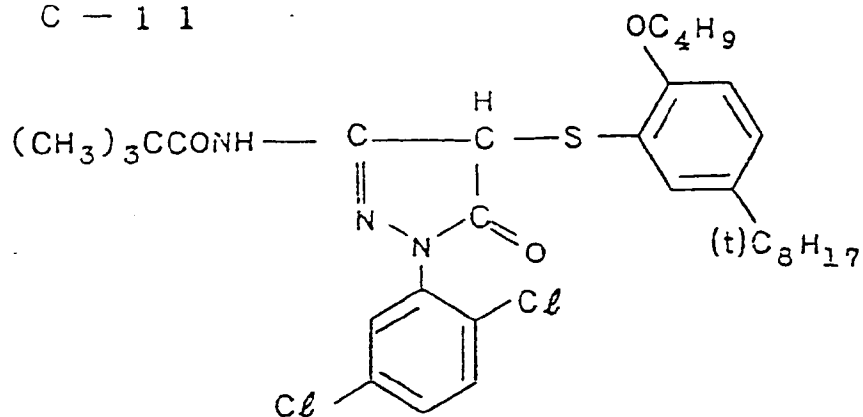
35

40

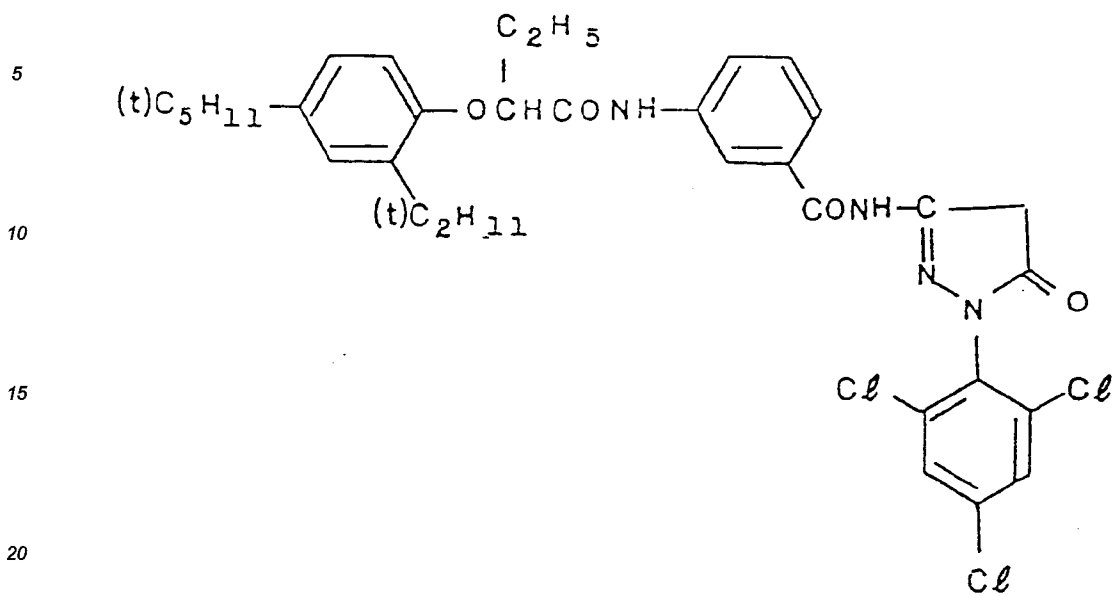
45

50

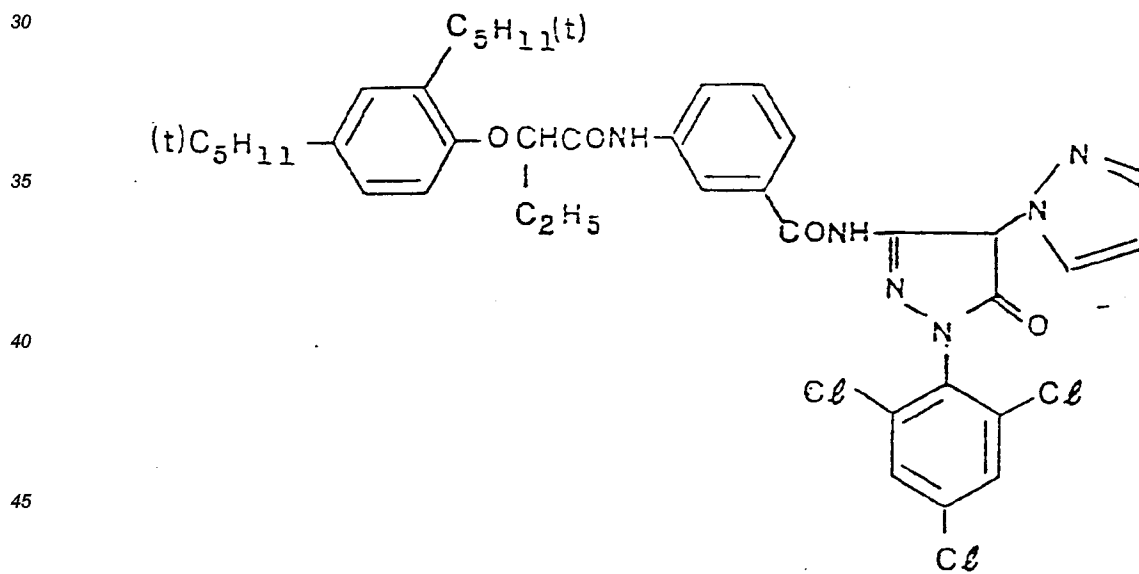
55



C - 1 2



C - 1 3



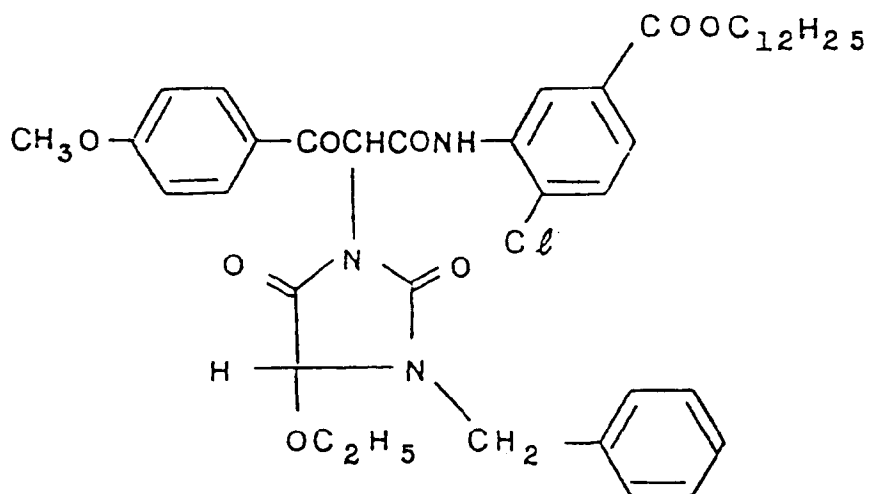
C - 1 4

5

10

15

20



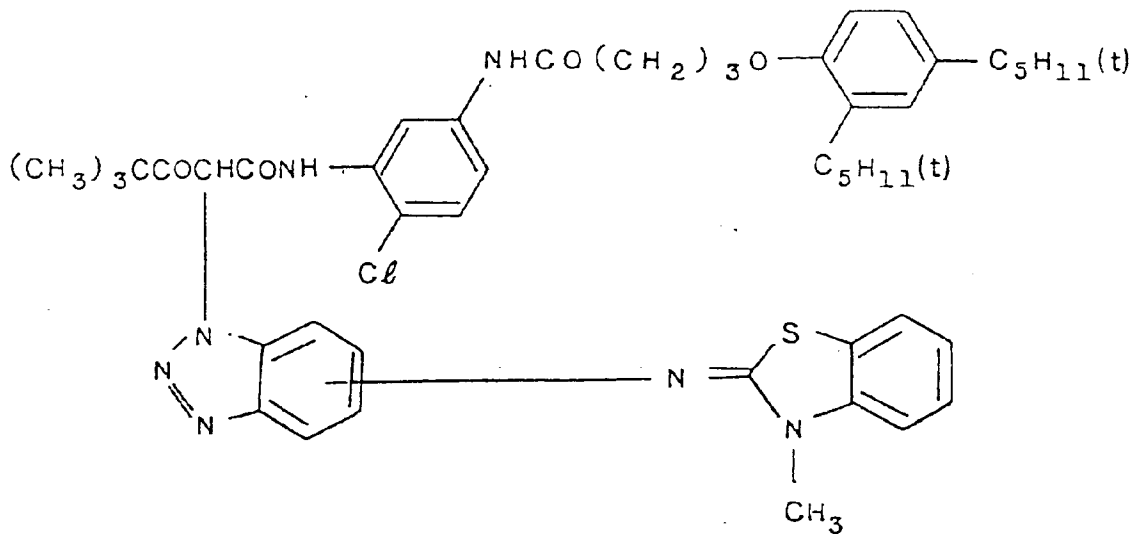
C-15

25

30

35

40

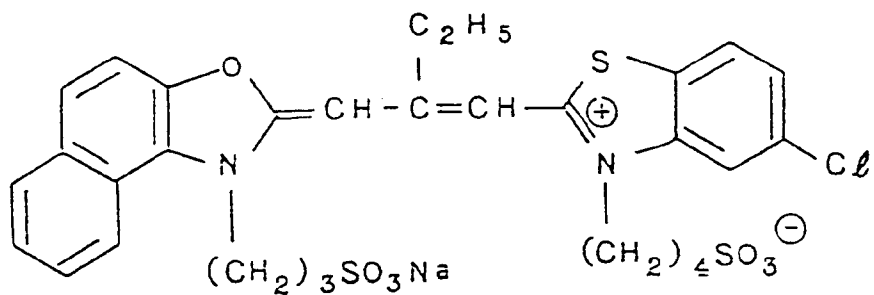


Sensitizing dye I

45

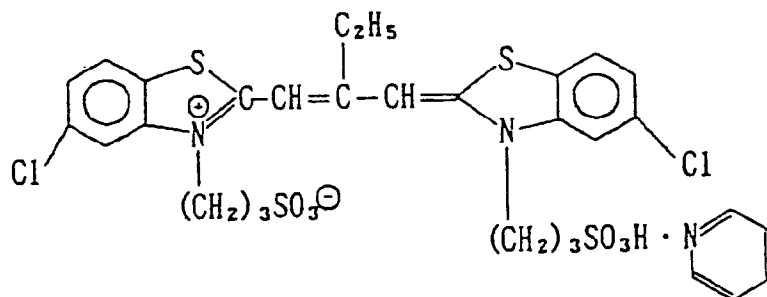
50

55



Sensitizing dye II

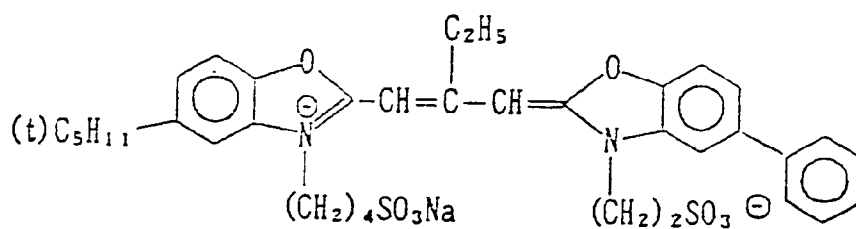
5



10

Sensitizing dye III

15

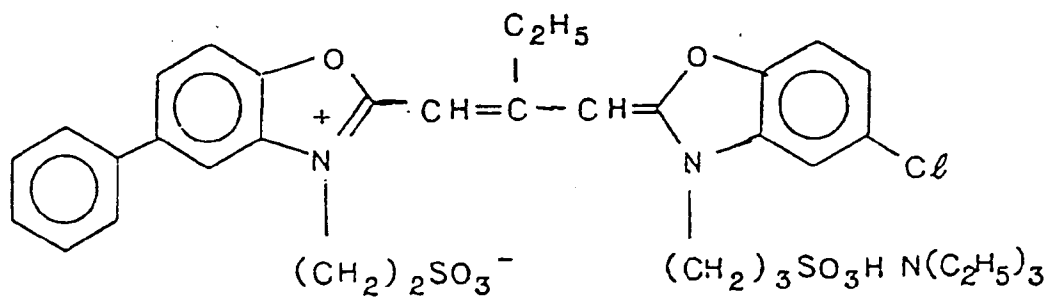


20

25

Sensitizing dye IV

30

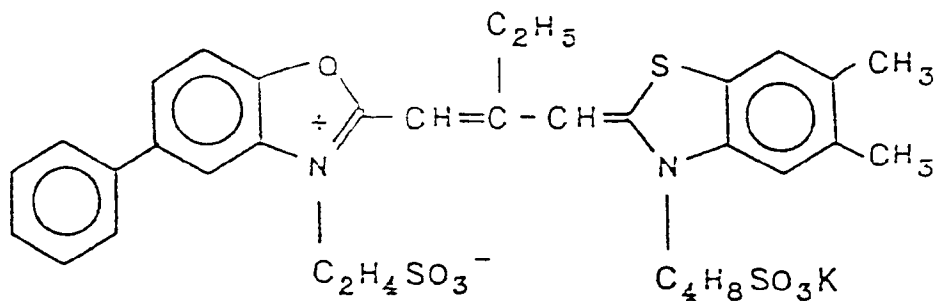


35

40

Sensitizing dye V

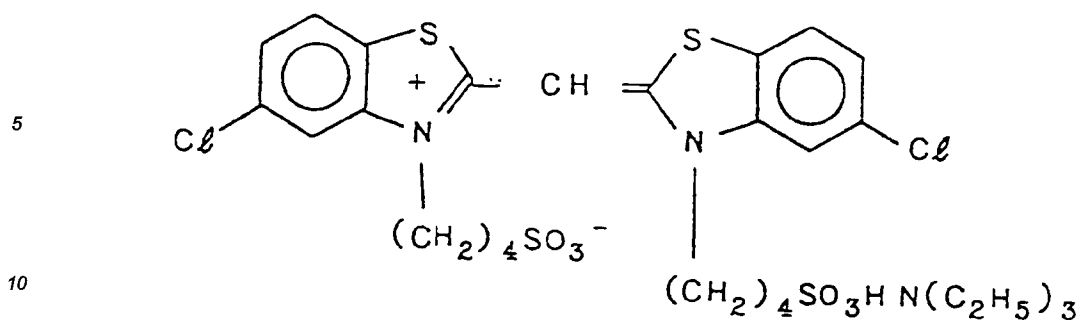
45



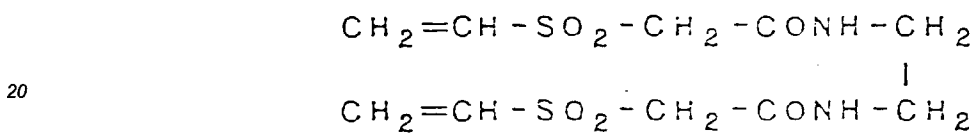
50

Sensitizing dye VI

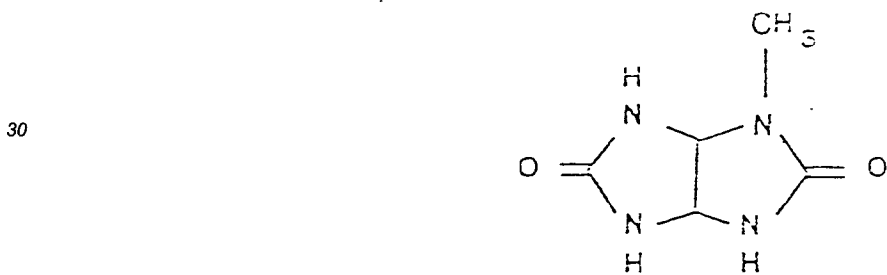
55



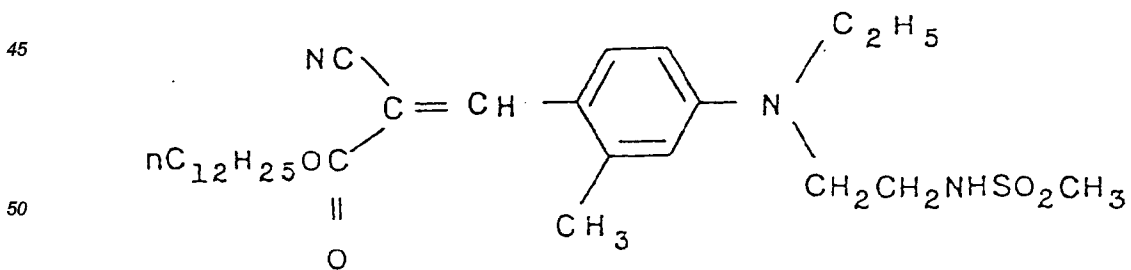
15 H - 1



25 S - 1

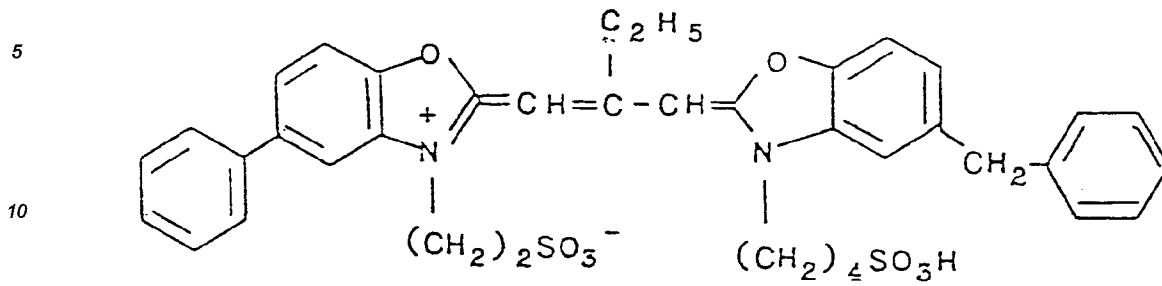


40 Y - 1



55

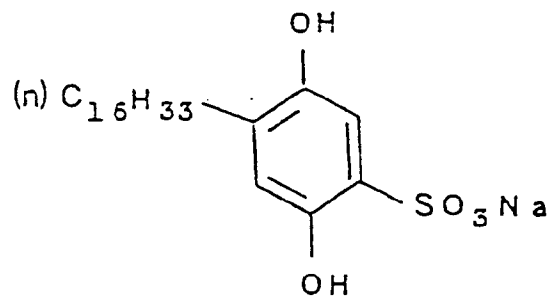
S - 6



15

Cpd A

20

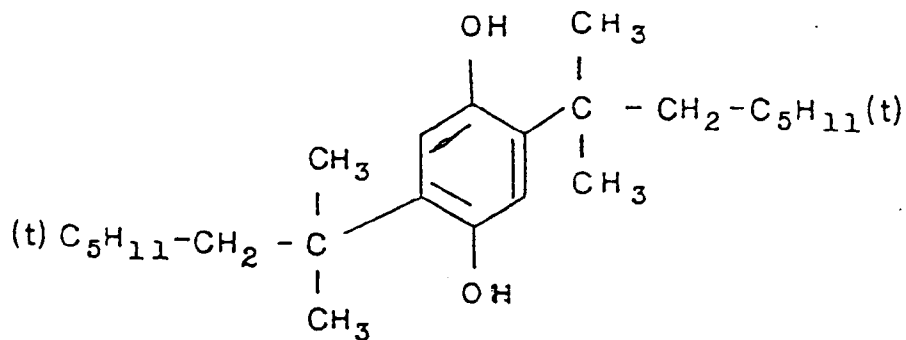


30

Cpd B

35

40



Comparative Sample 102 was prepared by using a 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.

50

(1) DIR coupler C-5 was added to the seventh layer in an amount of 0.03 g/m² and the total amount of the seventh layer was increased by 70%.

(2) DIR coupler C-5 was added to the eighth layer in an amount of 0.01 g/m² and the total amount of the eighth layer was increased by 50%.

55

(3) DIR coupler C-5 was added to the eleventh layer in an amount of 0.03 g/m² and the total amount of the eleventh layer was increased by 60%.

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

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

Comparative Sample 103 wherein the concentration of yellow filter layer was increased was prepared to

improve the 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.

5 (2) The silver iodobromide emulsion in the fifth layer was replaced with one having a mean grain size of $0.75\ \mu\text{m}$ and the total amount 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 $0.85\ \mu\text{m}$ and the total amount 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.

10 (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}

15 (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 total amount of the ninth layer was increased by 5%.

20 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.

25 (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}

30 (2) The amounts of the sensitizing dyes in the eighth layer were changed to the following amounts, and the total amount 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}

35 (3) The amounts of the sensitizing dyes in the ninth layer were changed to the following amounts, and the total amount 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}

40 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}

45 (2) The amounts of the sensitizing dyes in the eighth layer were changed to the following amounts, and the total amount 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}

50 (3) The amounts of the sensitizing dyes in the ninth layer were changed to the following amounts, and the total amount 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}

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

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

(2) The average particle size of the silver iodobromide emulsion in the fifth layer was changed to 0.75 μm , and the total amount 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 total amount of the ninth layer was increased by 10%.

5 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 in the tenth layer nondiffusing yellow dye YD-13 was used in an amount of 0.17 g/m² in place of yellow colloidal silver.

10 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.

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

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

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

20 The 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. A commercially available interference filter of Line double Filter was used to obtain monochromatic light of 480 nm. Half width was 8 nm. Development was carried out in the following stages.

| 25 | <u>Stage</u> | <u>Processing Time</u> | <u>Processing Temperature</u> |
|----|-------------------|------------------------|-------------------------------|
| | Color development | 3 min 15 s | 38°C |
| 30 | Bleaching | 6 min 30 s | 38°C |
| | Rinse | 2 min 10 s | 24°C |
| | Fixing | 4 min 20 s | 38°C |
| 35 | Rinse (1) | 1 min 5 s | 24°C |
| | Rinse (2) | 2 min 10 s | 24°C |
| 40 | Stabilization | 1 min 5 s | 38°C |
| | Drying | 4 min 20 s | 55°C |

45 Each processing solution had the following composition.

50

55

Color Developing Solution

Unit: g

| | | |
|----|--|--------------|
| 5 | Diethylenetriaminepentaacetic acid | 1.0 |
| | 1-Hydroxyethylidene-1,1-diphosphonic acid | 3.0 |
| 10 | Sodium sulfite | 4.0 |
| | Potassium carbonate | 30.0 |
| | Potassium bromide | 1.4 |
| 15 | Potassium iodide | 1.5 mg |
| | Hydroxylamine sulfite | 2.4 |
| 20 | 4-(N-Ethyl-N- β -hydroxyethyl-amino)-2-methylaniline sulfate | 4.5 |
| | Add water | 1.0 <i>l</i> |
| 25 | pH | 10.05 |

Bleaching Solution

Unit: g

| | | |
|----|---|--------------|
| 30 | Ethylenediaminetetraacetic acid iron(III) sodium trihydrate | 100.0 |
| | Disodium ethylenediaminetetraacetate | 10.0 |
| 35 | Ammonium bromide | 140.0 |
| | Ammonium nitrate | 30.0 |
| | Ammonia water (27%) | 6.5 ml |
| 40 | Add water | 1.0 <i>l</i> |
| | pH | 6.0 |

45

50

55

Fixing Solution

Unit: g

| | | |
|----|--|----------|
| 5 | Disodiummethylenediaminetetraacetate | 0.5 |
| | Sodium sulfite | 7.0 |
| | Sodium bisulfite | 5.0 |
| 10 | Ammonium thiosulfate (70% aqueous solution) | 170.0 ml |
| | Add water | 1.0 ℓ |
| 15 | pH | 6.7 |

Stabilizing Solution

Unit: g

| | | |
|----|---|---------|
| 20 | Formalin (37%) | 2.0 ml |
| | Polyoxyethylene-p-monononylphenyl ether (average degree of polymerization: 10) | 0.3 |
| 25 | Disodium ethylenediaminetetraacetate | 0.05 |
| | Add water | 1.0 ℓ |
| 30 | 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 that are commercially available were photographed and printing was made on color paper, commercially available, so that a grey sheet having an optical density of 0.7 reproduced lightness as well as hue.

35 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 were insufficient. The comparative sample 102 shows the chroma in acceptable level, however, the fidelity of Bluish Green is bad. Among the comparative samples 103 to 107 and 113, none of the samples satisfies requirements of the chroma and fidelity simulta-
40 neously.

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

45

50

55

5
10
15
20
25
30
35
40
45
50
55

Table 1

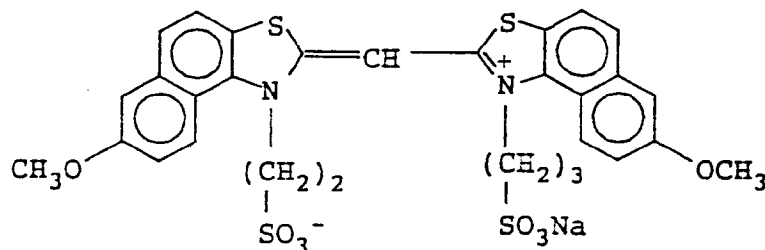
| Sample No. | Kind | ISO Sensitivity | S _{480-S480} _G | Peak Density of Yellow Filter Layer | Chroma of Blue | Fidelity of Blue | Fidelity of Bluish Green |
|------------|-----------|-----------------|------------------------------------|-------------------------------------|----------------|------------------|--------------------------|
| 101 | Comp. Ex. | 75 | -0.80 | 0.85 | xx | x | ○-△ |
| 102 | " | 80 | -0.95 | 0.85 | ○ | ○-△ | x-xx |
| 103 | " | 78 | -1.20 | 1.70 | ○ | ○-⊙ | xx |
| 104 | " | 73 | -0.65 | 0.85 | ○-△ | △ | ○ |
| 105 | " | 77 | -0.50 | 0.85 | ○-△ | △-x | ○-⊙ |
| 106 | " | 75 | -0.35 | 0.85 | △ | x | ⊙ |
| 107 | " | 71 | -0.90 | 1.70 | ○ | ○-⊙ | x |
| 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 | △ | ○ | x |

⊙: Very superior △: Slightly inferior xx: Very inferior
 ○: Superior x: Inferior

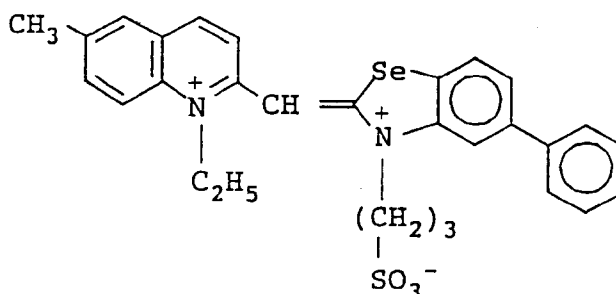
EXAMPLE 2

Samples 201 to 204 were prepared in the same manner as 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



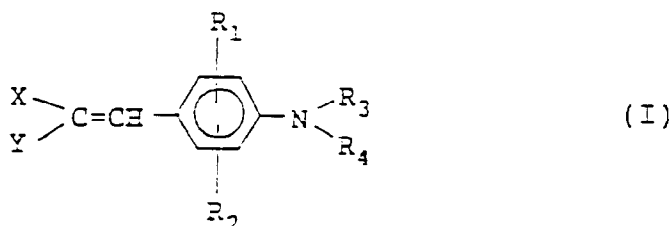
Samples 203, 204



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.

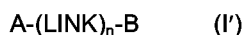
Claims

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 monochromatic light of 480 nm and the sensitivity (S_B^{480}) of the blue-sensitive emulsion layer to monochromatic light of 480 nm ranges from $-0.85 \leq S_G^{480} - S_B^{480} \leq 0.2$ 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 s, and the optical density of the yellow filter layer at the peak wavelength is 1.0 or more.
2. The silver halide color photographic material according to claim 1, wherein the relationship ranges from $-0.75 \leq S_G^{480} - S_B^{480} \leq 0$.
3. The silver halide color photographic material according to claim 1, wherein the relationship ranges from $-0.70 \leq S_G^{480} - S_B^{480} \leq -0.1$.
4. The silver halide color photographic material according to claim 1, wherein the optical density of the yellow filter layer is at least 1.2.
5. The silver halide color photographic material according to claim 4, wherein the optical density is at least 1.4.
6. The silver halide color photographic material according to claim 1, wherein the yellow filter layer contains a dye represented by formula:



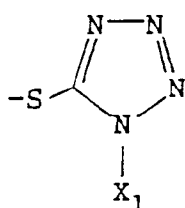
10 wherein R_1 and R_2 may be the same or different and each is selected from a hydrogen atom, a halogen atom, an alkyl group, an alkoxy group, a hydroxyl group, a carboxyl group, a substituted amino group, a carbamoyl group, a sulfamoyl group, a nitro group or an alkoxy carbamoyl group; R_3 and R_4 may be the same or different and each is 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 combine to form a 5-membered or 6-membered ring; and X and Y may be the same or different and each is an electron attractive group.

7. The 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. The 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. The silver halide color photographic material according to claim 1, further comprising a compound represented by formula:

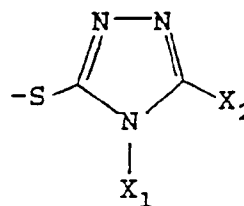


wherein A represents a residue of a coupler which releases $(\text{LINK})_n-B$ by the coupling reaction with the oxidant of an aromatic primary developing agent; LINK represents a group which is attached to the coupling active site of A and is capable of releasing B after it is released from A by the 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 or 1 and when $n=0$, B is directly attached to A.

Formula (IIa)

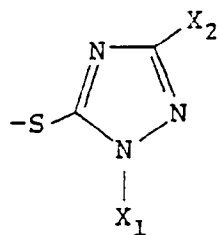


Formula (IIb)



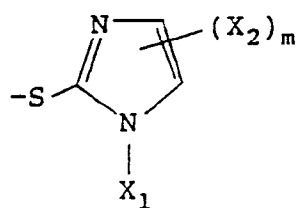
5

Formula (IIc)



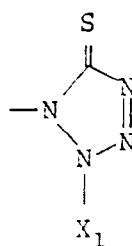
10

Formula (IIId)



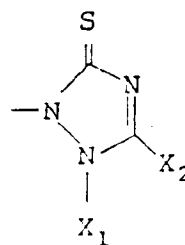
15

Formula (IIe)



20

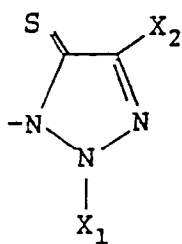
Formula (IIIf)



25

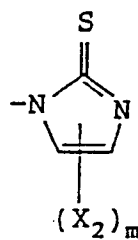
30

Formula (IIg)



35

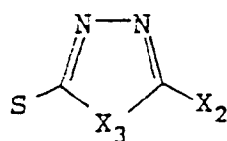
Formula (IIh)



40

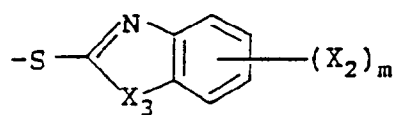
45

Formula (IIIi)



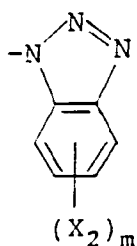
50

Formula (IIIj)

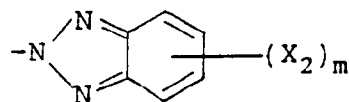


55

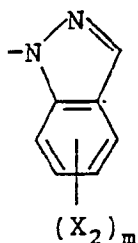
Formula (IIk)



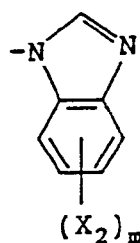
Formula (IIℓ)



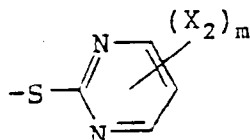
Formula (IIm)



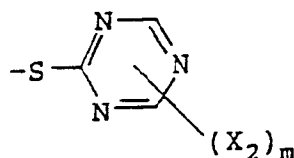
Formula (IIn)



Formula (IIo)



Formula (IIp)



40

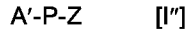
45

50

55

wherein X₁ 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, a hydroxyl group, an acylamino group, a carbamoyl group, a sulfonyl group, a sulfonamido group, a sulfamoyl group, an amino group, an acylamino group, a cyano group, a ureido group, an acyl group and an alkylthio group or X₁ is a substituted phenyl group wherein the substituent group has not more than 3 carbon atoms and is selected from the group consisting of a hydroxyl group, an alkoxycarbonyl group, an acylamino group, a carbamoyl group, a sulfonyl group, a sulfonamido group, a sulfamoyl group, an acyloxy group, a ureido group, a carboxyl group, a cyano group, a nitro group, an amino group and an acyl group; X₂ is a hydrogen atom, an aliphatic group, a halogen, a hydroxyl group, an alkoxy group, an alkylthio group, an alkoxycarbonyl group, an acylamino group, a carbamoyl group, a sulfonyl group, a sulfonamido group, a sulfamoyl group, an acyloxy group, a ureido group, a cyano group, a nitro group, an amino group, an alkoxycarbonylamino group, an aryloxy carbonyl group or an acyl group; X₃ is an oxygen atom, a sulfur atom or an imino group having not more than 4 carbon atoms; m is an integer of 1 or 2; the total number of carbon atoms of mX₂ is not more than 8; and when m=2, two X₂ may be the same or different groups.

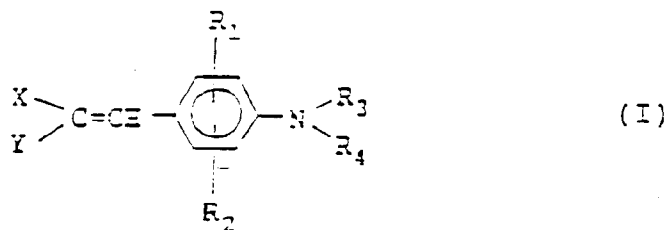
10. The silver halide color photographic material according to claim 1, further comprising a compound of formula:



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'.

Patentansprüche

1. Farbphotographisches Silberhalogenidmaterial, umfassend mindestens eine rotempfindliche Emulsionsschicht, mindestens eine grünempfindliche Emulsionsschicht, mindestens eine blauempfindliche Emulsionsschicht und mindestens eine Gelbfilterschicht auf einem Träger, worin das Verhältnis zwischen der Empfindlichkeit (S_G^{480}) der grünempfindlichen Emulsionsschicht für monochromatisches Licht mit 480 nm und der Empfindlichkeit (S_B^{480}) der blauempfindlichen Emulsionsschicht für monochromatisches Licht mit 480 nm im Bereich von $-0,85 \leq S_G^{480} - S_B^{480} \leq 0,2$ liegt, wenn sie gemessen wird, nachdem das farbphotographische Silberhalogenidmaterial mit einer ISO-Empfindlichkeit S einheitlich mit weißem Licht mit 2/S Lux s belichtet wurde, und die optische Dichte der Gelbfilterschicht bei der Peak-Wellenlänge 1,0 oder mehr beträgt.
2. Farbphotographisches Silberhalogenidmaterial nach Anspruch 1, worin das Verhältnis im Bereich von $-0,75 \leq S_G^{480} - S_B^{480} \leq 0$ liegt.
3. Farbphotographisches Silberhalogenidmaterial nach Anspruch 1, worin das Verhältnis im Bereich von $-0,70 \leq S_G^{480} - S_B^{480} \leq -0,1$ liegt.
4. Farbphotographisches Silberhalogenidmaterial nach Anspruch 1, worin die optische Dichte der Gelbfilterschicht mindestens 1,2 beträgt.
5. Farbphotographisches Silberhalogenidmaterial nach Anspruch 4, worin die optische Dichte mindestens 1,4 beträgt.
6. Farbphotographisches Silberhalogenidmaterial nach Anspruch 1, worin die Gelbfilterschicht einen Farbstoff enthält, der durch die Formel dargestellt ist:



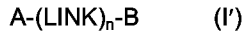
worin R_1 und R_2 gleich oder verschieden sein können und jeweils gewählt sind aus einem Wasserstoffatom, einem Halogenatom, einer Alkylgruppe, einer Alkoxygruppe, einer Hydroxylgruppe, einer Carboxylgruppe, einer substituierten Aminogruppe, einer Carbamoylgruppe, einer Sulfamoylgruppe, einer Nitrogruppe oder einer Alkoxy-carbamoylgruppe; R_3 und R_4 gleich oder verschieden sein können und jeweils gewählt sind aus einem Wasserstoffatom, einer unsubstituierten oder substituierten Alkylgruppe, einer unsubstituierten oder substituierten Alkenylgruppe, einer unsubstituierten oder substituierten Arylgruppe, einer Acylgruppe oder einer Sulfonylgruppe, und R_3 und R_4 sich miteinander verbinden können, um einen 5-gliedrigen oder 6-gliedrigen Ring zu bilden; und X und Y gleich oder verschieden sein können und jedes eine elektronenziehende Gruppe ist.

7. Farbphotographisches Silberhalogenidmaterial nach Anspruch 1, worin die für mindestens eine der blauempfindlichen Schichten verwendete Silberhalogenidemulsion monodispersiert ist.

8. Farbphotographisches Silberhalogenidmaterial nach Anspruch 1, worin mindestens eine Emulsions-
schicht eine Menge von ultra-tafelförmigen Silberkörnern mit einem Durchmesser von mindestens dem
5-fachen der Dicke des Kornes enthält, wobei diese Menge mindestens 50% der gesamten projizierten Flä-
che der gesamten Körner ausmacht.

5

9. Farbphotographisches Silberhalogenidmaterial nach Anspruch 1, weiterhin umfassend eine Verbindung,
die durch die Formel dargestellt ist,

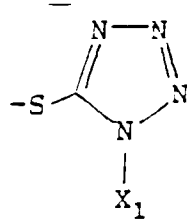


10

worin A einen Rest eines Kupplers darstellt, welcher $(\text{LINK})_n-B$ durch die Kupplungsreaktion mit dem Oxi-
dationsmittel eines aromatischen primären Entwicklungsmittels freisetzt; LINK eine Gruppe darstellt, wel-
che an der Kupplungsstelle von A hängt und B freisetzen kann, nachdem sie von A durch die Kupplungs-
reaktion freigesetzt wurde; B eine Gruppe darstellt, die durch die folgenden allgemeinen Formeln (IIa),
(IIb), (IIc), (IId), (IIe), (IIf), (IIg), (IIh), (Iii), (IIj), (IIk), (III), (IIm), (IIn), (IIo) oder (IIp) dargestellt ist; und n eine
ganze Zahl von 0 oder 1 darstellt und wenn $n=0$, B direkt an A gebunden ist.

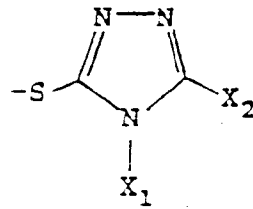
15

Formel (IIa)



20

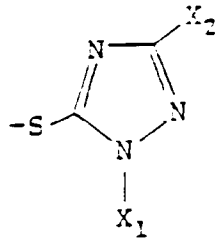
Formel (IIb)



25

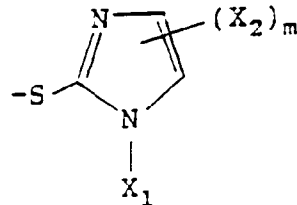
30

Formel (IIc)



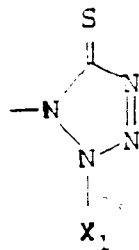
35

Formel (IId)



40

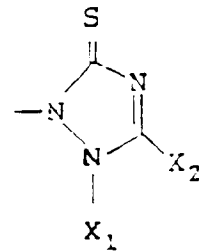
Formel (IIe)



45

50

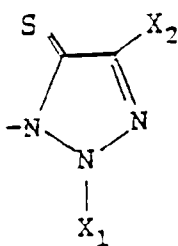
Formel (IIf)



55

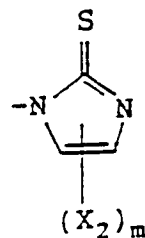
Formel (IIg)

5



10

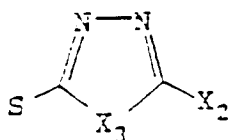
Formel (IIh)



15

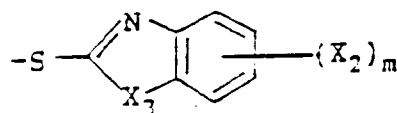
Formel (IIIi)

20



25

Formel (IIj)



30

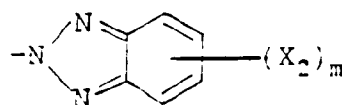
Formel (IIk)

35



40

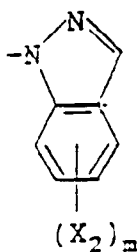
Formel (IIIl)



45

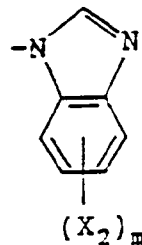
Formel (IIIm)

50

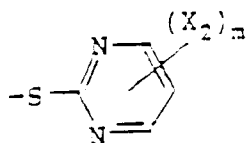


55

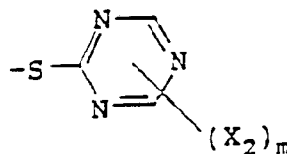
Formel (IIIn)



Formel (IIo)



Formel (IIp)



worin X_1 eine substituierte-oder unsubstituierte aliphatische Gruppe mit 1 bis 4 Kohlenstoffatomen ist, worin die Substituentengruppe nicht mehr als 3 Kohlenstoffatome hat und gewählt ist aus der Gruppe bestehend aus einer Alkoxygruppe, einer Alkoxy-carbonylgruppe, einer Hydroxylgruppe, einer Acylamino-gruppe, einer Carbamoylgruppe, einer Sulfonylgruppe, einer Sulfonamidogruppe, einer Sulfamoylgruppe, einer Aminogruppe, einer Acylaminogruppe, einer Cyanogruppe, einer Ureidogruppe, einer Acylgruppe und einer Alkylthiogruppe, oder X_1 eine substituierte Phenylgruppe ist, worin die Substituentengruppe nicht-mehr als 3 Kohlenstoffatome hat und gewählt ist aus der Gruppe bestehend aus einer Hydroxylgruppe, einer Alkoxy-carbonylgruppe, einer Acylaminogruppe, einer Carbamoylgruppe, einer Sulfonylgruppe, einer Sulfonamidogruppe, einer Sulfamoylgruppe, einer Acyloxygruppe, einer Ureidogruppe, einer Carboxylgruppe, einer Cyanogruppe, einer Nitrogruppe, einer Aminogruppe und einer Acylgruppe: X_2 ein Wasserstoffatom, eine aliphatische Gruppe, ein Halogen, eine Hydroxylgruppe, eine Alkoxygruppe, eine Alkylthiogruppe, eine Alkoxy-carbonylgruppe, eine Acylaminogruppe, eine Carbamoylgruppe, eine Sulfonylgruppe, eine Sulfonamidogruppe, eine Sulfamoylgruppe, eine Acyloxygruppe, eine Ureidogruppe, eine Cyanogruppe, eine Nitrogruppe, eine Aminogruppe, eine Alkoxy-carbonylaminogruppe, eine Aryloxy-carbonylgruppe oder eine Acylgruppe ist; X_3 ein Sauerstoffatom, ein Schwefelatom oder eine Iminogruppe mit nicht mehr als 4 Kohlenstoffatomen ist; m eine ganze Zahl von 1 oder 2 ist; die Gesamtzahl der Kohlenstoffatome von mX_2 nicht mehr als 8 beträgt; und wenn $m=2$, zwei X_2 die gleichen oder verschiedene Gruppen sein können.

10. Farbphotographisches Silberhalogenidmaterial nach Anspruch 1, weiterhin umfassend eine Verbindung der Formel:



worin A' einen Kupplungsbestandteil, der mit den Oxidationsmitteln von Farbentwicklungsmitteln reagieren kann und einen Bestandteil, der die -P-Z-Gruppe durch Reaktion mit den Oxidationsmitteln der Farbentwicklungsmittel freisetzen kann, darstellt; Z einen Entwicklungsverzögerer darstellt und -P-Z eine Gruppe darstellt, welche einen Verzögerer durch die Reaktion mit den Oxidationsmitteln der Entwicklungsmittel nach der Abspaltung von der Gruppe A' bildet.

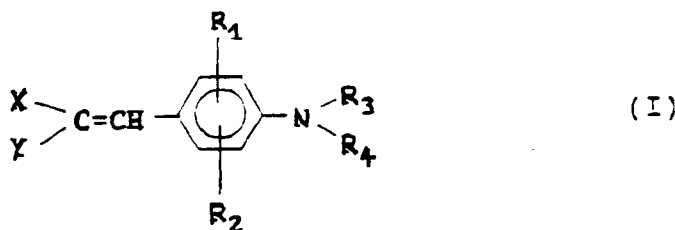
Revendications

- Un matériau photographique en couleur à l'halogénure d'argent comprenant au moins une couche d'émulsion sensible au rouge, au moins une couche d'émulsion sensible au vert, au moins une couche d'émulsion sensible au bleu et au moins une couche de filtre jaune prévues sur un support, où la relation entre la sensibilité (S_G^{480}) de la couche d'émulsion sensible au vert à la lumière monochromatique de 480 nm et la sensibilité (S_B^{480}) de la couche d'émulsion sensible au bleu à la lumière monochromatique de 480 nm est dans l'intervalle de $-0,85 \leq S_G^{480} - S_B^{480} \leq 0,2$ lorsqu'elle est mesurée après que le matériau photographique en couleur à l'halogénure d'argent ayant une sensibilité ISO de S soit uniformément exposée à la lumière blanche de 2/S lux s, et que la densité optique de la couche de filtre jaune à la longueur d'onde de pic soit de 1,0 ou plus.
- Le matériau photographique en couleur à l'halogénure d'argent selon la revendication 1, selon laquelle la relation est dans l'intervalle de $-0,75 \leq S_G^{480} - S_B^{480} \leq 0$.
- Le matériau photographique en couleur à l'halogénure d'argent selon la revendication 1, selon laquelle la relation est dans l'intervalle de $-0,70 \leq S_G^{480} - S_B^{480} \leq -0,1$.
- Le matériau photographique en couleur à l'halogénure d'argent selon la revendication 1, selon laquelle

la densité optique de la couche de filtre jaune est d'au moins 1,2.

5. Le matériau photographique en couleur à l'halogénure d'argent selon la revendication 4, selon laquelle la densité optique est d'au moins 1,4.

6. Le matériau photographique en couleur à l'halogénure d'argent selon la revendication 1, selon laquelle la couche de filtre jaune contient un colorant représenté par la formule :

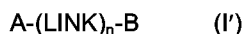


dans laquelle R_1 et R_2 peuvent être identiques ou différents et est choisi chacun parmi un atome d'hydrogène, un atome d'halogène, un groupe alkyle, un groupe alcoxy, un groupe hydroxyle, un groupe carboxyle, un groupe amino substitué, un groupe carbamoyle, un groupe sulfamoyle, un groupe nitro ou un groupe alcoxycarbamoyle ; R_3 et R_4 peuvent être identiques ou différents et sont choisis chacun parmi un atome d'hydrogène, un groupe alkyle substitué ou non substitué, un groupe alcényle substitué ou non substitué, un groupe aryle substitué ou non substitué, un groupe acyle ou un groupe sulfonyle, et R_3 et R_4 peuvent se combiner pour former un noyau à cinq chaînons ou à six chaînons ; et X et Y peuvent être identiques et différents et représentent chacun un groupe attracteur d'électron.

7. Le matériau photographique en couleur à l'halogénure d'argent selon la revendication 1, selon laquelle l'émulsion d'halogénure d'argent utilisée pour au moins l'une des couches sensibles au bleu est mono-dispersée.

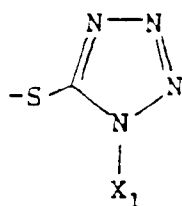
8. Le matériau photographique en couleur à l'halogénure d'argent selon la revendication 1, selon laquelle au moins une couche d'émulsion contient une quantité de grains d'argent ultratabulaires ayant un diamètre d'au moins cinq fois l'épaisseur du grain, en quantité d'au moins 50 % de la surface projetée totale des grains totaux.

9. Le matériau photographique en couleur à l'halogénure d'argent selon la revendication 1, comprenant en outre un composé représenté par la formule :

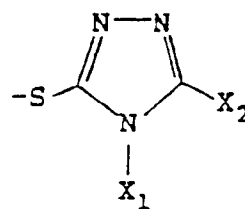


dans laquelle A représente un résidu d'un agent de couplage qui libère $(\text{LINK})_n-B$ par la réaction de couplage avec l'oxydant d'un agent de développement primaire aromatique ; LINK représente un groupe qui est attaché au site actif de couplage de A et qui est capable de libérer B après avoir été libéré de A par la réaction de couplage ; B représente un groupe représenté par les formules générales suivantes : (IIa), (IIb), (IIc), (IId), (IIe), (IIf), (IIg), (IIh), (IIi), (IIj), (IIk), (III), (IIl), (IIm), (IIn), (IIo) ou (IIp) ; et n représente un nombre entier de 0 ou 1 et lorsque $n = 0$, B est directement attaché à A.

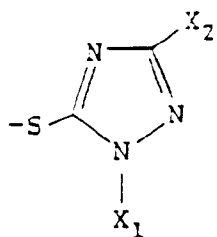
Formule (IIa)



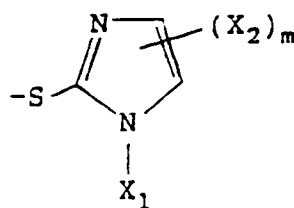
Formule (IIb)



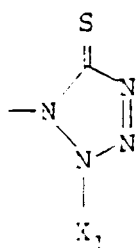
Formule (IIc)



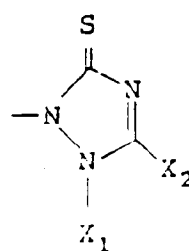
(Formule II d)



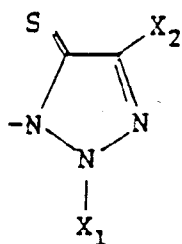
Formule (IIe)



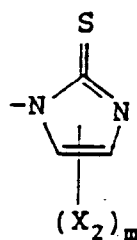
(Formule II f)



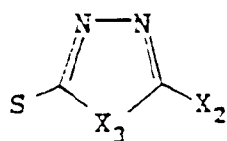
Formule (IIg)



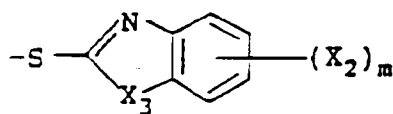
Formule (IIh)



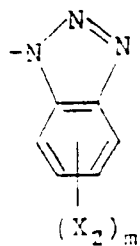
Formule (IIi)



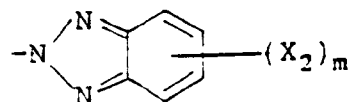
Formule (IIj)



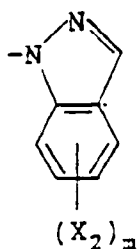
Formule (IIk)



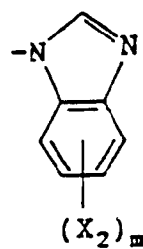
Formule (III)



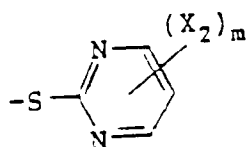
Formule (IIm)



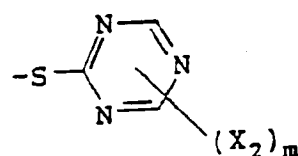
Formule (IIn)



Formule (IIo)

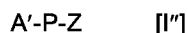


Formule (IIp)



dans lesquelles X_1 est un groupe aliphatique substitué ou non substitué ayant de 1 à 4 atomes de carbone où le groupe substituant n'a pas plus de 3 atomes de carbone et est choisi dans le groupe constitué d'un groupe alcoxy, d'un groupe alcoxycarbonyle, d'un groupe hydroxyle, d'un groupe acylamino, d'un groupe carbamoyle, d'un groupe sulfonyle, d'un groupe sulfonamido, d'un groupe sulfamoyle, d'un groupe amino, d'un groupe acylamino, d'un groupe cyano, d'un groupe uréido, d'un groupe acyle et d'un groupe alkylthio ou bien X_1 est un groupe phényle substitué où le groupe substituant n'a pas plus de 3 atomes de carbone et est choisi dans le groupe constitué d'un groupe hydroxyle, d'un groupe alcoxycarbonyle, d'un groupe acylamino, d'un groupe carbamoyle, d'un groupe sulfonyle, d'un groupe sulfonamido, d'un groupe sulfamoyle, d'un groupe acyloxy, d'un groupe uréido, d'un groupe carboxyle, d'un groupe cyano, d'un groupe nitro, d'un groupe amino et d'un groupe acyle ; X_2 est un atome d'hydrogène, un groupe aliphatique, un halogène, un groupe hydroxyle, un groupe alcoxy, un groupe alkylthio, un groupe alcoxycarbonyle, un groupe acylamino, un groupe carbamoyle, un groupe sulfonyle, un groupe sulfonamido, un groupe sulfamoyle, un groupe acyloxy, un groupe uréido, un groupe cyano, un groupe nitro, un groupe amino, un groupe alcoxycarbonylamino, un groupe aryloxy carbonyle ou un groupe acyle ; X_3 est un atome d'oxygène, un atome de soufre ou un groupe imino n'ayant pas plus de 4 atomes de carbone ; m est un nombre entier de 1 ou 2 ; le nombre total d'atomes de carbone de mX_2 n'est pas supérieur à 8 ; et lorsque $m = 2$, deux X_2 peuvent être les mêmes groupes ou des groupes différents.

10. Le matériau photographique en couleur à l'halogénure d'argent selon la revendication 1, comprenant en outre un composé de formule :



dans laquelle A' représente un composant de couplage capable de réagir avec les oxydants des agents de développement en couleur et un composant capable de libérer le groupe -P-Z par réaction avec les oxydants des agents de développement en couleur ; Z représente un agent retardateur de développement et -P-Z représente un groupe qui forme un retardateur par la réaction avec les oxydants des agents de développement après clivage à partir du groupe A'.

FIG. 1

