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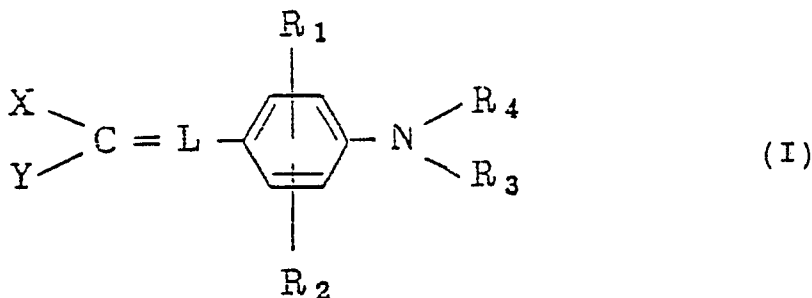
EUROPEAN PATENT APPLICATION

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D-5600 Wuppertal 1(DE)**(54) **Silver halide photographic materials.**

(57) Disclosed is a silver halide photographic material containing at least one dye compound of the following formula (I) and a yellow colloidal silver:



wherein all the symbols are defined in the specification.

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By the combination of the dye compound and the yellow colloidal silver, the filter effect and the antihalation effect are improved. The dye compound (I) may be discolored or dissolved out after the material has been photographically processed so that this does not have any bad influence on the photographic property of the material. Further, the compound (I) is stable after the material has been stored long.

SILVER HALIDE PHOTOGRAPHIC MATERIALS

FIELD OF THE INVENTION

The present invention relates to a silver halide photographic material containing at least one yellow dye
 5 and a yellow colloidal silver.

BACKGROUND OF THE INVENTION

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It is generally well known in the field of silver halide photographic materials that a dye capable of absorbing a light having a particular wavelength may be incorporated into a layer which constitutes the material as a light absorbing filter dye or for the purpose of antihalation or of adjustment of the sensitivity of the light-sensitive emulsion in the material. Accordingly, it has heretofore been known to color a hydrophilic
 15 colloid layer with such a dye.

More precisely, a silver halide photographic material may have various hydrophilic colloid layers such as red, green, and blue light-sensitive silver halide emulsion layers, respectively, formed on a support, and when the material is imagewise exposed so as to record a multicolor image in the various light-sensitive silver halide emulsion layers, it is desirable to control the spectral composition of the light as introduced into
 20 the various silver halide emulsion layers so as to adjust the photographic sensitivity of the material. In this case, in general, a dye which may absorb a light having a wavelength range unnecessary for the said silver halide emulsion layer is incorporated into a hydrophilic colloid layer which is in a remoter position from the support than the said light-sensitive silver halide emulsion layer to form a filter layer so that only the light having the intended wavelength range may penetrate the said filter layer to go into the light-sensitive silver
 25 halide emulsion layer.

An antihalation layer may be provided so as to improve the sharpness of the image to be formed on a photographic material. More precisely, an antihalation layer may be provided between the light-sensitive emulsion layer and the support or on the rear surface of the support in the material so that the layer may absorb any harmful reflected light in the interface between the emulsion layer and the support or on the
 30 rear surface of the support thereby to improve the sharpness of the image to be formed.

Dyes which are used for such purposes must satisfy various conditions. They should have a good absorption spectrum characteristic in accordance with the use and the object thereof, they should be readily discolored during photographic processing or be easily dissolved out from silver halide photographic materials so that they do not cause any substantial coloration or staining of the materials developed, they
 35 should not have any bad influence on photographic emulsions, for example, fogging or desensitization of photographic emulsions, they should not diffuse from the colored layer to any other layers, and they should be excellent in stability with the lapse of time in processing solutions and in silver halide emulsion layers and be hardly worsened therein.

Numerous efforts have been made in this technical field so as to develop dyes which satisfy the above-mentioned conditions. For example, dyes which have heretofore been found effective for the purpose include the pyrazolone oxonol dyes described in British Patent 506,385; the barbituric acid oxonol dyes described in U.S. Patent 3,247,127; the azo dyes described in U.S. Patent 2,390,707; the styryl dyes described in U.S. Patent 2,255,077; the hemioxonol dyes described in British Patent 584,609; the merocyanine dyes described in U.S. Patent 2,493,747; the cyanine dyes described in U.S. Patent
 45 2,843,486; and the open-chain methylene type benzylidene dyes described in U.S. Patent 4,420,555, JP-A-61-204630, JP-A-61-205934, JP-A-62-56958, JP-A-62-222248 and JP-A-63-40143 (the term "JP-A" as used herein refers to a "published unexamined Japanese patent application").

Among these dyes, those described in U.S. Patent 4,420,555, JP-A-61-204630, JP-A-61-205934, JP-A-62-56958, JP-A-62-222248, and JP-A-63-40143 are preferred, and the layer containing such dye has a fairly
 50 good performance as a filter layer or an antihalation layer.

However, the dyes described in U.S. Patent 4,420,555 have a drawback in that they diffuse into other layers thereby to desensitize a blue-sensitive emulsion layer. Regarding the dyes described in JP-A-62-222248, although these do not diffuse to other layers, they do cause residual coloration, though slightly, of the processed materials. Accordingly, it has been extremely difficult to obtain dyes which could completely satisfy both the nondiffusibility in storage and the discolorability in photographic processing.

SUMMARY OF THE INVENTION

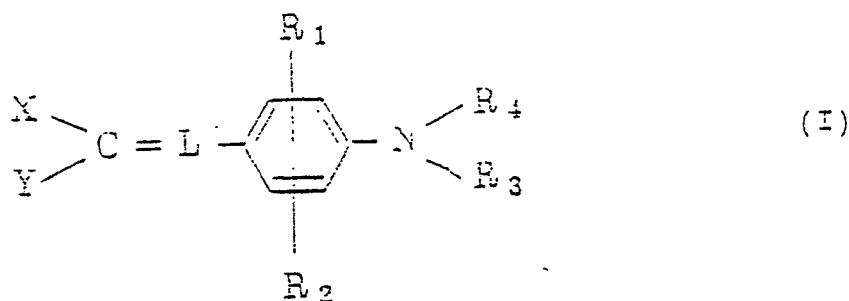
The first object of the present invention is to provide a silver halide photographic material containing at least one yellow dye and a yellow colloidal silver which are excellent in the filter effect, the antihalation effect and the effect of adjusting the sensitivity of light-sensitive emulsions.

The second object of the present invention is to provide a silver halide photographic material containing at least one yellow dye and a yellow colloidal silver which may selectively dye a particular layer but do not diffuse into other layers.

The third object of the present invention is to provide a silver halide photographic material containing at least one yellow dye and a yellow colloidal silver which may be discolored or dissolved out by photographic processing so that they do not have any bad influence on the photographic property of the material.

The fourth object of the present invention is to provide a silver halide photographic material which is stable even in storage for a long period of time without lowering the photographic property and which is excellent in stability during processing.

The present inventors repeatedly and widely experimented so as to obtain photographic materials satisfying the above-mentioned objects and have found that the objects may be attained by a silver halide photographic material containing at least one dye compound represented by the following general formula (I) and a yellow colloidal silver.



wherein X and Y may be the same or different and each represents a cyano group, a carboxyl group, an alkylcarbonyl group, an arylcarbonyl group, an alkoxycarbonyl group, an aryloxy carbonyl group, a carbamoyl group, a sulfonyl group or a sulfamoyl group, or X and Y may be bonded to each other to form a ring; R₁ and R₂ may be the same or different and each represents 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 or an alkoxycarbonyl group; R₃ and R₄ may be the same or different and each represents a hydrogen atom, an alkyl group, an alkenyl group, an aryl group, an acyl group or a sulfonyl group, or R₃ and R₄ may be bonded to each other to form a 5-membered or 6-membered ring; R₁ and R₃, and/or R₂ and R₄ may be bonded to each other to form a 5-membered or 6-membered ring; and L represents a methine group.

DETAILED DESCRIPTION OF THE INVENTION

The compounds of the formula (I) for use in the present invention will be explained in detail.

In the formula (I), X and Y may be the same or different and each represents a cyano group, a carboxyl group, an alkylcarbonyl group which may optionally be substituted (for example, acetyl, propionyl, heptanoyl, dodecanoyl, hexadecanoyl, 1-oxo-7-chloroheptyl, 4-methoxybutanoyl, 4-dimethylaminobutanoyl), an arylcarbonyl group which may optionally be substituted (for example, benzoyl, 4-aminobenzoyl, 4-nitrobenzoyl, 4-methanesulfonylaminobenzoyl, 4-ethanesulfonylaminobenzoyl, 4-propanesulfonylaminobenzoyl, 4-trifluoromethanesulfonylaminobenzoyl, 4-trifluoroacetylaminobenzoyl, 4-trichloroacetylaminobenzoyl, 3-hydroxy-4-methanesulfonylaminobenzoyl, 3-methanesulfonylaminobenzoyl, 3-propanesulfonylaminobenzoyl, 2-methanesulfonylaminobenzoyl, 4-methoxybenzoyl, 3-nitrobenzoyl, 4-methylaminocarbonylaminobenzoyl, 4-ethylaminocarbonylaminobenzoyl, 4-ethoxycarbonylaminosulfonylaminobenzoyl, 4-methoxycarbonylaminosulfonylaminobenzoyl, 3-methylaminocarbonylaminobenzoyl, 4-methoxy-3-methanesul-

fonylaminobenzoyl, 4-ethoxy-3-methanesulfonylaminobenzoyl, 4-(2-hydroxyethoxy)-2-hydroxybenzoyl, 3-chlorobenzoyl), an alkoxy carbonyl group which may optionally be substituted (for example, methoxycarbonyl, ethoxycarbonyl, butoxycarbonyl, t-amylloxycarbonyl, hexyloxycarbonyl, 2-ethylhexyloxycarbonyl, octyloxycarbonyl, decyloxycarbonyl, dodecyloxycarbonyl, hexadecyloxycarbonyl, octadecyloxycarbonyl, 2-butoxyethoxycarbonyl, 2-methylsulfonylethoxycarbonyl, 2-cyanoethoxycarbonyl, 2-(2-chloroethoxy)-ethoxycarbonyl, 2-[2-(2-chloroethoxy)ethoxy]ethoxycarbonyl), an aryloxycarbonyl which may optionally be substituted (for example, phenoxycarbonyl, 3-ethylphenoxycarbonyl, 4-ethylphenoxycarbonyl, 4-fluorophenoxycarbonyl, 4-nitrophenoxycarbonyl, 4-methoxyphenoxycarbonyl, 2,4-di(t-amyl)phenoxycarbonyl), a carbamoyl group which may optionally be substituted (for example, carbamoyl, ethylcarbamoyl, dodecylcarbamoyl, phenylcarbamoyl, 4-methoxyphenylcarbamoyl, 2-bromophenylcarbamoyl, 4-chlorophenylcarbamoyl, 4-ethoxycarbonylphenylcarbamoyl, 4-propylsulfonylphenylcarbamoyl, 4-cyanophenylcarbamoyl, 3-methylphenylcarbamoyl, 4-hexyloxyphenylcarbamoyl, 2,4-di(t-amyl)phenylcarbamoyl, 2-chloro-3-(dodecyloxycarbonyl)phenylcarbamoyl, 3-(hexyloxycarbonyl)phenylcarbamoyl), a sulfonyl group which may optionally be substituted (for example, methylsulfonyl, decylsulfonyl, phenylsulfonyl) or a sulfamoyl group which may optionally be substituted (for example, sulfamoyl, methylsulfamoyl).

X and Y may be bonded to each other to form a ring (for example, pyrazolone, pyrazolotriazole, pyrazoloimidazole, oxyndole, oxyindazopyridine, isoxazolone, barbituric acid, dioxetetrahydropyridine or indanedione ring).

R₁ and R₂ may be the same or different and each represents a hydrogen atom, a halogen atom (e.g., F, Cl, Br, I), an alkyl group which may optionally be substituted (for example, methyl, ethyl, 2-chloroethyl, propyl, hexyl), an alkoxy group which may optionally be substituted (for example, methoxy, ethoxy, 2-chloroethoxy, butoxy, hexyloxy, octyloxy), a hydroxyl group, a carboxyl group, a substituted amino group (for example, an amino group substituted by an acyl group derived from an aliphatic carboxylic acid or sulfonic acid, such as an alkylcarbonamido group (e.g., acetyl amino, hexylcarbonyl amino) or an alkylsulfonamido group (e.g., methanesulfonyl amino, ethanesulfonyl amino, hexanesulfonyl amino), or an alkylamino group (e.g., methyl amino, ethyl amino, propyl amino, hexyl amino), a dialkylamino group (e.g., dimethyl amino, diethyl amino, dipropyl amino)), a carbamoyl group which may optionally be substituted (for example, carbamoyl, methylcarbamoyl, ethylcarbamoyl), a sulfamoyl group which may optionally be substituted (for example, sulfamoyl, methylsulfamoyl, ethylsulfamoyl) or an alkoxy carbonyl group (for example, methoxycarbonyl, ethoxycarbonyl, pentyloxycarbonyl, octyloxycarbonyl).

R₃ and R₄ may be the same or different and each represents a hydrogen atom, an alkyl group which may optionally be substituted (for example, methyl, ethyl, propyl, butyl, isobutyl, pentyl, hexyl, 2-ethylhexyl, octyl, dodecyl, hexadecyl, 2-chloroethyl, 3-chloropropyl, 2-bromoethyl, 2-hydroxyethyl, cyanomethyl, 2-cyanoethyl, 3-cyanopropyl, 2-methoxyethyl, 3-methoxypropyl, 2-ethoxyethyl, 2-octyloxyethyl, 3-ethoxypentyl, 2-isopropoxyethyl, acetylmethyl, 2-acetyloethyl, benzoylmethyl, acetyloxymethyl, 2-(ethylcarbonyloxy)ethyl, 2-(heptanoyloxy)ethyl, 2-(isopropylcarbonyloxy)ethyl, benzoyloxymethyl, 4-chlorobenzoyloxymethyl, 4-nitrobenzoyloxyethyl, acetyl aminoethyl, 2-(ethylcarbonylamino)ethyl, methylcarbamoylmethyl, 2-methyl aminoethyl, 2-(ethyl amino)ethyl, 2-(dimethyl amino)ethyl, 2-(diethyl amino)ethyl, 2-methylureidoethyl, carboxymethyl, 2-carboxyethyl, 3-carboxypropyl, 6-carboxyhexyl, methoxycarbonylmethyl, ethoxycarbonylmethyl, butoxycarbonylmethyl, 2-(butoxycarbonyl)ethyl, 3-(octyloxycarbonyl)propyl, 2,2,2-trifluoroethoxycarbonylmethyl, propyloxycarbonylmethyl, isopropyloxycarbonylmethyl, 2-(propyloxycarbonyl)ethyl, 3-(t-amylloxycarbonyl)propyl, 2-(ethylhexyl)oxycarbonylmethyl, 2-(ethoxycarbonyl)ethyl, phenyloxycarbonylmethyl, ethylsulfonylmethyl, 2-(methylsulfonyl)ethyl, 2-(butylsulfonyl)ethyl, methylsulfonylaminomethyl, 2-(methylsulfonylaminomethyl), 2-(ethylsulfonyl amino)ethyl, 3-(ethylsulfonyl amino)propyl, methylsulfamoylethyl, 2-methylureidoethyl, phenylmethyl), an alkenyl group which may optionally be substituted (for example, 3-hexenyl), an aryl group which may optionally be substituted (for example, phenyl, 4-chlorophenyl, 4-cyanophenyl, 4-hydroxyphenyl, 4-carboxyphenyl, 2-methoxyphenyl, 4-methoxyphenyl, 4-ethoxyphenyl, 4-octyloxyphenyl, 4-methylphenyl, 4-nitrophenyl), an acyl group which may optionally be substituted (for example, acetyl, propionyl, benzoyl, 4-methoxybenzoyl) or a sulfonyl group which may optionally be substituted (for example, methylsulfonyl, ethylsulfonyl, hexylsulfonyl, phenylsulfonyl, 4-chlorophenylsulfonyl, 4-cyanophenylsulfonyl).

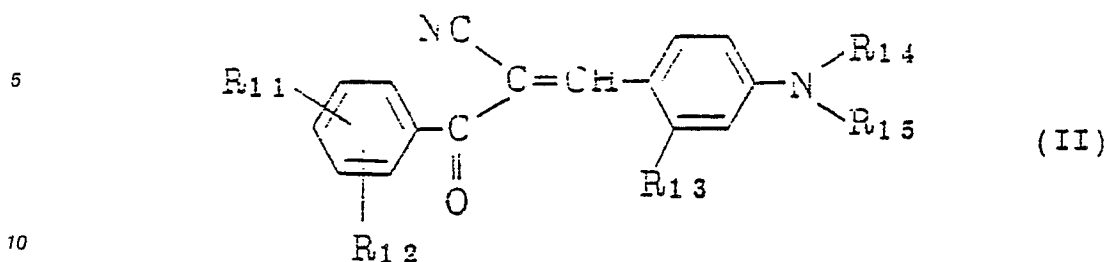
R₃ and R₄ may together form a 5-membered or 6-membered hetero ring (for example, piperidine or morpholine ring).

R₁ and R₃ and/or R₂ and R₄ may be bonded to each other to each form a 5-membered or 6-membered hetero ring.

L represents a methine group, which may optionally be substituted by, for example, a methyl or cyano group.

Among the compounds of the formula (I), those as represented by the following general formula (II) are

preferred.



15 In formula (II) R_{11} represents a hydrogen atom or an electron donating group, preferably an electron donating group having a Hammett's σ_p value lower than -0.05, for example, an alkyl group (e.g., methyl, ethyl, propyl, butyl, t-butyl, carboxymethyl, 2-hydroxyethyl), a cycloalkyl group (e.g., cyclohexyl), a hydroxyl group, an alkoxy group (e.g., methoxy, ethoxy, butoxy, carboxymethoxy, 2-methoxyethoxy, 2-hydroxyethoxy), an amino group (e.g., amino, methylamino, dimethylamino, diethylamino) or a ureido group (e.g., ureido, methylureido, ethylureido). The said Hammett's σ_p value may be selected on the basis of the Table described in Relation between Structure and Activity in Pharmaceutical Substances (published by Nansando Publishing), pages 96 to 103, 1979).

20 R_{12} represents a hydroxyl group or a group of RSO_2NH- , $RCONH-$ or $RNHCONH-$ in which R represents a hydrocarbon residue having from 1 to 6 carbon atoms (e.g., methyl, ethyl, propyl, butyl, i-butyl, pentyl, trifluoromethyl, trichloromethyl, chloromethyl, phenyl, 4-hydroxyphenyl).

25 R_{13} represents a hydrogen atom, a halogen atom (e.g., F, Cl, Br, I), a hydroxyl group, an alkyl group having from 1 to 3 carbon atoms (e.g., methyl, ethyl, propyl), an alkoxy group having from 1 to 3 carbon atoms (e.g., methoxy, ethoxy, propoxy), an alkylsulfonamido group having from 1 to 3 carbon atoms (e.g., methanesulfonamido, ethanesulfonamido) or an alkylcarbonamido group having from 1 to 3 carbon atoms (e.g., acetamino, α -chloroacetamino, trifluoroacetamino).

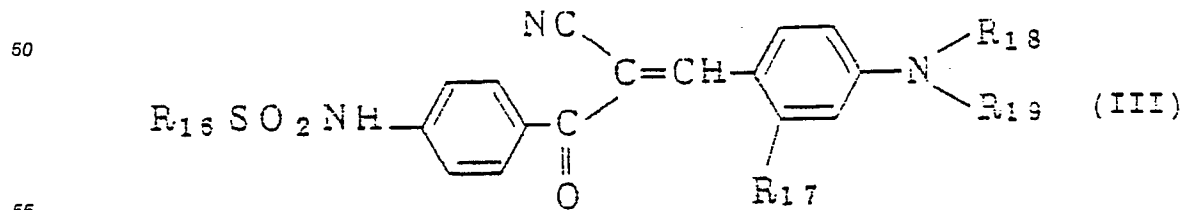
30 R_{14} and R_{15} may be the same or different and each represents an alkyl group having from 1 to 7 carbon atoms which may optionally be substituted or a phenyl group which may optionally be substituted.

As specific examples of the substituents for the alkyl group for R_{14} or R_{15} , there may be mentioned a halogen atom (e.g., F, Cl, Br, I), a hydroxyl group, an alkoxy group (e.g., methoxy, ethoxy, butoxy), an aryloxy group (e.g., phenoxy, p-methylphenoxy), a cyano group, an alkylsulfonyl group (e.g., methanesulfonyl, ethanesulfonyl), an acyloxy group (e.g., acetyloxy, propionyloxy), an alkylsulfonamido group (e.g., methanesulfonamido, propanesulfonamido), an alkylcarbonamido group (e.g., acetamino, trifluoroacetamino, propionylamino), a ureido group (e.g., ureido, methylureido), an alkylcarbonyl group (e.g., acetyl, ethanoyl), an arylcarbonyl group (e.g., benzoyl, p-tert-butylbenzoyl), an alkoxy carbonyl group (e.g., ethoxycarbonyl, butoxycarbonyl, 2,2,2-trifluoroethoxycarbonyl), an aryloxy carbonyl group (e.g., phenoxy carbonyl, p-cyanophenoxy carbonyl), an alkoxy carbonylamino group (e.g., methoxycarbonylamino, ethoxycarbonylamino), an aryloxy carbonylamino group (e.g., phenoxy carbonylamino), an amino group, an alkylamino group (e.g., methylamino, ethylamino), a dialkylamino group (e.g., dimethylamino, diethylamino) and a phenyl group.

As the substituents for the phenyl group for R_{14} or R_{15} , there may be mentioned, for example, an alkyl group, an alkoxy group and a hydroxyl group.

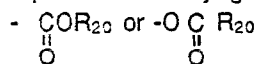
45 R_{14} and R_{15} may together form a ring (e.g., piperidine or morpholine ring).

Among the compounds of the above-mentioned formula (II), those as represented by the following general formula (III) are more preferred.



wherein R_{16} represents an alkyl group having from 1 to 3 carbon atoms; R_{17} represents a hydrogen atom

or an alkyl group having from 1 to 3 carbon atoms; R_{18} and R_{19} may be the same or different and each represents an alkyl group having from 1 to 3 carbon atoms, and at least one of them has



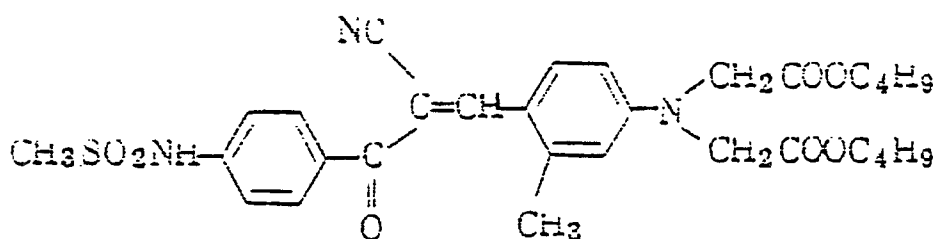
at the terminal thereof; R_{20} represents an alkyl group having from 1 to 5 carbon atoms (e.g., methyl, ethyl, isopropyl, butyl, pentyl) and optionally substituted (e.g., methoxyethyl, trifluoromethyl, ethoxyethyl, 2,2,2-trifluoroethyl).

Specific examples of the compounds for use in the present invention are mentioned below. These example compounds are illustrative and should not be considered to restrict the scope of the present invention.

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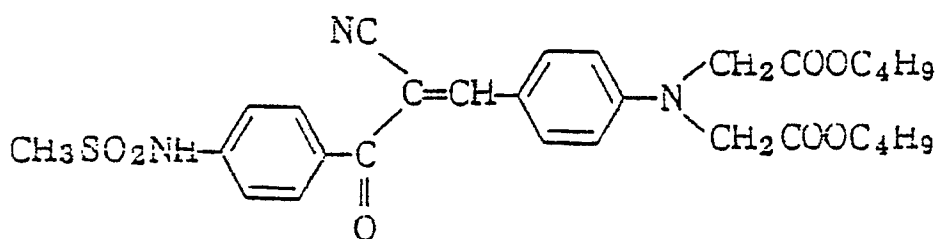


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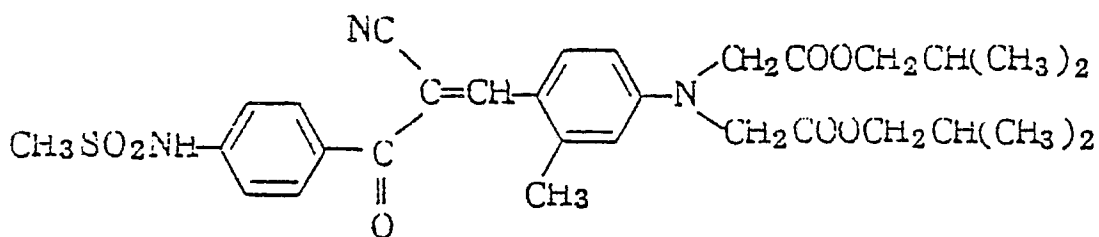
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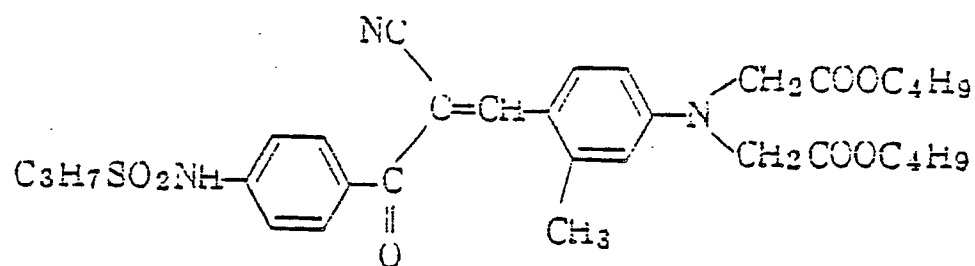
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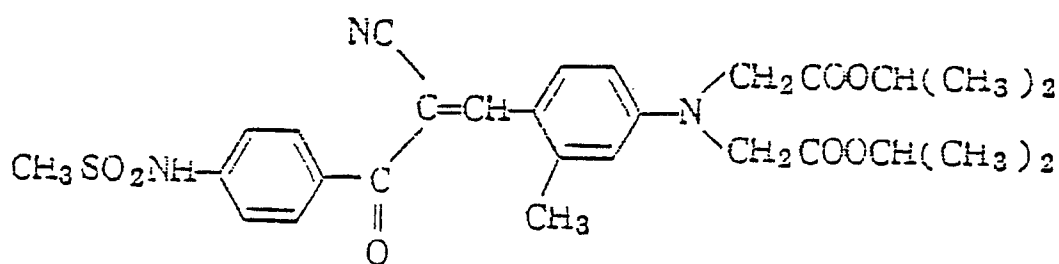
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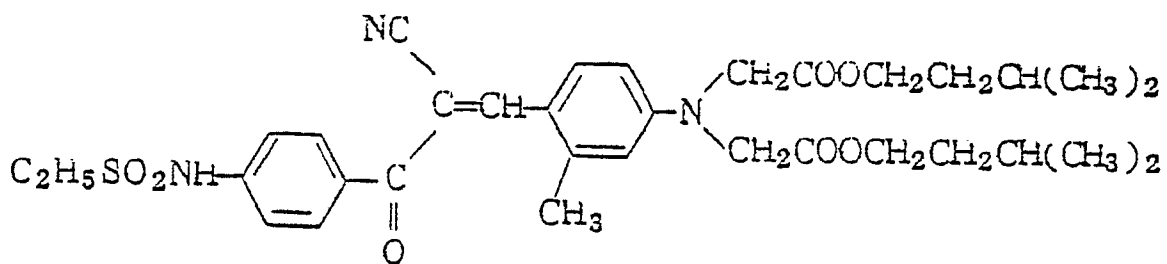
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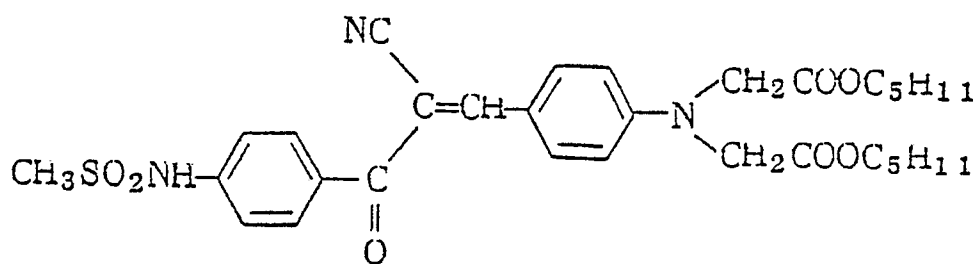
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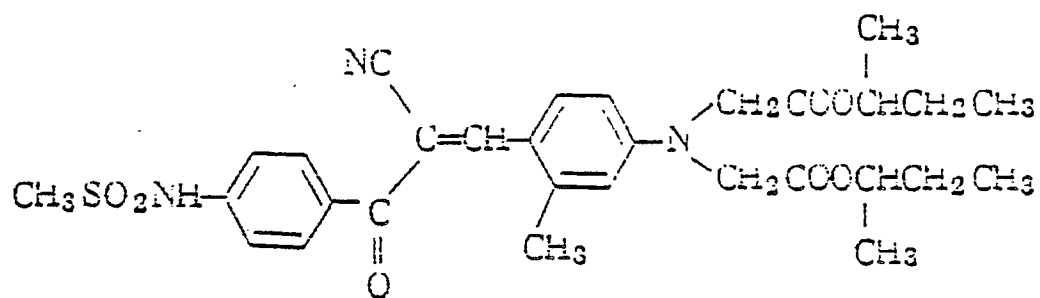
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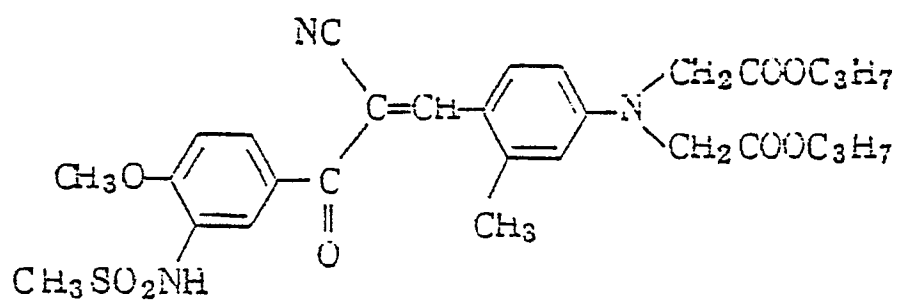
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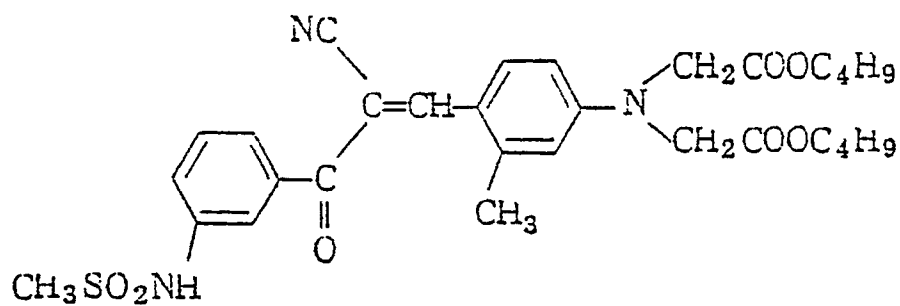
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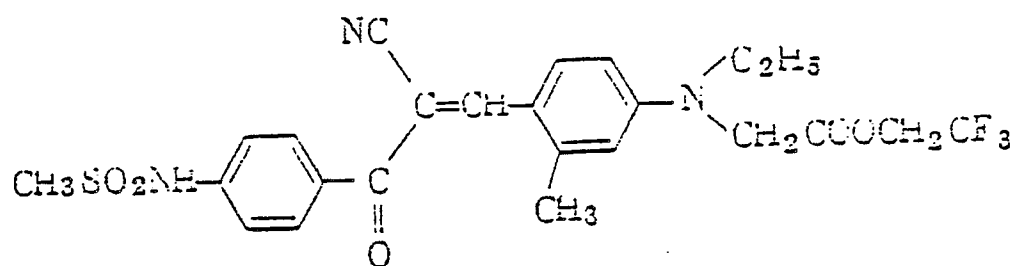
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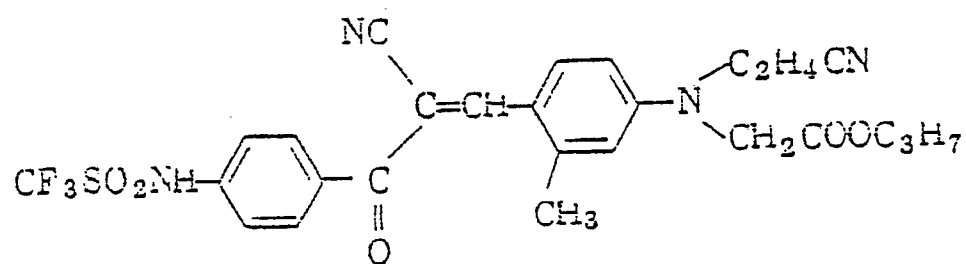
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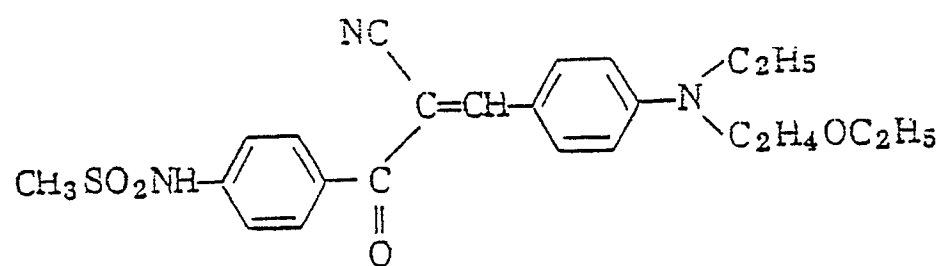
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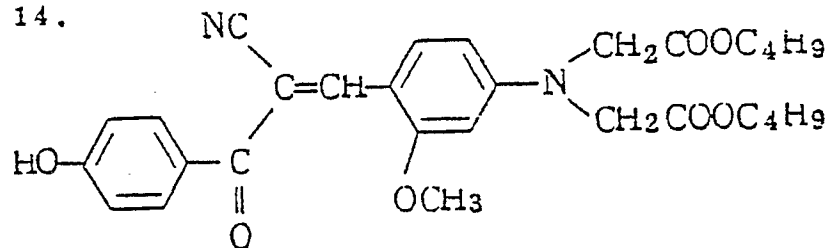
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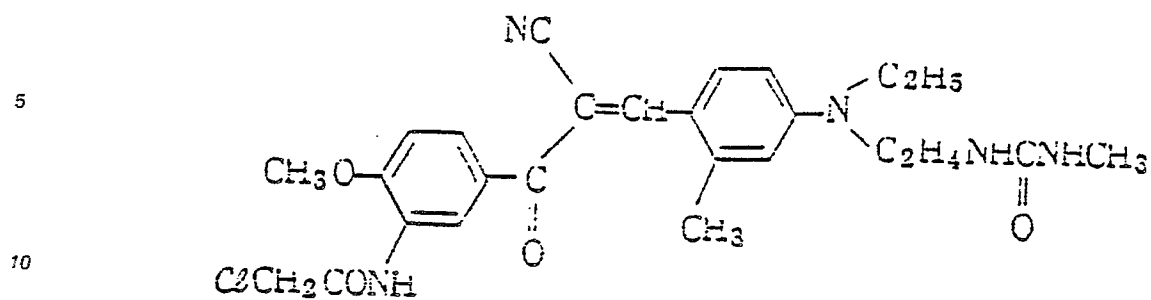
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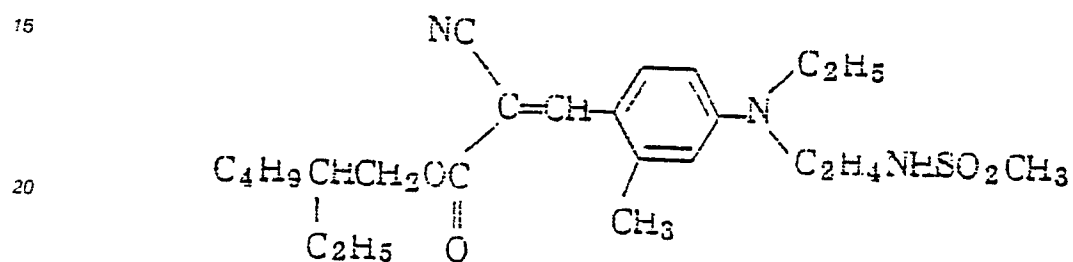
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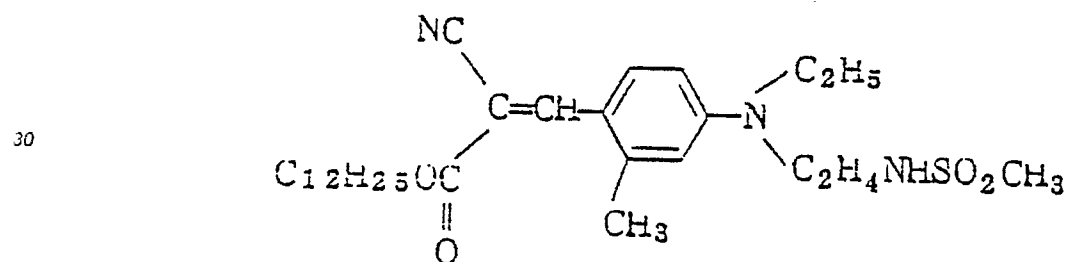
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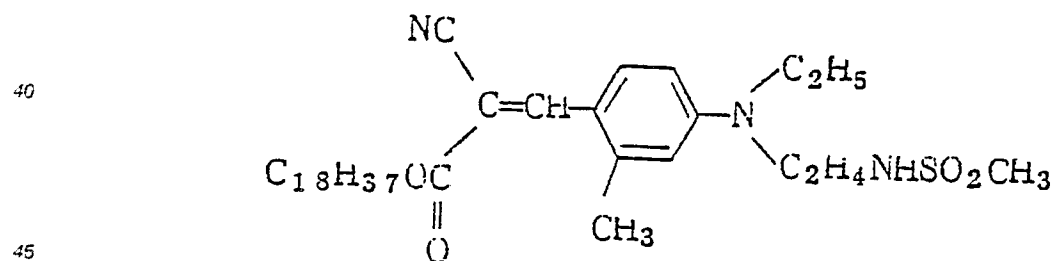
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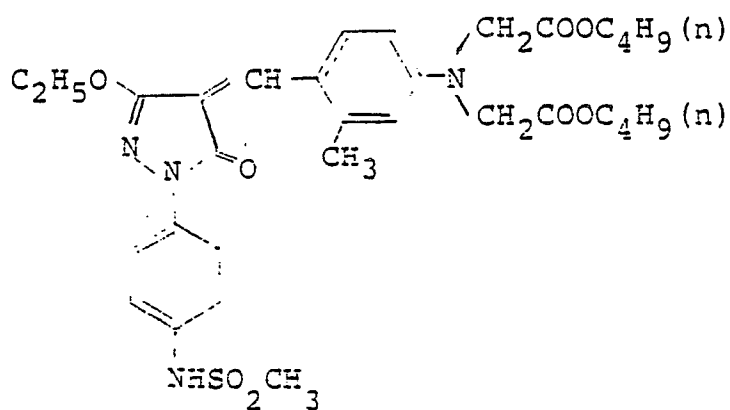
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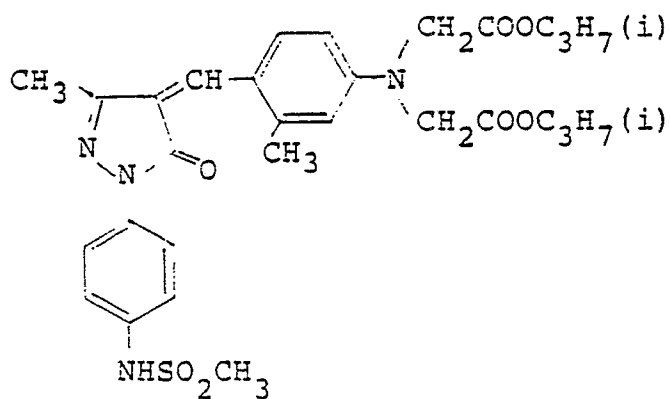
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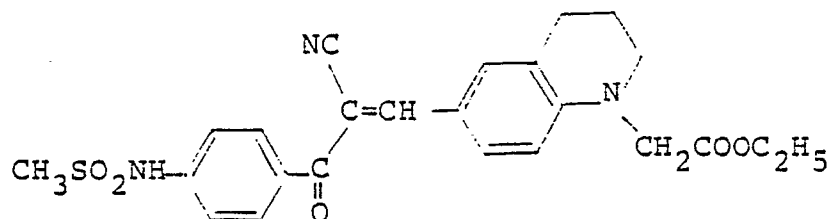
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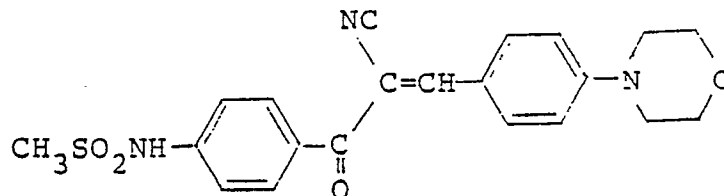
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The dye compounds of the formula (I) may easily be produced by the methods described in U.S. Patent 4,420,555, the disclosure of which is incorporated by reference, and JP-A-62-222248, JP-A-62-56958 and JP-A-63-40143.

In general, the dye compound of the formula (I) is incorporated into the photographic material in an amount of from 1 to 800 mg per m² of the material, preferably from 1 to 400 mg/m². The yellow colloidal silver is incorporated in the material in an amount of from 1 to 400 mg per m² of the material, preferably from 1 to 300 mg/m².

The dye compound of the formula (I) and the yellow colloidal silver may be incorporated into the same layer or into different layers in the photographic material. Preferably, both are incorporated into layer(s) which is(are) remoter from the support than the green-sensitive emulsion layer.

The amount ratio of the dye compound of the formula (I) to the yellow colloidal silver is preferably from 90/10 to 30/70 by weight.

When the dye compound of the formula (I) is used as a filter dye or an antihalation dye, it is preferably used in an amount that the optical density of the material may be adjusted to fall within the range of from 0.05 to 3.0. Regarding the time of the addition of the dye, it may be added to a coating composition at any stage before coating.

The dye compound of the present invention may be dispersed into an emulsion layer or any other hydrophilic colloid layer(s) (e.g., interlayer, protective layer, antihalation layer, filter layer) by various known methods, for example, as mentioned below.

(1) A method where the dye compound of the present invention is directly dissolved or dispersed into an emulsion layer or a hydrophilic colloid layer, or after the dye compound has been dissolved or dispersed in an aqueous solution or solvent, the resulting solution or dispersion is incorporated into an emulsion layer or a hydrophilic colloid layer. The dye may be dissolved in a suitable solvent, for example, methyl alcohol, ethyl alcohol, propyl alcohol, methyl cellosolve, the halogenated alcohol described in JP-A-48-9715 and U.S. Patent 3,756,830, acetone, water or pyridine or a mixed solvent thereof, and the resulting solution may be added to an emulsion.

(2) A method where a solution formed by dissolving the dye compound in a high boiling point solvent which is substantially insoluble in water and which has a boiling point of about 160°C or higher is dispersed into a hydrophilic colloid solution. As the high boiling point organic solvent, the compounds described in U.S. Patent 2,322,027 can be used, for example, an alkyl phthalate (e.g., dibutyl phthalate, dioctyl phthalate), a phosphoric acid ester (e.g., diphenyl phosphate, triphenyl phosphate, tricresyl phosphate, dioctylbutyl phosphate), a citric acid ester (e.g., tributyl acetylcitrate), a benzoic acid ester (e.g., octyl benzoate), an alkylamide (e.g., diethylaurylamide), a fatty acid ester (e.g., dibutoxyethyl succinate, diethyl azelate) and a trimesic acid ester (e.g., tributyl trimesate). In addition, an organic solvent having a boiling point of from about 30°C to about 150°C, such as lower alkyl acetates (e.g., ethyl acetate, butyl acetate), ethyl propionate, secondary butyl alcohol, methyl isobutyl ketone, β -ethoxyethyl acetate or methyl cellosolve acetate, as well as a solvent which is easily soluble in water, such as alcohols (e.g., methanol, ethanol) may also be used in the method.

The amount ratio of the dye to the high boiling point organic solvent to be used in the method is preferably from 10/1 to 1/10 (by weight).

(3) A method where the dye compound of the present invention and other additives are incorporated into the photographic material in the form of a polymer latex composition to be incorporated in the photographic emulsion layers or other hydrophilic colloid layers.

As the polymer latex for use in the method, for example, there are polyurethane polymers and polymers obtained by polymerization of vinyl monomers. Suitable vinyl monomers include acrylic acid esters (e.g., methyl acrylate, ethyl acrylate, butyl acrylate, hexyl acrylate, octyl acrylate, dodecyl acrylate, glycidyl acrylate, α -substituted acrylic acid esters (e.g., methyl methacrylate, butyl methacrylate, octyl methacrylate, glycidyl methacrylate), acrylamides (e.g., butylacrylamide, hexylacrylamide), α -substituted acrylamides (e.g., butyl methacrylamide, dibutyl methacrylamide), vinyl esters (e.g., vinyl acetate, vinyl butyrate), vinyl halides (e.g., vinyl chloride), vinylidene halides (e.g., vinylidene chloride), vinyl ethers (e.g., vinyl methyl ether, vinyl octyl ether), styrene, α -substituted styrene (e.g., α -methylstyrene), nucleus-substituted styrenes (e.g., hydroxystyrene, chlorostyrene, methylstyrene), as well as ethylene, propylene, butylene, butadiene and acrylonitrile. These may be used singly or in the form of combination of two or more of them. In addition, any other vinyl monomers may be blended with the said monomers, as a minor component. As examples of additional vinyl monomers, there may be mentioned itaconic acid, acrylic acid, methacrylic acid, hydroxyalkyl acrylates, hydroxyalkyl methacrylates, sulfoalkyl acrylates, sulfoalkyl methacrylates and styrenesulfonic acid.

The above polymer latexes may be produced in accordance with the methods described in JP-B-51-39853 (the term "JP-B" as used herein refers to an "examined Japanese patent publication"), and JP-A-51-59943, JP-A-53-137131, JP-A-54-32552, JP-A-54-107941, JP-A-55-133465, JP-A-56-19043, JP-A-56-19047, JP-A-56-126830 and JP-A-58-149038.

The proportion of the dye to the polymer latex to be used in the method is preferably from 10/1 to 1/10 (by weight).

(4) A method of dissolving the dye compound into water in the presence of a surfactant.

The surfactant for use in the method may be in the form of oligomers or polymers.

The details of the polymers are described in JP-A-60-158437.

(5) An alternative method for the abovementioned method (2), in which a hydrophilic polymer is used in place of or in addition to the high boiling point organic solvent. This method is described in detail, for example, in U.S. Patent 3,619,195 and West German Patent 1,957,467.

5 (6) The microcapsulating method described in JP-A-59-113434, in which a polymer having a carboxyl group or a sulfonic acid group in the side chains is used for microcapsulation.

In addition, a hydrosol of an oleophilic polymer, for example, that as described in JP-B-51-39835, may be added to the hydrophilic colloid dispersion obtained in the above-mentioned methods.

10 As the hydrophilic colloid for use in the present invention, gelatin is typical, but any other substances which have heretofore been known to be photographically useful may also be used.

Preparation of yellow colloidal silver is well known, and, for example, the yellow colloidal silver for use in the present invention may be prepared in accordance with the methods described in U.S. Patents 4,094,811 and 4,429,038, the disclosures of which are incorporated herein by reference, and JP-A-51-89722 and JP-A-58-91103.

15 The following are examples of the preparation of the yellow colloidal silver for use in the present invention, which are not to be construed as limiting the scope of the present invention.

1. To a distilled water 0.1 to 10 kg of dextrin was dissolved and 0.01 to 3 liters of a hydrogen peroxide solution (31 wt%) was added thereto. The pH was adjusted to 10 to 13 with sodium hydroxide and then a solution containing 1 kg of silver nitrate was added thereto with preferably keeping the temperature
20 of the mixture at about 25° C to 70° C. The higher temperature could provide a yellow colloidal silver having an absorption spectrum of longer wavelength.

2. To a distilled water 0.02 to 2 kg of sodium boron hydride was dissolved and the pH was adjusted to 10 to 13 with sodium hydroxide, and then a solution containing 1 kg of silver nitrate was added thereto with preferably keeping the temperature of the mixture at about 20° C to 70° C. In this case, the higher
25 temperature could also provide a yellow colloidal silver having an absorption spectrum of longer wavelength.

3. The pH of a solution containing 1 kg of silver nitrate was adjusted to 10 to 13 with sodium hydroxide, and then 0.01 to 10 kg of hydroquinone and 0.05 to 20 kg of sodium sulfite were added thereto with preferably keeping the temperature of the mixture at about 20° C to 70° C. Thus, a yellow colloidal
30 silver was obtained.

It was preferred that a chlorine ion or a bromine ion was added to the yellow colloidal silver at the preparation thereof or at the preparation of a coating solution for a yellow-colored filter layer by using alkali metal chloride, ammonium chloride, alkali metal bromide or ammonium bromide.

35 The light-sensitive silver halide emulsion for use in the present invention may comprise any one of silver bromide, silver iodobromide, silver iodochlorobromide, silver chlorobromide and silver chloride. Preferred examples of the silver halide for use in the present invention include silver bromide, silver chlorobromide, silver iodobromide and silver iodochlorobromide.

The silver halide grains in the photographic emulsion layer of the photographic material of the present
40 invention may have a regular crystal form such as cubic or octahedral form or may have an irregular crystal form such as spherical or tabular form, or the grains may also have a composite form composed of different crystal forms. The grains may also be a mixture comprising grains of various crystal forms.

The silver halide grains may have different phases in the inside and the surface layer in each grain, or they may have a uniform phase throughout the whole grain. The grains may be such that form a latent
45 image mainly in the surface part thereof (for example, negative emulsion grains) or such that form a latent image mainly in the inside thereof (for example, internal latent image type emulsion grains or prefogged direct reversal type emulsion grains).

The silver halide emulsion for use in the present invention may be such that contains tabular grains having a thickness of 0.5 μm or less, preferably 0.3 μm or less, a diameter of preferably 0.6 μm or more
50 and a mean aspect ratio of 5 or more, in a proportion of 50% or more of the total projected area. Combination of the emulsion containing tabular grains with an aspect ratio of 5 or more and the filter dye of the present invention is preferred to provide a silver halide color photographic material which is extremely excellent in sharpness and color reproducibility. The details of the tabular grain emulsion and the use thereof are described, for example, in Research Disclosure, Item 22534, pages 20 to 58 (January, 1983),
55 ibid., Item 22530, pages 237 to 240 (May, 1985).

The silver halide emulsion for use in the present invention may be a monodispersed emulsion in which grains having a grain size falling within the range of the mean grain size $\pm 40\%$ account for 95% by number of the grains or more.

The photographic emulsion for use in the present invention may be prepared by the methods described in P. Giakides, Chimie et Physique Photographique (published by Paul Montel, 1967), G.F. Duffin, Photographic Emulsion Chemistry (published by Focal Press, 1966), and V.L. Zelikman et al., Making and Coating Photographic Emulsion (published by Focal Press, 1964).

5 In formation of the silver halide grains for use in the present invention, a silver halide solvent may be used so as to control the growth of the grains, which includes, for example, ammonia, potassium thiocyanate, ammonium thiocyanate, thioether compounds (such as those described in U.S. Patents 3,271,157, 3,574,628, 3,704,130, 4,297,439 and 4,276,374), thione compounds such as those described in JP-A-53-144319, JP-A-53-82408 and JP-A-55-77737) and amine compounds (such as those described in
10 JP-A-54-100717).

The silver halide grains may be formed or physically ripened in the presence of a cadmium salt, a zinc salt, a thallium salt, an iridium salt or a complex salt thereof, a rhodium salt or a complex salt thereof, or an iron salt or a complex salt thereof.

The silver halide emulsion for use in the present invention is generally chemically sensitized. For
15 chemical sensitization, for example, the method described in H. Frieser, Die Grundlagen der Photographischen Prozesse mit Silberhalogeniden (published by Akademische Verlagsgesellschaft, 1968) may be used.

Briefly, a sulfur sensitization method using an active gelatin or a sulfur-containing compound capable of reacting with silver (for example, thiosulfates, thioureas, mercapto compounds, rhodanines), a reduction
20 sensitization method using a reducing substance (for example, stannous salts, amines, hydrazine derivatives, formamidinesulfinic acids, silane compounds, and a noble metal sensitization method using a noble metal (for example, gold metal complexes as well as complexes of metals of the VIII Group of the Periodic Table, such as Pt, Ir or Pd) may be used singly or in combination thereof.

The photographic emulsion for use in the present invention may contain various compounds for the
25 purpose of preventing fog during manufacture, storage and photographic processing of the photographic material or for the purpose of stabilizing the photographic property of the material. For example, various kinds of compounds which are known as an antifoggant or stabilizer may be used for the said purpose, which include azoles such as benzothiazolium salts, nitroindazoles, triazoles, benzotriazoles and benzimidazoles (especially nitro- or halogen-substituents); heterocyclic mercapto compounds such as mercaptothiazoles, mercaptobenzothiazoles, mercaptobenzimidazoles, mercaptothiadiazoles, mercaptotetrazoles
30 (especially 1-phenyl-5-mercaptotetrazole) and mercaptopyrimidines; the said heterocyclic mercapto compounds having a water-soluble group such as a carboxyl group or a sulfone group; thioketo compounds such as oxazolinethione; azaindenes such as tetraazaindenes (especially 4-hydroxy-substituted (1,3,3a,7)-tetraazaindenes); benzenethiosulfonic acids; benzenesulfinic acids; etc.

Various kinds of color couplers can be used in the present invention, and examples of color couplers
35 which may be used in the present invention are described in the patent publications as referred to in the aforesaid Research Disclosure (RD), Item 17643, VII-C to G. As the dye-forming couplers, those capable of giving one of three primary colors in subtractive color process (that is, yellow, magenta and cyan) by color development are important. Examples of nondiffusible 4-equivalent or 2-equivalent couplers are mentioned
40 in the patent publications as referred to in the aforesaid RD, Item 17643, VII-C to D, which may be used in the present invention. In addition, the following couplers are preferably used in the present invention.

As the yellow couplers for use in the present invention, there are known oxygen atom-releasing type yellow couplers and nitrogen atom-releasing type yellow couplers as the typical examples. In particular, α -pivaloylacetanilide couplers are excellent in fastness, especially light fastness of colored dyes formed, and
45 α -benzoylacetanilide couplers are excellent in coloring density.

As the magenta couplers for use in the present invention, there are hydrophobic ballast group-containing 5-pyrazolone couplers and pyrazoloazole couplers. As the 5-pyrazolone couplers, those substituted by an arylamino group or an acylamino group at the 3-position thereof are preferred from the viewpoint of the hue and coloring density of the colored dyes formed.

50 As the cyan couplers for use in the present invention, there are hydrophobic and nondiffusible naphthol couplers and phenol couplers. Preferably, oxygen atom-releasing type 2-equivalent naphthol couplers are mentioned as the typical examples. Couplers capable of forming cyan dyes which are durable to humidity and temperature are preferably used, and specific examples of such couplers include the phenol cyan couplers having an alkyl group of 2 or more carbon atoms at the meta-position of the phenol nucleus described in U.S. Patent 3,772,002, as well as 2,5-diacylamino-substituted phenol couplers and phenol
55 couplers having a phenylureido group at the 2-position and an acylamino group at the 5-position.

In the present invention, by using couplers giving colored dyes having a proper diffusibility together with the aforesaid color couplers, the graininess of color images formed can be improved. Specific

examples of magenta couplers of this type are described in U.S. Patent 4,366,237, and specific examples of yellow, magenta or cyan couplers of this type are described in European Patent 96,570.

The dye-forming couplers and the abovementioned specific couplers for use in the present invention may form dimers or higher polymers. Typical examples of the polymerized dye-forming couplers are described in U.S. Patent 3,451,820. Also, specific examples of the polymerized magenta couplers are described in U.S. Patent 4,367,282.

Couplers capable of releasing a photographically useful group along with coupling may also preferably be used in the present invention. As DIR couplers capable of releasing a development inhibitor, the couplers described in the patent publications as referred to in the aforesaid RD, Item 17643, VII-F are useful for the present invention.

The photographic material of the present invention can contain a coupler which may imagewise release a nucleating agent or a development accelerator or a precursor thereof in development. Examples of such compounds are described in British Patents 2,097,140 and 2,131,188.

The photographic emulsion for use in the present invention can contain, for example, polyalkylene oxides or ether, ester or amine derivatives thereof, thioether compounds, thiomorpholines, quaternary ammonium salt compounds, urethane derivatives, urea derivatives, imidazole derivatives and 3-pyrazolidones, for the purpose of elevation of sensitivity, enhancement of contrast and acceleration of developability.

The silver halide photographic emulsion for use in the present invention can contain any other known water-soluble dyes (for example, oxonol dyes, hemioxonol dyes, merocyanine dyes) than the particular dyes as specifically defined in the present invention, as a filter dye or for the purpose of antiirradiation and for other various purposes, the said known water-soluble dyes being incorporated into the emulsion together with the particular dye of the present invention. Further, the emulsion may also contain any other known cyanine dyes, merocyanine dyes or hemicyanine dyes than the particular dyes of the present invention, as a spectral sensitizer which is to be incorporated into the emulsion together with the particular dye of the invention.

The photographic emulsion for use in the present invention can contain various surfactants for various purposes of coating aid, static charge prevention, reduction of friction, emulsification and dispersion, prevention of surface blocking and improvement of photographic characteristics (for example, acceleration of developability, enhancement of contrast and elevation of sensitivity).

The photographic material of the present invention can contain various additives such as anti-fading agent, hardening agent, color fogging inhibitor, ultraviolet absorbent, and protective colloid (e.g., gelatin). Examples of these additives are described in the aforesaid RD, Item 17643.

The finished emulsion is coated on a suitable support, for example, baryta paper, resin-coated paper, synthetic paper, triacetate film, polyethylene terephthalate film and other plastic base or glass plate.

As examples of the silver halide photographic material of the present invention, there may be mentioned color positive film, color paper, color negative film, color reversal film (containing or not containing coupler), photomechanical photographic material (e.g., lith film, lith dupe film), photographic material for cathode ray display (e.g., photographic material for X-ray recording in emulsion, photographic material for direct or indirect photographing with screen), photographic material for silver salt diffusion transfer process, photographic material for color diffusion transfer process, photographic material for imbibition transfer process, heat developing photographic material, etc.

In order to obtain photographic images, the photographic material of the present invention may be exposed in a conventional manner. For example, various kinds of known light sources such as natural light (sunlight), tungsten lamp, fluorescent lamp, mercury lamp, xenon arc lamp, carbon arc lamp, xenon flash lamp or cathode ray flying spot may be used for exposure of the photographic material of the present invention. The exposure time may be from 1/1,000 second to 1 second, like the case for conventional camera. However, this is not limitative and may be shorter than 1/1,000 second, for example, from $1/10^4$ to $1/10^6$ second, like the case using a xenon flash lamp or cathode ray tube, or on the contrary may be longer than 1 second. If necessary, a color filter may be used so as to control the spectral composition of the light used for exposure. A laser ray may also be used for exposure. Further, the photographic material may also be exposed with a light as emitted from a fluorescent substance excited by electron ray, X-ray, α -ray or γ -ray.

For photographically processing the photographic material of the present invention, any known methods and known processing solutions, for example, those described in the aforesaid RD, Item 17643, may be employed. The processing temperature is generally selected from the range between 18°C and 50°C, but it may be lower than 18°C or higher than 50°C. It is especially preferred that the photographic material of the present invention is processed by color development so as to form color images.

The color developer which may be used for processing the photographic material or the present invention is an alkaline aqueous solution containing a color developing agent. The color developing agent may be a known primary aromatic amine developing agent of phenylenediamines, such as 4-amino-N,N-diethylaniline, 3-methyl-4-amino-N,N-diethylaniline, 4-amino-N-ethyl-N- β -hydroxyethylaniline, 3-methyl-4-amino-N-ethyl-N- β -hydroxyethylaniline, 3-methyl-4-amino-N-ethyl-N- β -methanesulfonamidoethylaniline or 4-amino-3-methyl-N-ethyl-N- β -methoxyethylaniline.

In addition, the developers described in L.F.A. Mason, Photographic Processing Chemistry (published by Focal Press, 1966), pages 226 to 229, U.S. Patents 2,193,015 and 2,592,364 and JP-A-48-64933 may also be used.

The developer may additionally contain a pH buffer such as alkali metal sulfites, bisulfites, carbonates, borates or phosphates, as well as a development inhibitor or an antifoggant such as bromides, iodides or organic antifoggants. In addition, it may also contain, if desired, a water softener, a preservative such as hydroxylamine, an organic solvent such as benzyl alcohol or diethylene glycol, a development accelerator such as polyethylene glycol, quaternary ammonium salts or amines, a dye-forming coupler, a competing coupler, a foggant such as sodium boron hydride, an auxiliary developing agent such as 1-phenyl-3-pyrazolidone, a tackifier, the polycarboxylic acid chelating agent as described in U.S. Patent 4,083,723, and the antioxidant described in West German Patent Application (OLS) No. 2,622,950.

The developer is preferred to have a pH value of 8 or more, especially preferably 9 or more. The concentration of the sulfite or bisulfite in the developer is preferably 10^{-3} mol/liter or more, especially preferably 10^{-2} mol/liter or more.

The fixing solution or bleach-fixing solution to be used for processing the photographic material of the present invention preferably contains a sulfite or bisulfite.

The bleaching solution and bleach-fixing solution as well as the prebath thereof may contain a compound which is known as a bleaching accelerator, for example, the mercapto group or disulfide group-containing compounds described in U.S. Patent 3,893,858, West German Patents 1,290,812 and 2,059,988, JP-A-53-32736, JP-A-53-57831, JP-A-53-37418, JP-A-53-65832, JP-A-53-72623, JP-A-53-95630, JP-A-53-95631, JP-A-53-104232, JP-A-53-124424, JP-A-53-141623 and JP-A-53-28426, and RD, Item 17129, the thiazolidine derivatives described in JP-A-50-140129, the thiourea derivatives described in JP-B-45-8506, JP-A-52-20832 and JP-A-53-32735, and U.S. Patent 3,706,561, the iodides described in West German Patent 1,127,715 and JP-A-58-16235, the polyethylene oxides described in West German Patents 966,410 and 2,748,430, the polyamine compounds described in JP-B-45-8836, and the 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.

The process for processing the photographic material of the present invention comprises the above-mentioned color development, bleaching and fixation steps. After the fixation or bleach-fixation step, the photographic material is generally rinsed in water or stabilized. If acceptable, the material may simply be rinsed in water only without being subjected to stabilization, or on the contrary, it may also simply be stabilized only without being rinsed in water.

As the stabilizing solution to be used in the stabilizing step, a processing solution capable of stabilizing the color image formed is used. For example, a solution having a buffer capacity of from pH 3 to pH 6 or a solution containing an aldehyde (such as formalin) can be used. If desired, the stabilizing solution may optionally contain a brightening agent, a chelating agent, a bactericide, a fungicide, a hardening agent and a surfactant.

If necessary, two or more tanks may be used for the stabilization step. For example, a so-called multistage countercurrent stabilization (e.g., from 2 to 9 stages) may be employed so as to economize the stabilizing solution to be used, and the rinsing-in-water step may be omitted.

The rinsing water to be used in the rinsing step may optionally contain known additives. For example, it may contain a chelating agent such as inorganic phosphoric acids, aminopolycarboxylic acids or organic phosphoric acids, a bactericide or fungicide capable of preventing propagation of various bacteria and algae, a hardening agent such as magnesium salts or aluminum salts, and a surfactant for preventing drying load or unevenness. In addition, the compounds described in L.E. West, Photographic Science and Engineering (Water Quality Criteria), Vol. 9, No. 6, pages 344 to 359 (1965) may also be incorporated into the rinsing water.

If necessary, two or more tanks may be used for the rinsing-in-water step. For example, a so-called multistage countercurrent rinsing (e.g., from 2 to 9 stages) may be employed so as to economize the rinsing water to be used.

As explained in detail in the above, the multilayer silver halide photographic material of the present invention has both the particular yellow dye and the yellow colloidal silver and therefore is excellent in the antihalation effect and the sensitivity adjusting effect in the light-sensitive emulsions of the material. In the

characteristic constitution of the silver halide photographic material of the present invention, the dye in the dye layer may have a proper spectral absorption to selectively dye the dye layer without diffusing into any other layers. The function of the dye is noticeable and excellent.

In particular, when the dye compound of the formula (II) and yellow colloidal silver are incorporated into a filter layer, the layer may easily be discolored and the dye compound may be dissolved out of the layer by photographic processing to give a low Dmin without lowering the sensitivity. Further, the sensitivity of the photographic material having such filter layer is hardly lowered even after the material has been stored long. This is another characteristic aspect of the invention.

As still another characteristic feature of the present invention, the silver halide photographic material of the present invention may form an image having an improved sharpness. Further, the photograph obtained from the silver halide photographic material of the present invention is hardly stained and the photographic property thereof is stable and does not deteriorate even after the photograph has been stored for a long period of time.

The following example is intended to illustrate the present invention in greater detail but not to limit it in any way.

EXAMPLES

A multilayer color photographic material (Comparative Sample No. 101) having no dye compound of formula (I) was prepared by forming the layers each having the composition mentioned below on a subbed cellulose triacetate film support.

Constitution of Light-Sensitive Layers:

The amount coated was represented by the unit of g/m² based on the amount of silver for the silver halide and colloidal silver, and by the unit of g/m² for the coupler, additives and gelatin. The amount of the sensitizing dye coated was represented by the unit of the number of mols per mol of the silver halide in the same layer. The symbols for additives have the meanings as mentioned below. When the additive used had plural functions, it was represented by the typical function thereof.

UV: Ultraviolet Absorbent

Solv: High Boiling Point Organic Solvent

ExF: Dye

ExS: Sensitizing Dye

ExC: Cyan Coupler

ExM: Magenta Coupler

ExY: Yellow Coupler

Cpd: Additive

First Layer: Antihalation Layer

Black colloidal silver 0.15

Gelatin 2.9

UV-1 0.03

UV-2 0.06

UV-3 0.07

Solv-2 0.08

ExF-1 0.01

ExF-2 0.01

Second Layer: Low-Sensitive Red-Sensitive Emulsion Layer

Silver iodobromide emulsion 0.4 as Ag

(AgI: 4 mol%, uniform sphere-corresponding
diameter: 0.4 μ m, fluctuation coefficient
of sphere-corresponding diameter: 37%,
tabular grains, aspect ratio of diameter/
thickness: 3.0)

	Gelatin	0.8
	ExS-1	2.3×10^{-4}
5	ExS-2	1.4×10^{-4}
	ExS-5	2.3×10^{-4}
	ExS-7	8.0×10^{-6}
10	ExC-1	0.17
	ExC-2	0.03
15	ExC-3	0.13

Third Layer: Middle Sensitive Red-Sensitive Emulsion

Layer

20	Silver iodobromide emulsion	0.65 as Ag
	(AgI: 6 mol%, core/shell (2/1) type	
25	with AgI-rich core, sphere-corresponding	
	diameter: 0.65 μm , fluctuation coefficient	
	of sphere-corresponding diameter: 25%,	
30	tabular grains, aspect ratio of diameter/	
	thickness: 2.0)	
35	Silver iodobromide emulsion	0.1 as Ag
	(AgI: 4 mol%, uniform AgI type, sphere-	
	corresponding diameter: 0.4 μm , fluctuation	
40	coefficient of sphere-corresponding	
	diameter: 37%, tabular grains, aspect ratio	
45	of diameter/thickness: 3.0)	

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	Gelatin	1.0
	ExS-1	2×10^{-4}
5	ExS-2	1.2×10^{-4}
	ExS-5	2×10^{-4}
	ExS-7	7×10^{-6}
10	ExC-1	0.31
	ExC-2	0.01
15	ExC-3	0.06
<u>Fourth Layer: High Sensitive Red-Sensitive Emulsion Layer</u>		
20	Silver iodobromide emulsion	0.9 as Ag
	(AgI: 6 mol%, core/shell (2/1) type with	
	AGI-rich core, sphere-corresponding	
25	diameter: 0.7 μ m, fluctuation coefficient	
	of sphere-corresponding diameter: 25%,	
	tabular grains, aspect ratio of diameter/	
30	thickness: 2.5)	
	Gelatin	0.8
35	ExS-1	1.6×10^{-4}
	ExS-2	1.6×10^{-4}
	ExS-5	1.6×10^{-4}
40	ExS-7	6×10^{-4}
	ExC-1	0.07
45	ExC-4	0.05
	Solv-1	0.07
	Solv-2	0.20
50	Cpd-7	4.6×10^{-4}

Fifth Layer: Interlayer

	Gelatin	0.6
5	UV-4	0.03
	UV-5	0.04
	Cpd-1	0.1
10	Polyethyl acrylate latex	0.08
	Solv-1	0.05

Sixth Layer: Low Sensitive Green-Sensitive Emulsion Layer

	Silver iodobromide emulsion	0.18 as Ag
20	(AgI: 4 mol%, uniform type, sphere- corresponding diameter: 0.4 μ m, fluctuation coefficient of sphere- corresponding diameter: 37%, tabular grains, aspect ratio of diameter/ thickness: 2.0)	
30	Gelatin	0.4
	ExS-3	2×10^{-4}
35	ExS-4	7×10^{-4}
	ExS-5	1×10^{-4}
40	ExM-5	0.11
	ExM-7	0.03
	ExY-8	0.01
45	Solv-1	0.09
	Solv-4	0.01

Seventh Layer: Middle Sensitive Green-Sensitive EmulsionLayer

5	Silver iodobromide emulsion	0.27 as Ag
	(AgI: 4 mol%, core/shell (1/1) type	
	with AgI-rich shell, sphere-corresponding	
10	type, sphere-corresponding diameter: 0.5 μ m,	
	fluctuation coefficient of sphere-	
15	corresponding diameter 20%, tabular grains,	
	aspect ratio of diameter/thickness: 4.0)	
20	Gelatin	0.6
	ExS-3	2×10^{-4}
	ExS-4	7×10^{-4}
25	ExS-5	1×10^{-4}
	ExM-5	0.17
	ExM-7	0.04
30	ExY-8	0.02
	Solv-1	0.14
35	Solv-4	0.02

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Eighth Layer: High Sensitive Green-Sensitive Emulsion
Layer

5	Silver iodobromide emulsion	0.7 as Ag
	(AgI: 8.7 mol%, multilayered grains with	
	silver ratio of 3/4/2 as the layers,	
10	AgI content of 24 mol%, 0 mol% and 3 mol%	
	in the order from the inside, sphere-	
15	corresponding diameter: 0.7 μm , fluctuation	
	coefficient of sphere-corresponding diameter:	
20	25%, tabular grains, aspect ratio of	
	diameter/thickness: 1.6)	
	Gelatin	0.8
25	ExS-4	5.2×10^{-4}
	ExS-5	1×10^{-4}
30	ExS-8	0.3×10^{-4}
	ExM-5	0.1
	ExM-6	0.03
35	ExY-8	0.02
	ExC-1	0.02
	ExC-4	0.01
40	Solv-1	0.25
	Solv-2	0.06
45	Solv-4	0.01
	Cpd-7	1×10^{-4}

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Ninth Layer: Interlayer

	Gelatin	0.6
5	Cpd-1	0.14
	Polyethyl acrylate latex	0.12
10	Solv-1	0.02

Tenth Layer: Interlayer Effect Donor Layer to Red-Sensitive Layer

15	Silver iodobromide emulsion	0.68 as Ag
	(AgI: 6 mol%, core/shell (2/1) type with	
20	AgI-rich core, sphere-corresponding	
	diameter: 0.7 μ m, fluctuation coefficient	
	of sphere-corresponding diameter: 25%,	
25	tabular grains, aspect ratio of diameter/	
	thickness: 2.0)	
30	Silver iodobromide emulsion	0.19 as Ag
	(AgI: 4 mol%, uniform type, fluctuation	
	coefficient of sphere-corresponding	
35	diameter: 37%, tabular grains, aspect	
	ratio of diameter/thickness: 3.0)	
40	Gelatin	1.0
	ExS-3	6×10^{-4}
	ExM-10	0.19
45	Solv-1	0.20

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Eleventh Layer: Yellow Filter Layer

	Yellow colloidal silver	0.12
5	Gelatin	0.8
	Solv-1	0.06
10	Cpd-1	0.07
	Cpd-6	0.002
	H-1	0.13

15 Twelfth Layer: Low Sensitive Blue-Sensitive Emulsion
Layer

20	Silver iodobromide emulsion	0.3 as Ag
	(AgI: 4.5 mol%, uniform AgI type, sphere-	
	corresponding diameter: 0.7 μ m, fluctuation	
25	coefficient of sphere-corresponding	
	diameter: 15%, tabular grains, aspect	
30	ratio of diameter/thickness: 7.0)	
	Silver iodobromide emulsion	0.15 as Ag
	(AgI: 3 mol%, uniform AgI type, sphere-	
35	corresponding diameter: 0.3 μ m, fluctuation	
	coefficient of sphere-corresponding	
40	diameter: 30%, tabular grains, aspect	
	ratio of diameter/thickness: 7.0)	
	Gelatin	1.8
45	ExS-6	9×10^{-4}
	ExC-1	0.06
50	ExC-4	0.03

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	ExY-9	0.14
5	ExY-11	0.89
	Solv-1	0.42
	<u>Thirteenth Layer: Interlayer</u>	
10	Gelatin	0.7
	ExY-12	0.20
15	Solv-1	0.34
	<u>Fourteenth Layer: High Sensitive Blue-Sensitive Emulsion</u>	
	<u>Layer</u>	
20	Silver iodobromide emulsion	0.5 as Ag
	(AgI: 10 mol%, AgI-rich core type,	
	sphere-corresponding diameter: 1.0 μm ,	
25	fluctuation coefficient of sphere-	
	corresponding diameter: 25%, multilayered	
30	twin tabular grains, aspect ratio of	
	diameter/thickness: 2.0)	
35	Gelatin	0.5
	ExS-6	1×10^{-4}
	ExY-9	0.01
40	ExY-11	0.20
	ExC-1	0.02
45	Solv-1	0.10
50		
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Fifteenth Layer: First Protective Layer

5	Fine silver bromide grain emulsion	0.12 as Ag
	(AgI: 2 mol%, uniform AgI type, sphere- corresponding diameter: 0.07 μ m)	
10	Gelatin	0.9
	UV-4	0.11
	UV-5	0.16
15	Solv-5	0.02
	H-1	0.13
20	Cpd-5	0.10
	Polyethyl acrylate latex	0.09

Sixteenth Layer: Second Protective Layer

25	Fine silver bromide grain emulsion	0.36 as As
	(AgI: 2 mol%, uniform AgI type, sphere- corresponding diameter: 0.07 μ m)	
30	Gelatin	0.55
	Polymethyl methacrylate grains	0.2
35	(diameter: 1.5 μ m)	
	H-1	0.17

40 The respective layers contained an emulsion stabilizer Cpd-3 (0.07 g/m² and a surfactant Cpd-4 (0.03 g/m²) as coating aids, in addition to the abovementioned components.

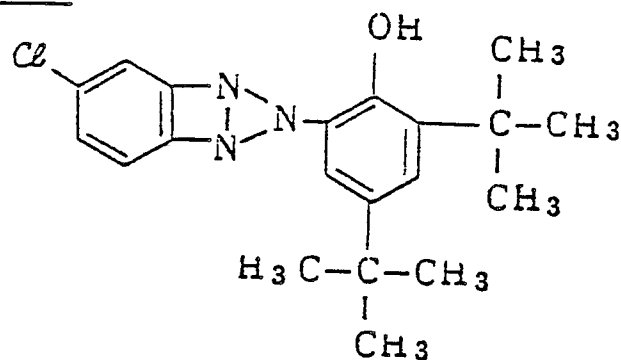
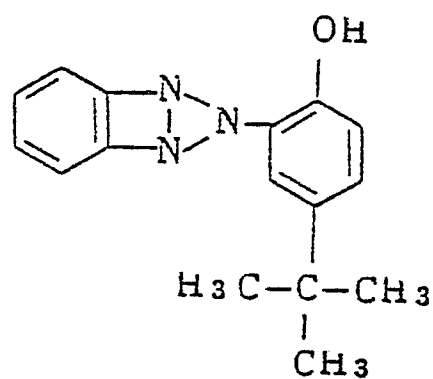
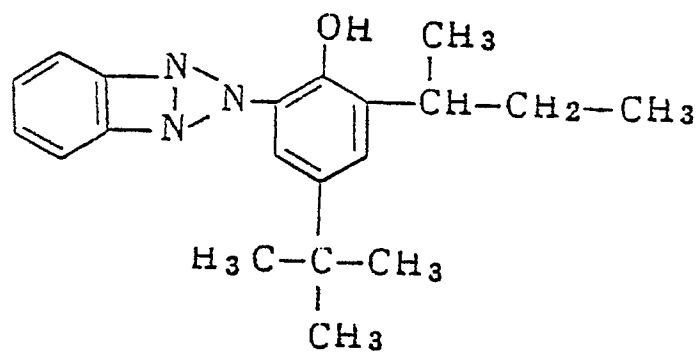
The yellow colloidal silver to be incorporated into the eleventh layer was prepared as follows:

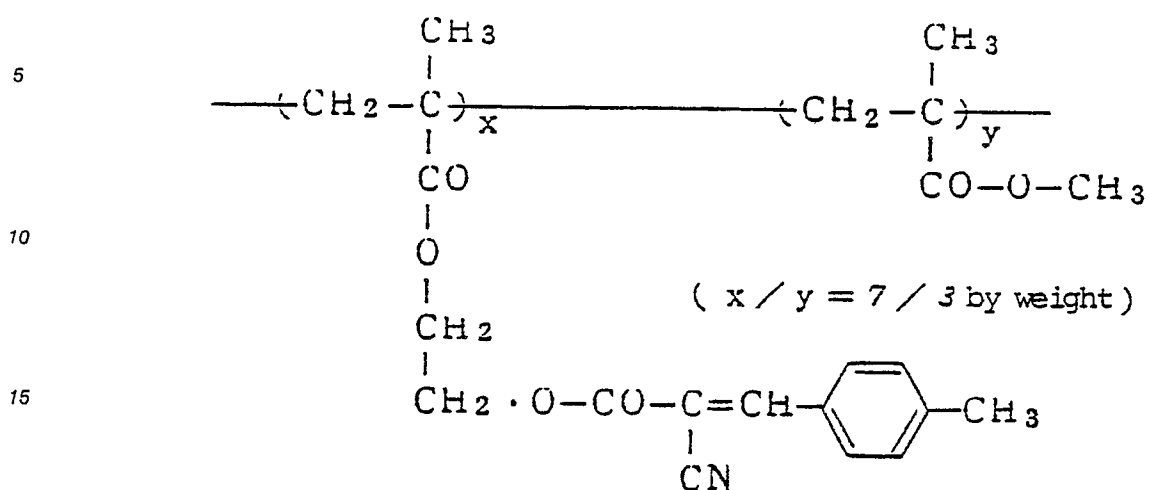
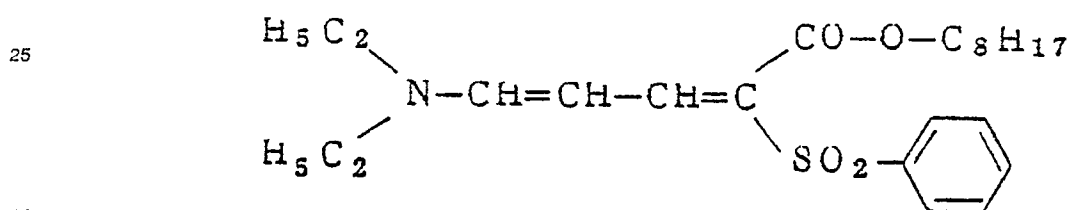
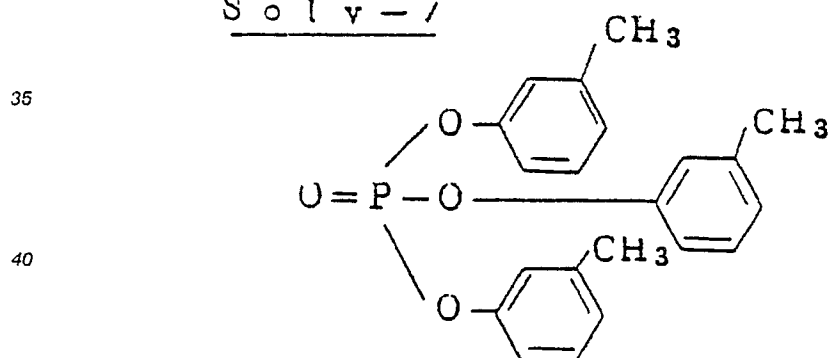
Dextrin was dissolved in a distilled water the pH of which was adjusted to 12.0 with sodium hydroxide and the temperature of which was maintained at about 40° C. To the thus-obtained dextrin solution, a
45 hydrogen peroxide solution and a silver nitrate solution were added in this order. After gelatin was added, desalting was conducted to obtain a yellow colloidal silver.

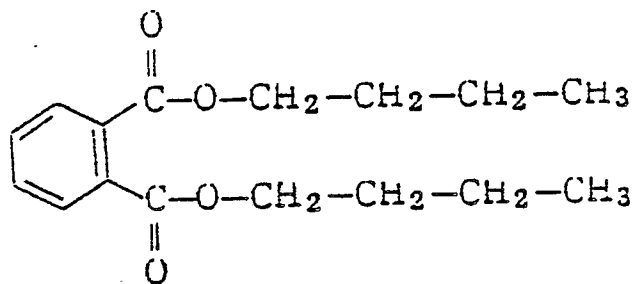
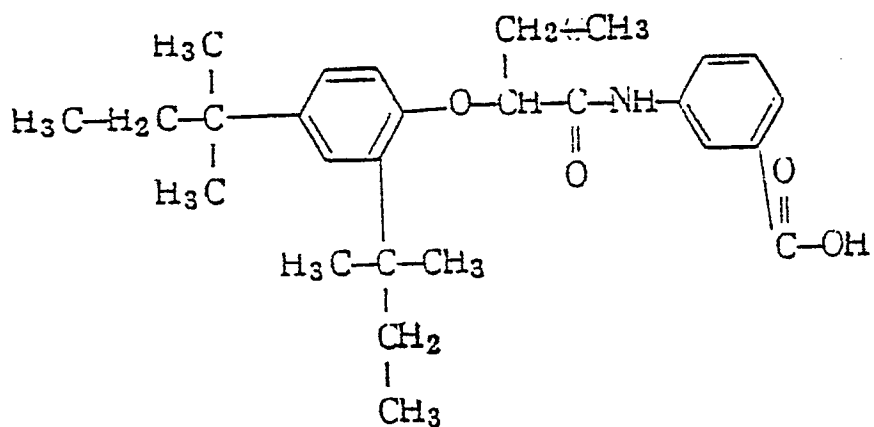
The compounds used in the layers were as follows:

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UV - 1UV - 2UV - 3

U V - 4U V - 5S o l v - 1

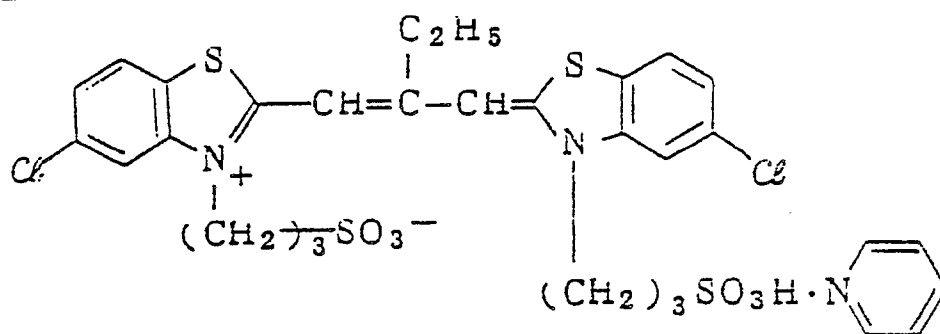
S o l v - 2S o l v - 4

Ex S - 2

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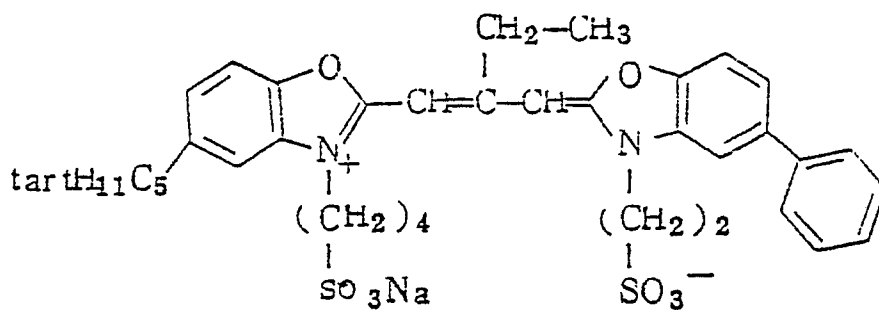
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Ex S - 3

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Ex S - 4

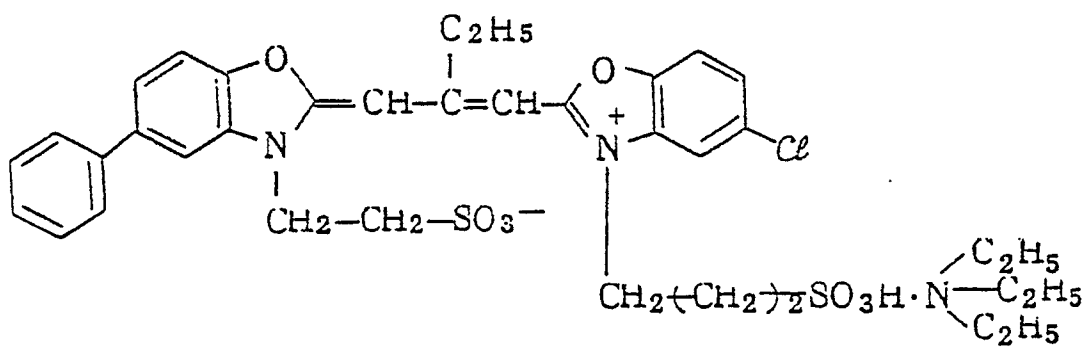
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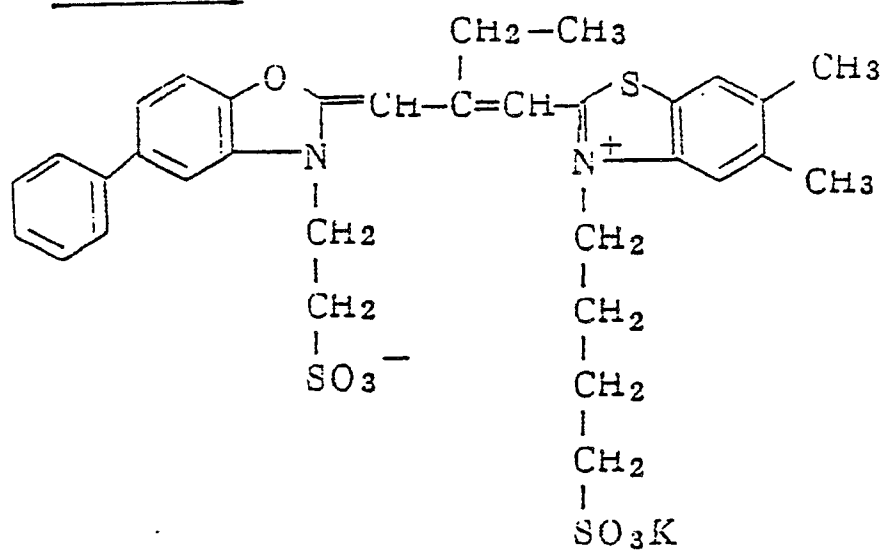
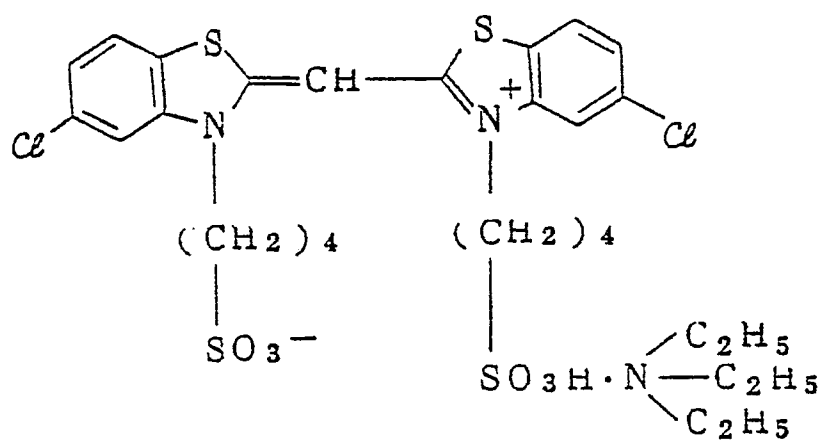
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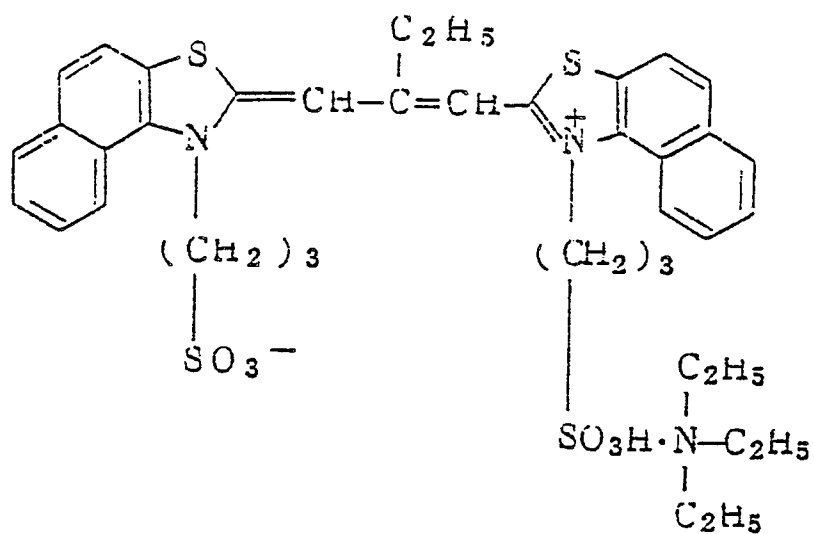
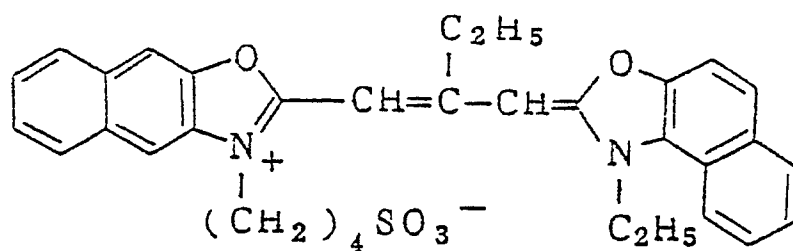
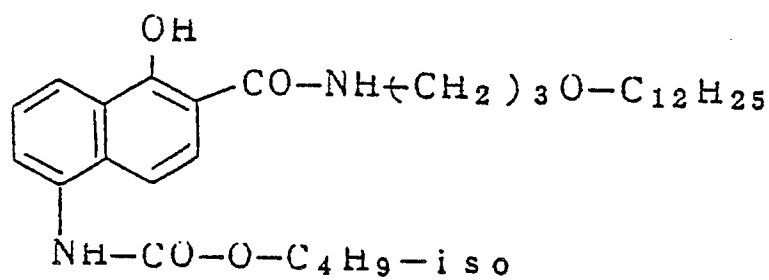
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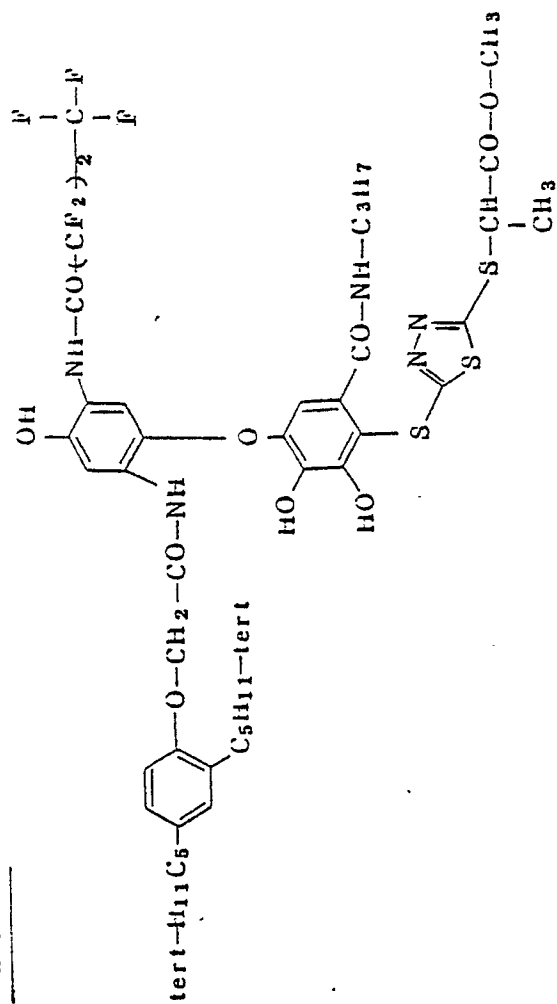
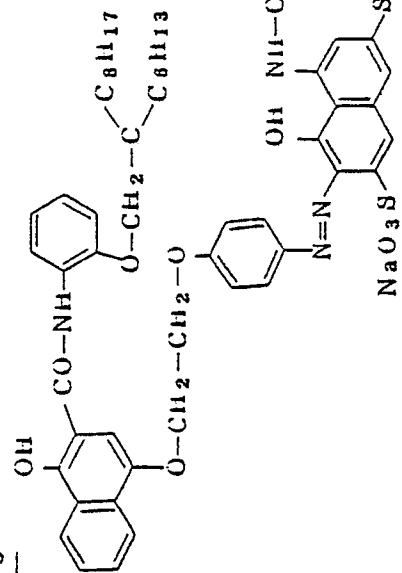
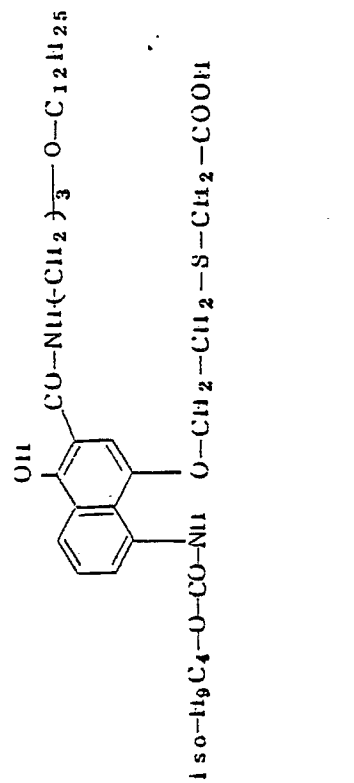
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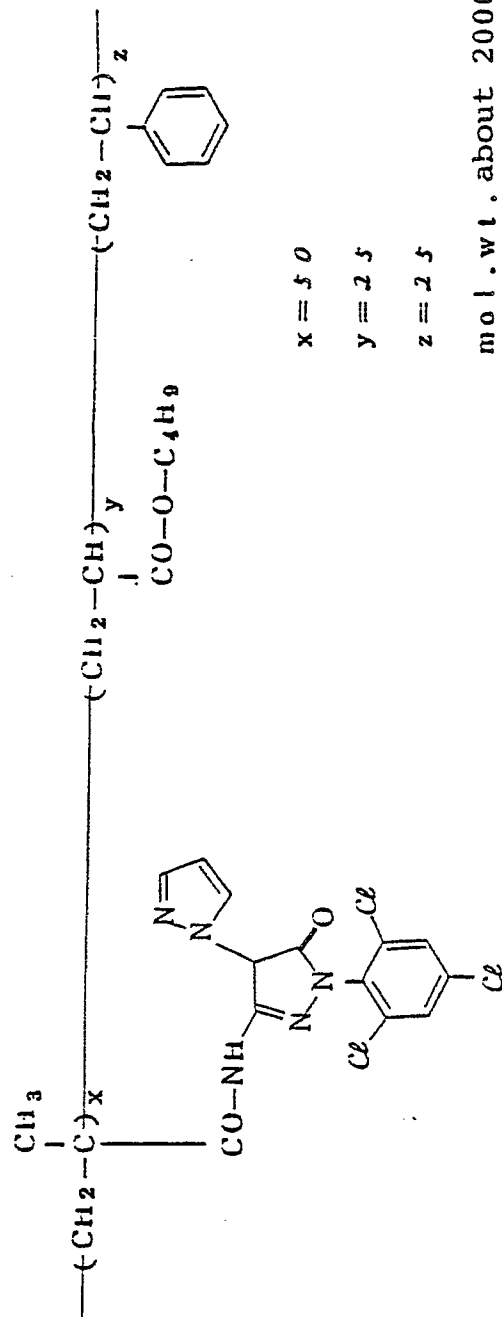
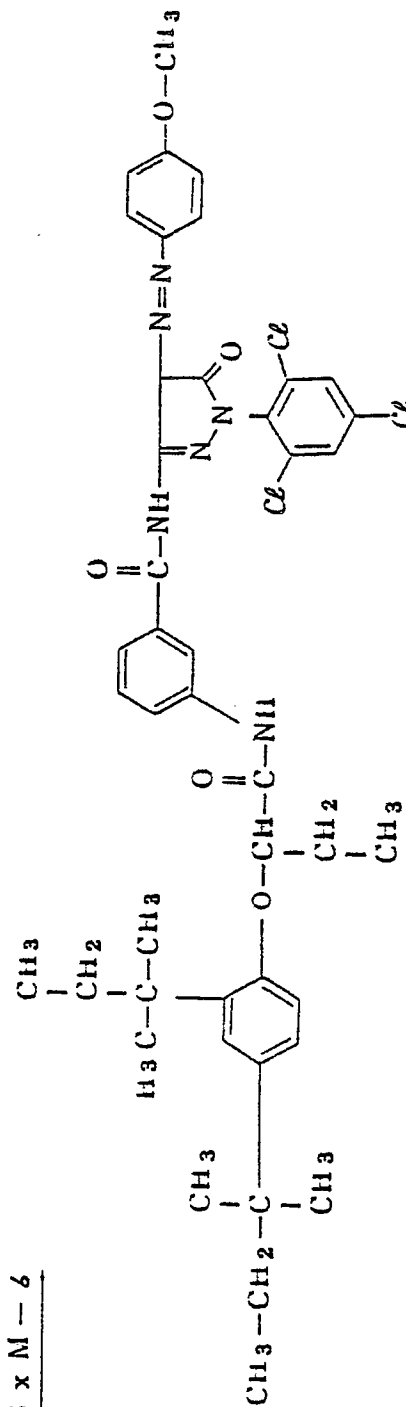
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Ex S - 5Ex S - 6

E x S - 7E x S - 8E x C - 1

Ex C - 2Ex C - 3Ex C - 4

Ex M - 5Ex M - 6

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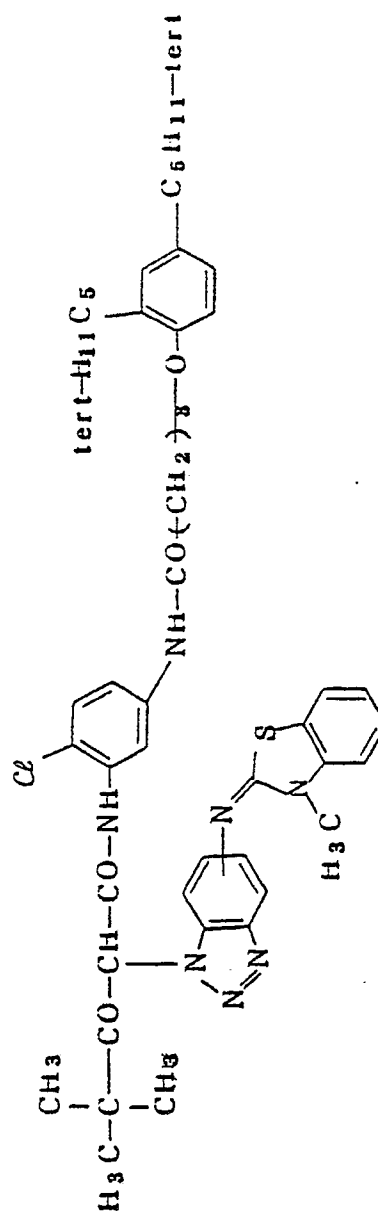
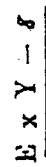
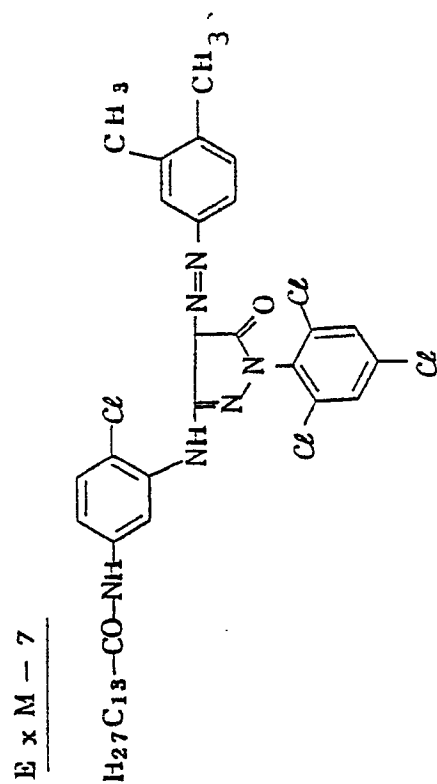
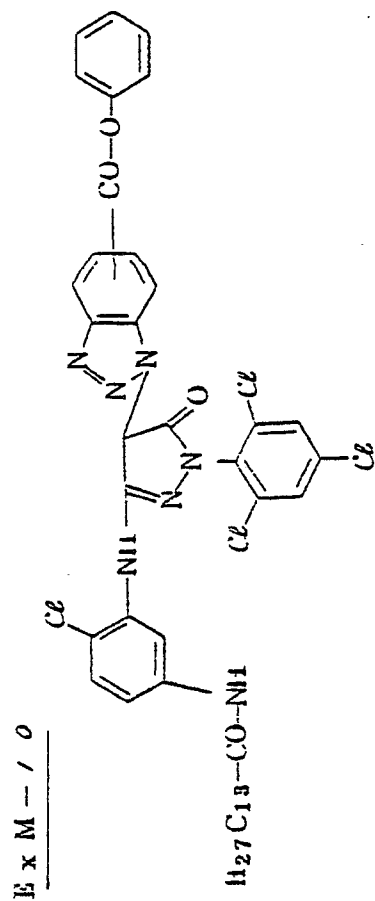
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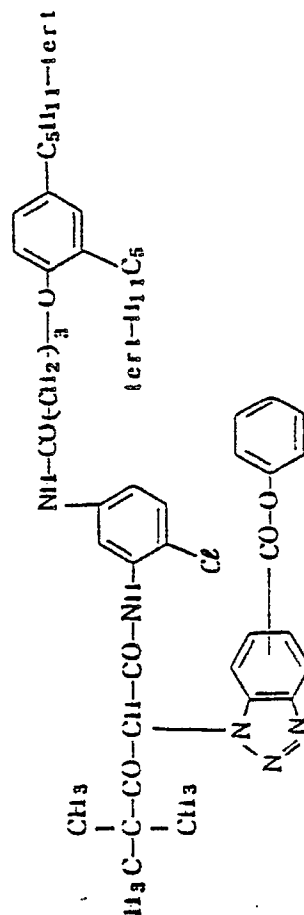
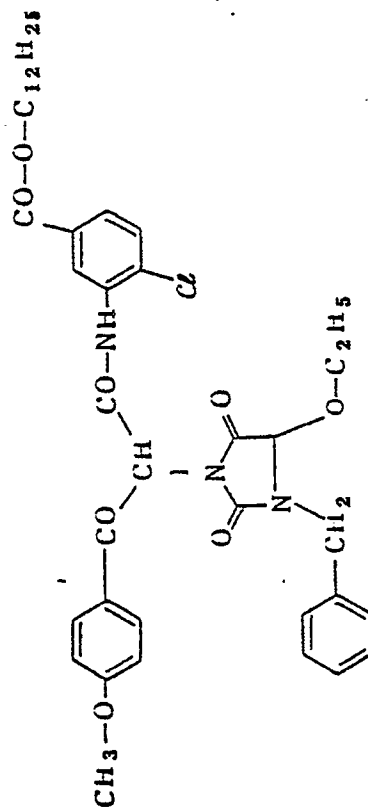
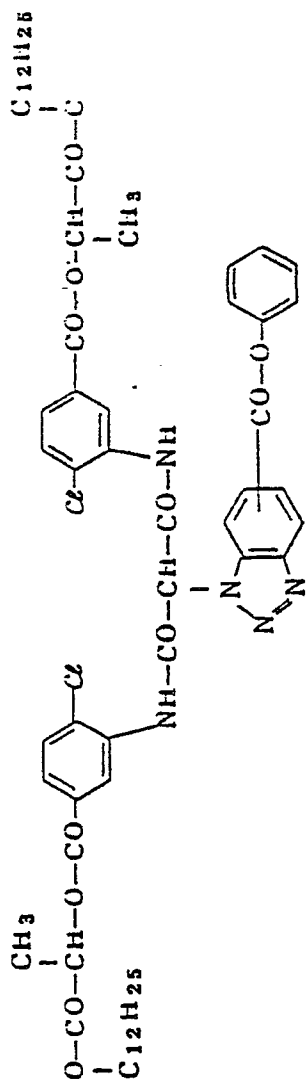
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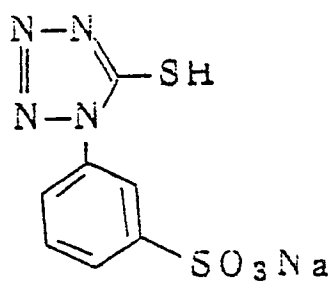


C p d - 7

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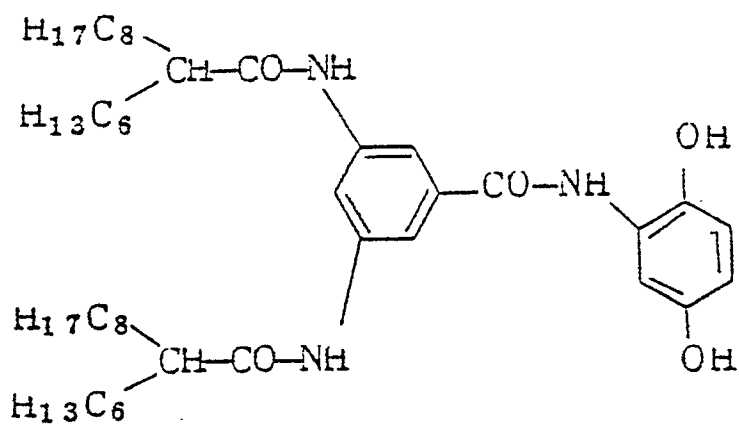
C p d - 1

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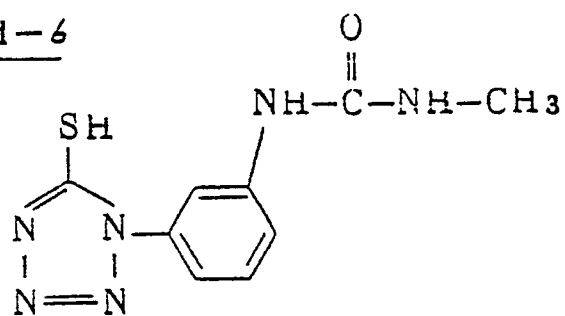
C p d - 6

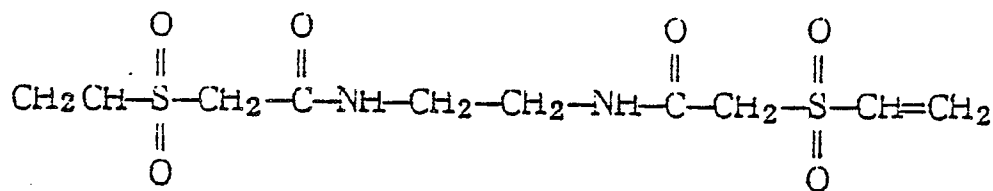
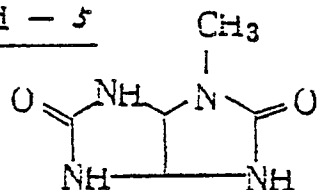
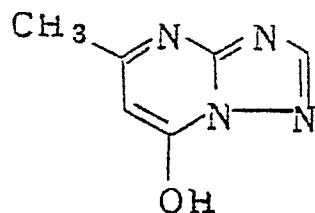
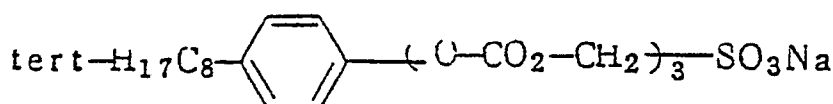
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H - 1C p d - 5C p d - 3C p d - 4Preparation of Comparative Sample Nos. 102 to 104:

Comparative Sample Nos. 102, 103 and 104 were prepared in the same manner as the preparation of Comparative Sample No. 101, except that a dispersion obtained by dissolving Dye Compound Nos. 5, 1 and 8 (of the invention, mentioned above), respectively, in tricresyl phosphate and ethyl acetate and emulsifying the resulting solution with gelatin was used in place of the yellow colloidal silver in the eleventh layer.

The amount of Dye Compound Nos. 5, 1 and 8 used was 0.26 g/m², and the amount of the tricresyl phosphate used was the same as that of the said compound.

Preparation of Sample Nos. 105 to 107:

Sample Nos. 105, 106 and 107 were prepared in the same manner as the preparation of Sample No.

101, except that the amount of the yellow colloidal silver in the eleventh layer was reduced to 0.06 g/m², and 0.13 g/m² of Compounds 5, 1 and 8, respectively, were added to the eleventh layer. The dye (Compounds 5, 1 and 8) was emulsified in the same manner as in the preparation of Sample Nos. 102 to 104.

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Preparation of Reference Sample No. 108:

Reference Sample No. 108 was prepared in the same manner as the preparation of Sample No. 101, except that the yellow colloidal silver was not added to the eleventh layer.

Sample Nos. 101 to 108 thus prepared were wedgewise exposed and then developed in accordance with the procedure mentioned below.

On the other hand, in order to evaluate the discolorability of the dye, a different color developer was prepared, which was the same as the color developer mentioned below but did not contain 4-(N-ethyl-N- β -hydroxyethylamino)-2-methylaniline sulfate, and this was used for processing the exposed samples. The other steps were the same as the Steps 2 to 6 mentioned below.

The discolorability of the dye in the thus processed samples was evaluated by the difference between the yellow density in each of Sample Nos. 101 to 107 and that in Sample No. 108 which was represented by $\Delta D_{\min}^B$.

In order to evaluate the stability with the lapse of time of these samples, they were stored for 7 days under the conditions of 40 °C and 80% relative humidity to simulate prolonged storage and then wedgewise exposed and developed in the same manner as mentioned above. The sensitivity of the blue-sensitive emulsion layer was compared between samples after stored under conditions of raised temperature and humidity and those before storage.

The results obtained were shown in Table 1 below.

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Development Procedure (38°C)

5	1. Color Development	3 min 15 sec
	2. Bleaching	6 min 30 sec
	3. Rinsing	3 min 15 sec
10	4. Fixation	6 min 30 sec
	5. Rinsing in Water	3 min 15 sec
	6. Stabilization	3 min 15 sec

15 Compositions of Processing Solutions:Color Developer:

20	Nitrilotriacetic Acid Sodium Salt	1.0 g
	Sodium Sulfite	4.0 g
	Sodium Carbonate	30.0 g
25	Potassium Bromide	1.4 g
	Hydroxylamine Sulfate	2.4 g
30	4-(N-Ethyl-N-β-hydroxyethylamino)-2-methylaniline Sulfate	4.5 g
	Water to make	1 liter

Bleaching Solution:

35	Ammonium Bromide	160.0 g
	Aqueous Ammonia (28 wt%)	25.0 ml
40	Ethylenediaminetetraacetic Acid Sodium Iron Complex	130.0 g
	Glacial Acetic Acid	14.0 ml
45	Water to make	1 liter

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Fixing Solution:

	Tetrapolyphosphoric Acid Sodium Salt	2.0 g
5	Sodium Sulfite	4.0 g
	Ammonium Thiosulfate (70 wt%)	175.0 ml
	Sodium Bisulfite	4.6 g
10	Water to make	1 liter

Stabilizing Solution:

15	Formalin	8.0 ml
	Water to make	1 liter

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TABLE 1

Sample No.	Eleventh Layer (yellow filter layer)	ΔD_{min}^B	Green-Sensitive Layer		Blue-Sensitive Layer
			Relative Sensitivity	Fog	
101 (Comparison)	Yellow Colloidal Silver Compound No. 5 Compound No. 1 Compound No. 8	0	100	0.08	0.95
102 (Comparison)		0.01	110	0.05	0.73
103 (Comparison)		0.03	111	0.04	0.95
104 (Comparison)		0.02	111	0.03	0.94
105 (Invention)	Yellow Colloidal Silver/Compound No. 5	<0.01	108	0.05	0.91
106 (Invention)	Yellow Colloidal Silver/Compound No. 1	0.01	108	0.04	0.97
107 (Invention)	Yellow Colloidal Silver/Compound No. 8	0.01	108	0.04	0.96

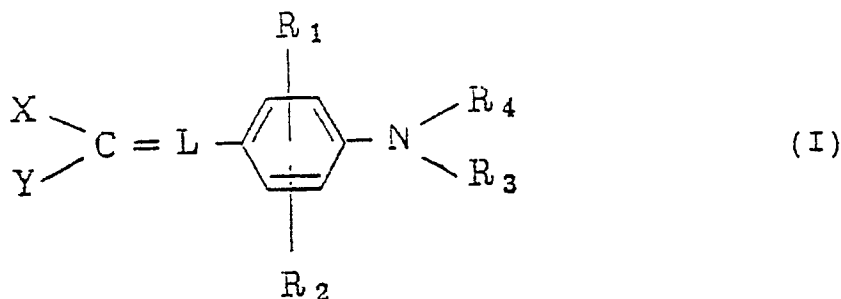
From the results in Table 1 above, the following facts are obvious: In Comparative Sample No. 102 containing only Compound No. 5 in the eleventh layer, the sensitivity of the blue-sensitive emulsion layer lowered after simulated prolonged storage, while in Sample No. 105 of the invention which contained both the yellow colloidal silver and Compound No. 5 in the eleventh layer, the lowering of the sensitivity was noticeably reduced. In Comparative Sample Nos. 103 and 104 containing Compound No. 1 and No. 8 only, respectively, residual coloration was somewhat noted in the processed samples; while in Sample Nos. 106 and 107 of the invention, the discolorability was evaluated as good. In addition, it was also evaluated that the sensitivity was higher but the fog was lower in the green-sensitive emulsion layer in the samples of the invention than that in Comparative Sample No. 101 containing the yellow colloidal silver but no dye of the present invention in the eleventh layer.

In accordance with the present invention, color photographic materials were obtained which are stable and excellent in the color reproducibility because of the yellow filter layer which may efficiently absorb a blue light without lowering the sensitivity of the blue-sensitive layer (outside filter layer) and which does not deteriorate after storage.

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

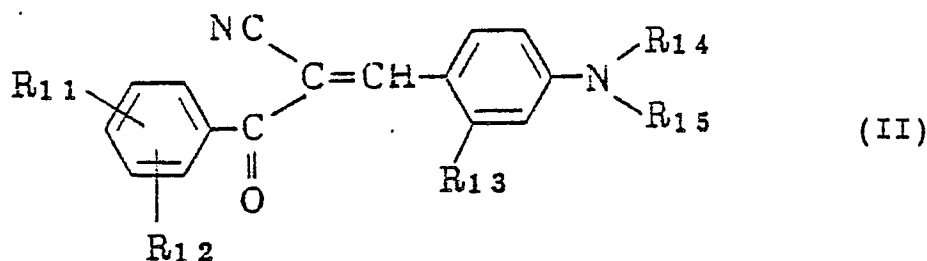
Claims

1. A silver halide photographic material containing at least one dye compound represented by general formula (I) and a yellow colloidal silver:



wherein X and Y may be the same or different and each represents a cyano group, a carboxyl group, an alkylcarbonyl group, an arylcarbonyl group, an alkoxycarbonyl group, an aryloxycarbonyl group, a carbamoyl group, a sulfonyl group or a sulfamoyl group, each of which may be further substituted, and wherein X and Y may be bonded to each other to form a ring; R₁ and R₂ may be the same or different and each represents 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 or an alkoxycarbonyl group, each of which groups may be further substituted; R₃ and R₄ may be the same or different and each represents a hydrogen atom, an alkyl group, an alkenyl group, an aryl group, an acyl group or a sulfonyl group, each of which groups may be further substituted, and wherein R₃ and R₄ may be bonded to each other to form a 5-membered or 6-membered ring; wherein R₁ and R₃ and/or R₂ and R₄ may be bonded to each other to form a 5-membered or 6-membered ring; and L represents a methine group.

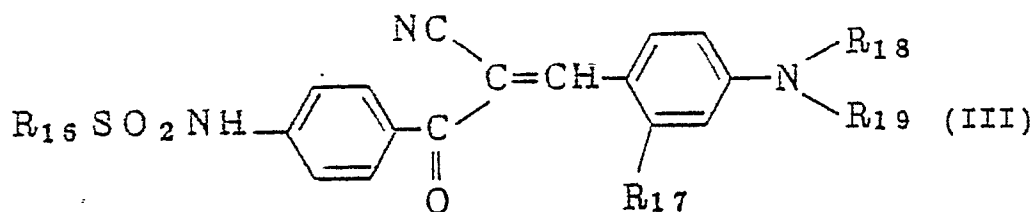
2. A silver halide photographic material as in Claim 1, wherein the dye compound is a compound represented by general formula (II)



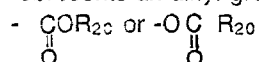
10 wherein R_{11} represents a hydrogen atom or an electron-donating group; R_{12} represents a hydroxyl group or a group selected from the group consisting of RSO_2NH- , $RCONH-$ or $RNHCONH-$, where R represents a hydrocarbon residue having from 1 to 6 carbon atoms; R_{13} represents a hydrogen atom, a halogen atom, a hydroxyl group, an alkyl group having from 1 to 3 carbon atoms, an alkoxy group having from 1 to 3 carbon atoms, an alkylsulfonamido group having from 1 to 3 carbon atoms or an alkyl carbonamido group having from 1 to 3 carbon atoms; and R_{14} and R_{15} may be the same or different and each represents an alkyl group having from 1 to 7 carbon atoms or a phenyl group, each of which may be further substituted.

15 3. A silver halide photographic material as in Claim 2, wherein R_{11} represents an electron donating group having a Hammett's σ_p value lower than -0.05.

20 4. A silver halide photographic material as in Claim 1, wherein the dye compound is a compound represented by general formula (III):



wherein R_{15} represents an alkyl group having from 1 to 3 carbon atoms; R_{17} represents a hydrogen atom or an alkyl group having from 1 to 3 carbon atoms; and R_{18} and R_{19} may be the same or different and each represents an alkyl group having from 1 to 3 carbon atoms, provided that at least one of them has



at the terminal thereof, where R_{20} represents an optionally substituted alkyl group having from 1 to 5 carbon atoms.

40 5. A silver halide photographic material as in Claim 1, wherein the amount of the dye compound to be incorporated is from 1 to 800 mg/m².

6. A silver halide photographic material as in Claim 1, wherein the amount of the dye compound to be incorporated is from 1 to 400 mg/m².

7. A silver halide photographic material as in Claim 1, wherein the amount of the yellow colloidal silver to be incorporated is from 1 to 400 mg/m².

45 8. A silver halide photographic material as in Claim 1, wherein the amount of the yellow colloidal silver to be incorporated is from 1 to 300 mg/m².

9. A silver halide photographic material as in Claim 1, wherein the amount ratio of the dye compound represented by general formula (I) to the yellow colloidal silver is from 90/10 to 30/70 by weight.

50 10. A silver halide photographic material as in Claim 1, wherein the dye of formula (I) and the yellow colloidal silver are incorporated into the same layer.

11. A silver halide photographic material as in Claim 10, wherein said layer containing the dye of the formula (II) and the yellow colloidal silver is remoter from the support than the green-sensitive emulsion layer.