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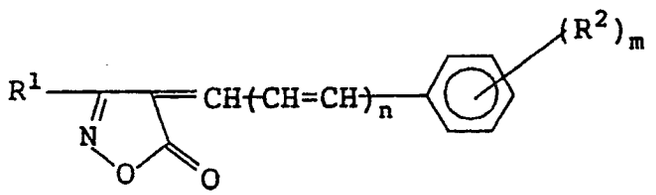
(54) Silver halide photographic light-sensitive materials.

(57) A silver halide photographic light-sensitive material is disclosed which comprises at least one dye which is insoluble in water and is represented by formula (1) below and a silver halide photographic light-sensitive material is also disclosed which comprises at least one dye which is insoluble in water and is represented by formula (1) and at least one dye which is insoluble in water and is represented by formula (2) below:



(1)

wherein R^1 represents an alkyl group, a cycloalkyl group, an aryl group, a heterocyclic group, a carboxyl group, an alkoxycarbonyl group, an aryloxycarbonyl group, a carbamoyl group or a cyano group; R^2 represents a hydrogen atom, a halogen atom, an alkyl group, an alkoxy group, a hydroxy group, an amino group, a carbamoyl group; a sulfamoyl group or an alkoxycarbonyl group; R^2 may form a five or six membered ring with the benzene ring; n represents 0 or 1, and m represents 1 to 5; with the proviso that at least one alkyl chain which has four or more carbon atoms is contained within R^1 and R^2; and where m is 2 or more the R^2 groups may be the same or different,

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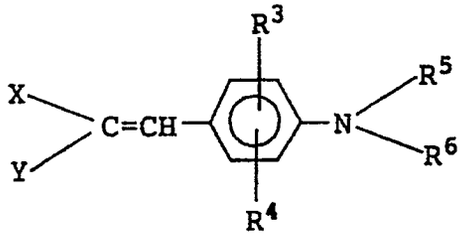


(2)

wherein X and Y may be the same or different, each representing 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, with the proviso that where the combination of X and Y is (cyano group, arylcarbonyl group), (cyan group, alkylcarbonyl group) or (cyano group, sulfonyl group) are excluded; R^3 and R^4 may be the same or different, each representing a hydrogen atom, a halogen atom, an alkyl group, an alkoxy group, a hydroxy group, a carboxyl group, an amino group, a carbamoyl group, a sulfamoyl group or an alkoxycarbonyl group; R^5 and R^6 may be the same or different, each representing a hydrogen atom, an alkyl group or an aryl group, and R^5 and R^6 may form a five or six membered ring; and R^3 and R^5, or R^4 and R^6, may be joined together to form a five or six membered ring.

SILVER HALIDE PHOTOGRAPHIC LIGHT-SENSITIVE MATERIALS

FIELD OF THE INVENTION

This invention relates to silver halide photographic light-sensitive materials which have a novel dye containing layer.

BACKGROUND OF THE INVENTION

The inclusion of dyes in the structural layers of a silver halide photographic light-sensitive material to adsorb light of a specified wavelength is generally well known for the purposes of absorbing or filtering light, for the prevention of halation or for adjusting the sensitivity of a light-sensitive emulsion.

The dyes which are used for such purposes must satisfy various conditions. For example, they must have absorption spectral characteristics which are satisfactory for the intended use, they must have no adverse effects, such as fogging or desensitization on the photographic emulsion, they must not diffuse from the colored layer into other layers and they must have excellent storage stability and aging stability and remain unchanged in solution or in the silver halide photographic light-sensitive material.

Much effort has been expended in the search for dyes which satisfy these conditions. For example, the pyrazolone oxonol dyes disclosed in British Patent 506,385, the barbituric acid oxonol dyes disclosed in U.S. Patent 3,247,127, the azo dyes disclosed in U.S. Patent 2,390,707, the styryl dyes disclosed in U.S. Patent 2,255,072, the hemi-oxonol dyes disclosed in British Patent 584,609, the merocyanine dyes disclosed in U.S. Patent 2,493,747, the cyanine dyes disclosed in U.S. Patent 2,843,486 and the benzylidene dyes disclosed in U.S. Patents 3,002,837, 3,847,621 and 4,420,555 can be cited as examples of such dyes.

In those cases where the layer which contains the above mentioned dyes functions as a filter layer or an anti-halation layer, it is essential that the layer itself is selectively colored, and the color should not spread into other layers. This is because if the other layers become essentially colored, then not only will there be a harmful optical effect on the other layers, but there will also be a weakening of the effect of the colored layer as a filter layer or anti-halation layer.

Methods in which so-called water soluble dyes which have sulfo groups or carboxyl groups are localized in a specified layer using mordants have long been known as a means of overcoming this problem. Furthermore, the use of oil soluble dyes for preventing diffusion to other layers has also been disclosed in JP-A-63-64044. (The term "JP-A" as used herein signifies an "unexamined published Japanese patent application".)

In those cases where oil soluble dyes are used, the dyes are not decolorized in practice during the course of photographic processing and since their presence is undesirable from the view point of color reproduction, it is necessary to make use of colour correcting dyes. The azo dyes and azomethine dyes disclosed in JP-A-63-64044 can be cited as examples of such color correcting dyes.

However, the effects on the photographic emulsion described above and the storage stability in the silver halide photographic light-sensitive material are unsatisfactory in those cases where these dyes are used.

Moreover, in cases where these dyes are used in combination, color reproduction and aging stability in the silver halide photographic light-sensitive materials have been unsatisfactory.

SUMMARY OF THE INVENTION

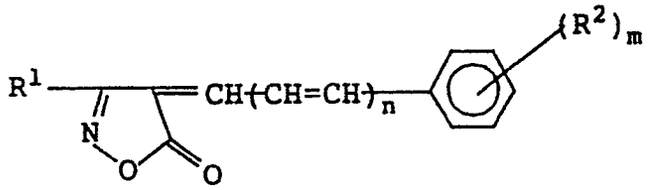
An object of the present invention is to provide silver halide photographic light-sensitive materials in which there is a dye layer which is stable in long term storage and which does not adversely affects photographic performance.

A second object of the present invention is to provide silver halide photographic light-sensitive materials in which there is a filter effect, an anti-halation effect or sensitivity controlling effect of a light-sensitive emulsion.

A third object of the present invention is to provide silver halide photographic light-sensitive materials which have excellent color reproduction properties.

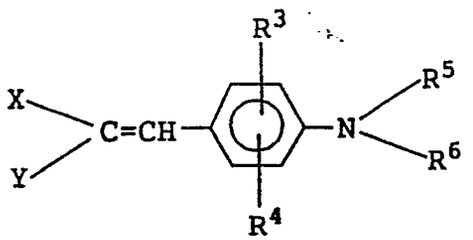
A fourth object of the present invention is to obtain silver halide photographic light-sensitive materials in which there are dyed layers in which specific layers are selectively dyed and the color is not spread into other layer.

It has been discovered in the present invention that the above mentioned objects can be realized by means of a silver halide photographic light-sensitive material which comprises at least one dye which is insoluble in water and is represented by formula (1) which is indicated below, or by means of a silver halide photographic light sensitive material which comprises at least one dye which is insoluble in water and is represented by formula (1) which is indicated below and at least one dye which is insoluble in water and is represented by formula (2) which is indicated below.



(1)

In formula (1), R^1 represents an alkyl group, a cycloalkyl group, an aryl group, a heterocyclic group, a carboxyl group, an alkoxycarbonyl group, an aryloxycarbonyl group, a carbamoyl group or a cyano group. R^2 represents a hydrogen atom, a halogen atom, an alkyl group, an alkoxy group, a hydroxy group, an amino group, a carbamoyl group, a sulfamoyl group or an alkoxycarbonyl group. R^2 may form a five or six membered ring with the benzene ring. Moreover, n represents 0 or 1, and m represents 1 to 5. The substituent groups R^1 and R^2 described above may be further substituted with other substituent groups. However, at least one alkyl chain which has four or more carbon atoms is contained within R^1 and R^2. Furthermore, in those cases where m is 2 or more the R^2 group may be the same or different.



(2)

In formula (2), X and Y may be the same or different, each representing 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. Furthermore, cases in which the combination of X and Y is (cyano group, arylcarbonyl group), (cyan group, alkylcarbonyl group) or (cyano group, sulfonyl group) are excluded. R^3 and R^4 may be the same or different, each representing a hydrogen atom, a halogen atom, an alkyl group, an alkoxy group, a hydroxy group, a carboxyl group, an amino group, a carbamoyl group, a sulfamoyl group or an alkoxycarbonyl group. R^5 and R^6 may be the same or different, each representing a hydrogen atom, an alkyl group or an aryl group, and R^5 and R^6 may form a five or six membered ring. R^3 and R^5, or R^4 and R^6, may be joined together and form a five or six membered ring. The substituent groups described above may be further substituted with other substituent groups.

DETAILED DESCRIPTION OF THE INVENTION

More precisely, the number of carbon atoms in the alkyl groups represented by R^1 to R^6 and in the alkyl moiety of the alkylcarbonyl groups represented by X and Y is from preferably 1 to 22. Furthermore, they may have a linear chain structure or they may be branched, and they may be substituted with

substituent groups such as halogen atoms, cyano groups, alkoxy groups, hydroxy groups, amino groups (described hereinafter) and aryloxycarbonyl groups (described hereinafter), for example.

The aryl groups represented by R^1, R^5 and R^6, and the aryl moieties of the arylcarbonyl groups represented by X and Y and of the aryloxycarbonyl groups represented by X, Y and R^1 are preferably phenyl groups or naphthyl groups. Furthermore, these may be substituted with alkyl groups (as described earlier), alkoxy groups (described hereinafter), halogen atoms, nitro groups, cyano groups, hydroxy groups, carboxyl groups, carbamoyl groups (described hereinafter) sulfo groups, sulfamoyl groups (described hereinafter), alkoxycarbonyl groups (described hereinafter) or amino groups, for example.

The alkyl moieties of the alkoxy groups represented by R^2, R^3 and R^4 and of the alkoxycarbonyl groups represented by R^1, R^2, R^3, R^4, X and Y have the same meaning as those described earlier.

The carbamoyl groups represented by R^1, R^2, R^3, R^4, X and Y and the sulfamoyl groups represented by R^2, R^3, R^4, X and Y may be substituted with the aforementioned alkyl groups and aryl groups, for example.

The sulfonyl groups represented by X and Y may be substituted with the aforementioned alkyl groups and aryl groups, for example.

The amino groups represented by R^2, R^3 and R^4 may be substituted with alkyl groups (as described earlier), aryl groups (as described earlier), COR' or SO_2R' (where R' is an alkyl group or an aryl group as described earlier), for example.

The cycloalkyl group represented by R^1 may be, for example, a cyclopentyl group, a cyclohepthyl group or a cyclooctyl group.

The heterocyclic group represented by R^1 is preferably a ring which contains nitrogen , oxygen or sulfur, for example. Examples of such groups include the thienyl group, the furyl group and the pyridyl group.

Fluorine, chlorine, bromine and iodine are cited as halogen atoms which can be represented by R^2, R^3 and R^4.

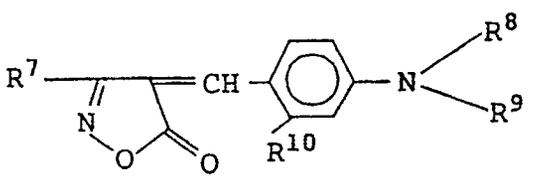
The following combinations of X and Y are excluded: (cyano group and aryloxycarbonyl group), (cyano group and alkylcarbonyl group) and (cyano group and sulfonyl group).

A five or six membered heterocyclic ring (for example, a piperidine ring or a morpholine ring) may be formed by R^5 and R^6.

Furthermore, R^3 and R^5, or R^4 and R^6, may be joined together to form a five or six membered ring.

Moreover, n represents 0 or 1, and m represents 1 to 5.

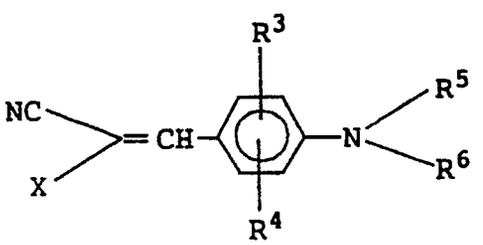
The dyes represented by formula (1) and formula (2) can be more preferably represented by formula (3) and formula (4) indicated below, respectively.



(3)

In formula (3), R^7 is an alkyl group, R^8 and R^9 may be the same or different, each representing an alkyl group (as described earlier), and a five or six membered ring may be formed by R^8 and R^9. R^{10} has the same meaning as R^2 described in connection with formula (1). At least one of the groups R^7, R^8, R^9 and R^{10} contains an alkyl chain which has at least four carbon atoms.

Moreover, the dyes of formula (3) are most desirably dyes in which the alkyl group of R^7 is branched.



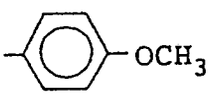
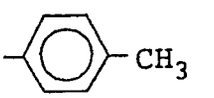
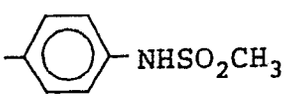
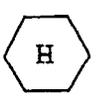
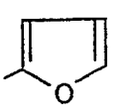
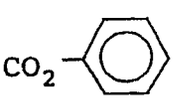
(4)

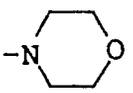
In formula (4), X represents an alkylcarbonyl group (as described earlier) or an arylcarbonyl group (as described earlier). R^3 to R^6 have the same meaning as described earlier.

Actual examples of compounds which can be used in the present invention are indicated below, but the compounds are not limited to these examples.

Actual examples of compounds represented by formula (1) are indicated below.

Compounds 1 to 23 are indicated by showing the actual groups represented by R^7, R^8, R^9 and R^{10} in formula (3).

Compound Number	R^7	R^8	R^9	R^{10}
1	$(t)C_4H_9$	$C_{12}H_{25}$	$C_{12}H_{25}$	CH_3
2	$(t)C_8H_{17}$	$C_{12}H_{25}$	$C_{12}H_{25}$	CH_3
3	CH_3	$C_{12}H_{25}$	$C_{12}H_{25}$	CH_3
4	CH_2Cl	$C_{12}H_{25}$	$C_{12}H_{25}$	CH_3
5	CF_3	$C_{12}H_{25}$	$C_{12}H_{25}$	CH_3
6		$C_{12}H_{25}$	$C_{12}H_{25}$	CH_3
7		$C_{12}H_{25}$	$C_{12}H_{25}$	CH_3
8		$C_{12}H_{25}$	$C_{12}H_{25}$	CH_3
9		$C_{12}H_{25}$	$C_{12}H_{25}$	CH_3
10		$C_{12}H_{25}$	$C_{12}H_{25}$	CH_3
11		$C_{12}H_{25}$	$C_{12}H_{25}$	CH_3
12		$C_{12}H_{25}$	$C_{12}H_{25}$	CH_3
13	$CONHCH_3$	$C_{12}H_{25}$	$C_{12}H_{25}$	CH_3
14	$(t)C_8H_{17}$	C_2H_5	C_2H_5	CH_3

Compound Number	R^7	R^8	R^9	R^{10}
15	(t)C_8H_{17}	$CH_2CO_2C_4H_9$	$CH_2CO_2C_4H_9$	CH_3
16	(t)C_8H_{17}	C_2H_5	C_2H_4Cl	CH_3
17	(t)C_8H_{17}	C_2H_5	$C_2H_4NHSO_2CH_3$	CH_3
18	(t)C_8H_{17}	C_2H_5	C_2H_4CN	CH_3
19	(t)C_8H_{17}	C_2H_5	$C_2H_4OC_2H_5$	CH_3
20	(t)C_8H_{17}	 is formed by R^8 and R^9		CH_3
21	(t)C_4H_9	$C_{12}H_{25}$	$C_{12}H_{25}$	OCH_3
22	(t)C_4H_9	$C_{12}H_{25}$	$C_{12}H_{25}$	$NHCOCH_3$
23	(t)C_4H_9	$C_{12}H_{25}$	$C_{12}H_{25}$	Cl

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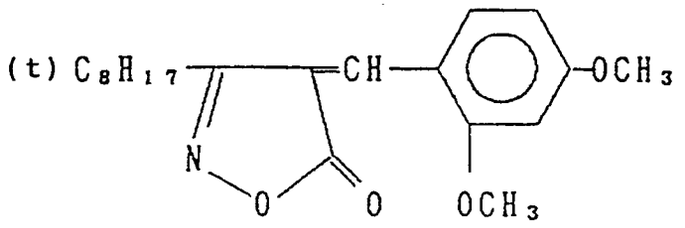

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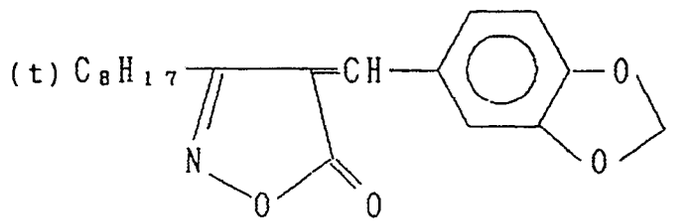

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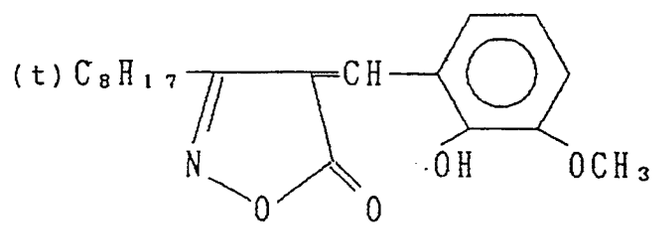

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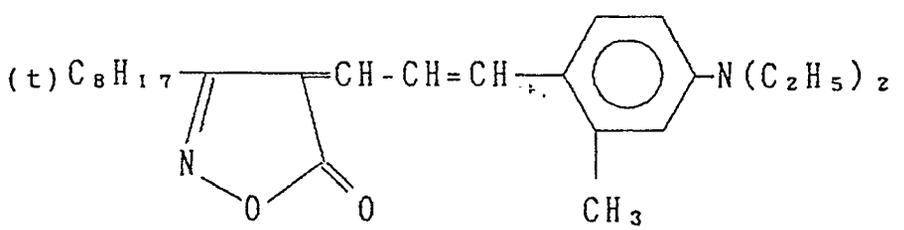

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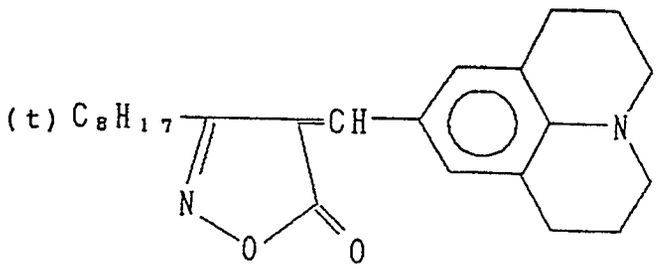

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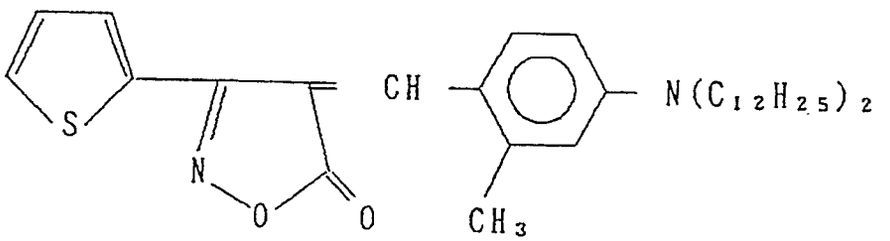

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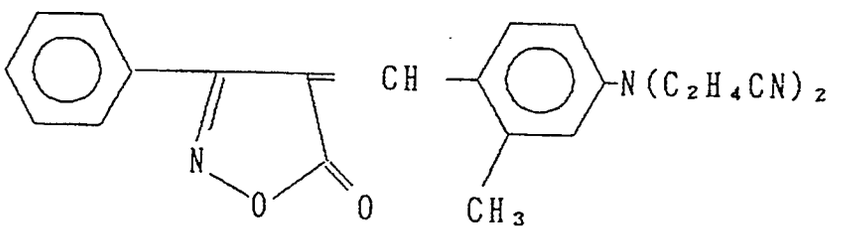

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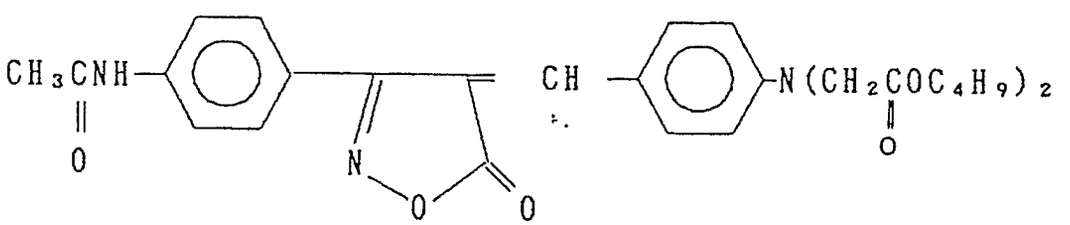

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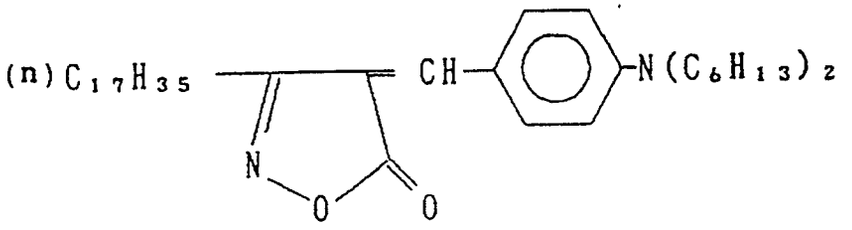

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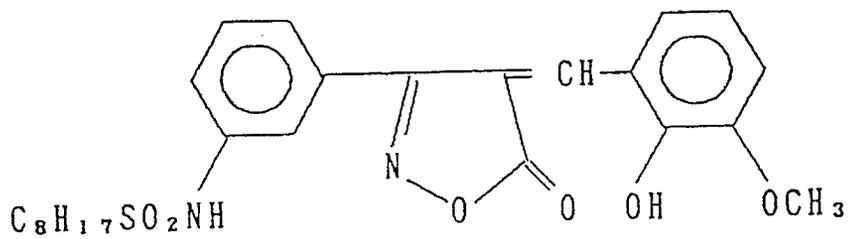

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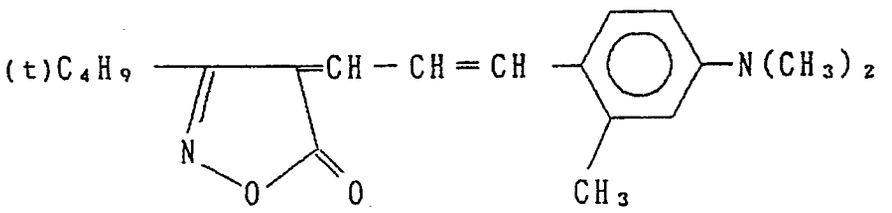

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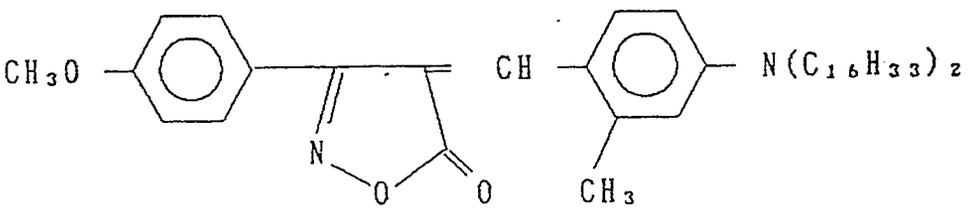

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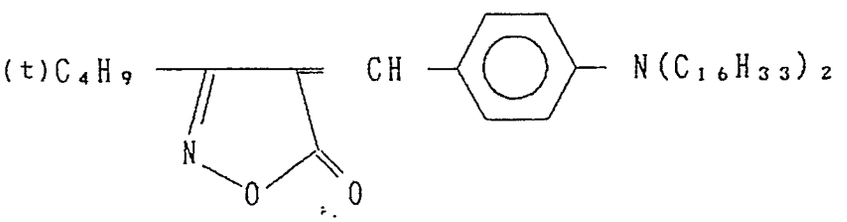

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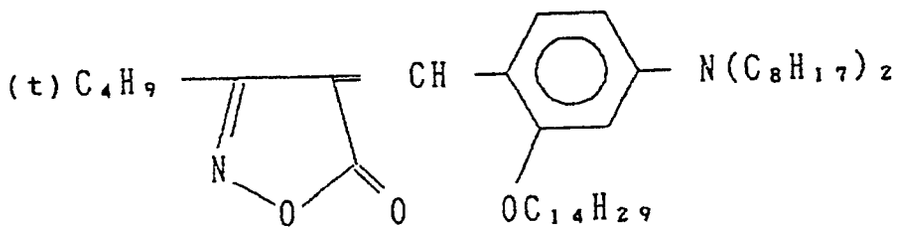

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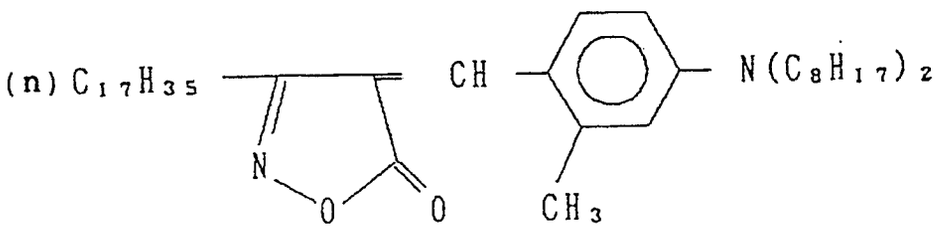

Actual examples of compounds represented by formula (2) are indicated below.

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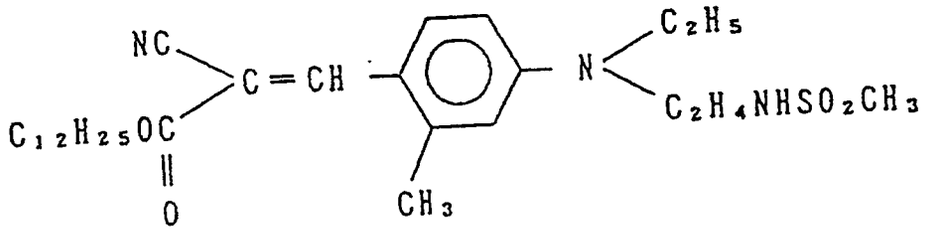

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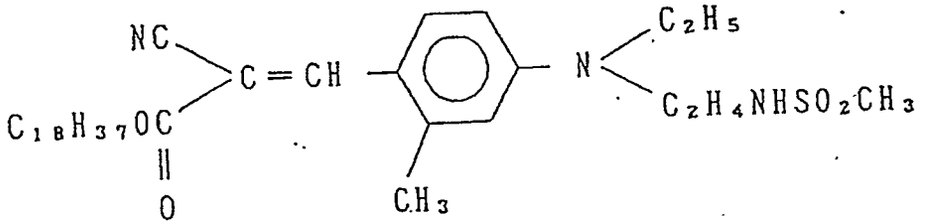

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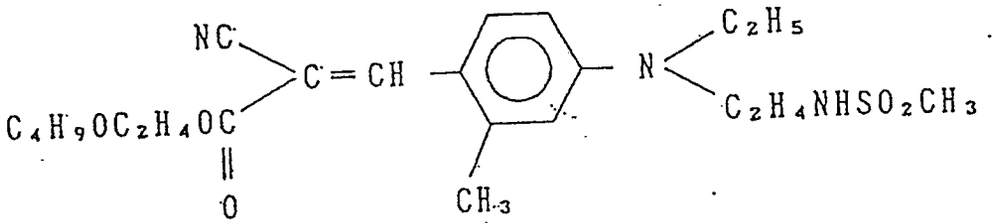

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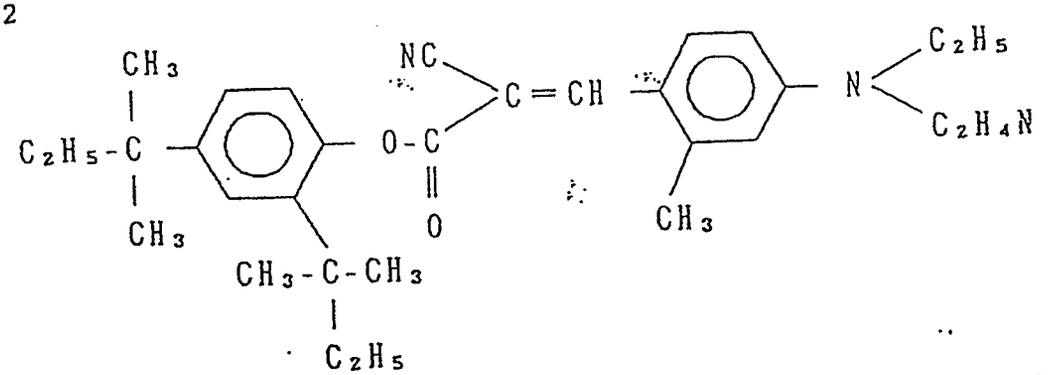

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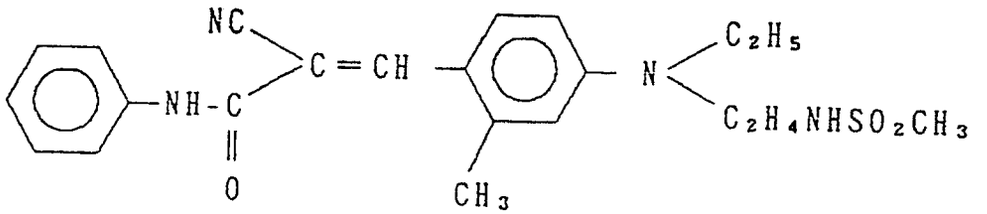

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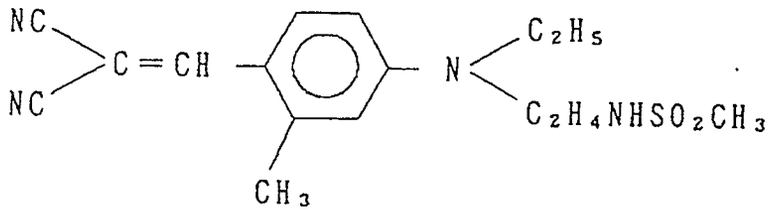

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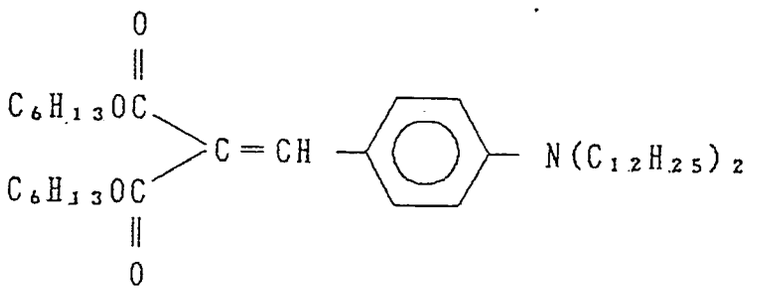

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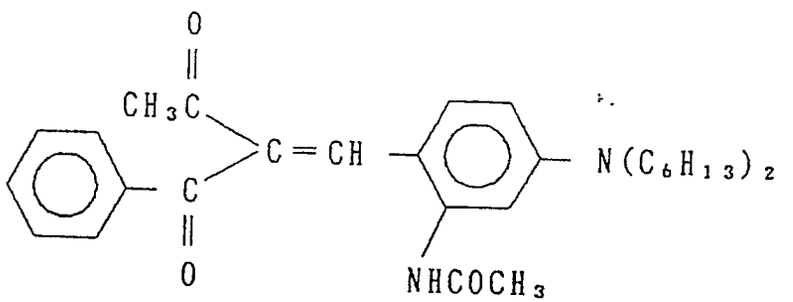

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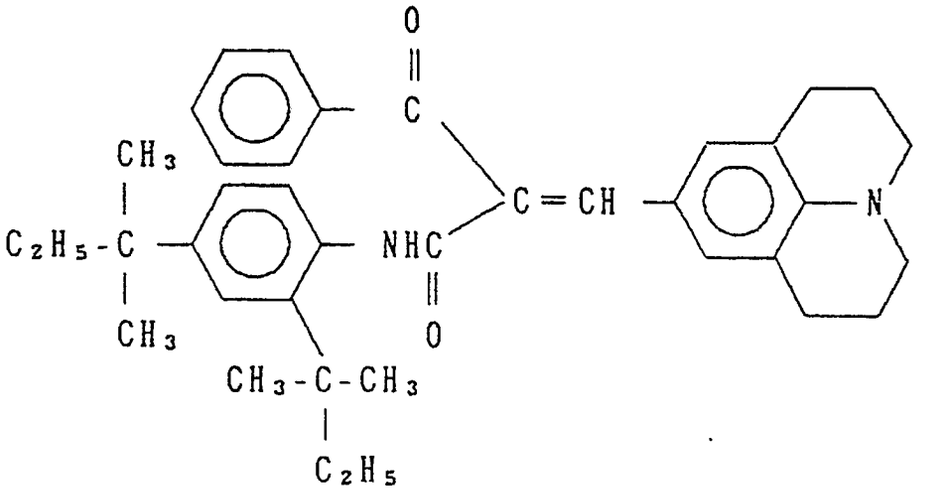

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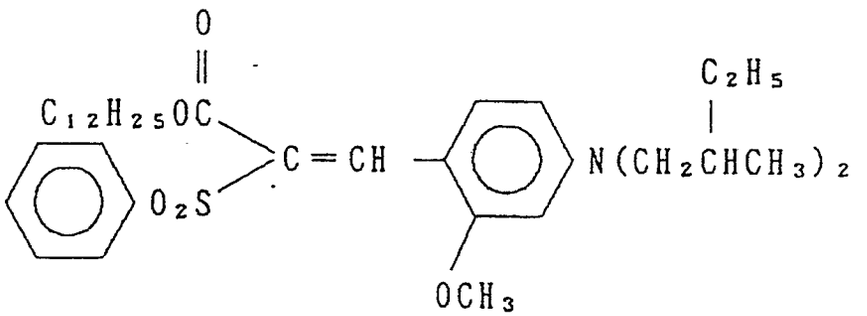

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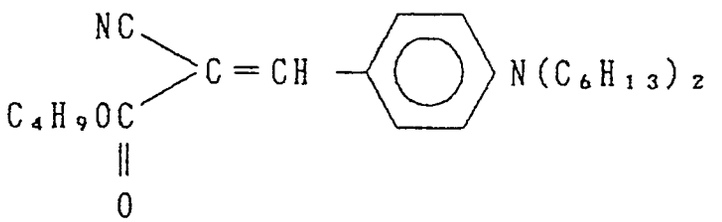

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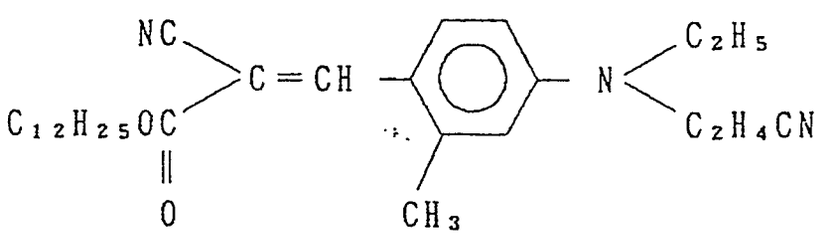

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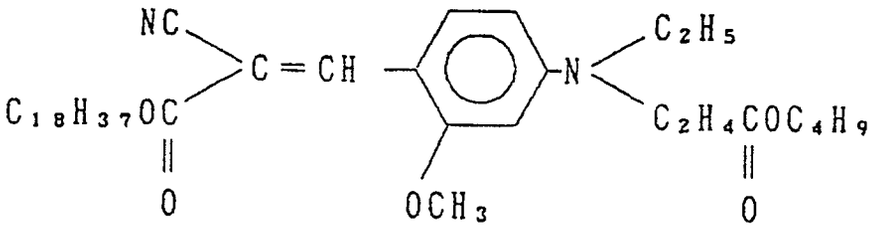

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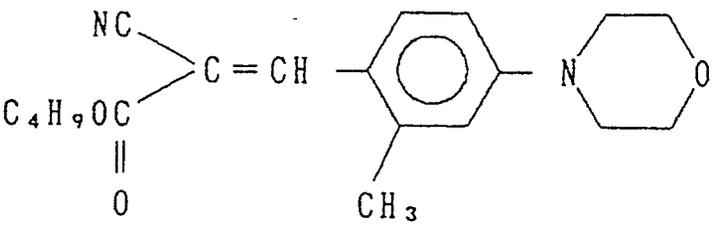

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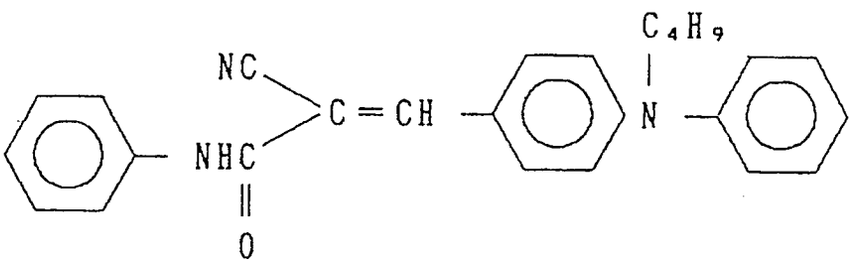

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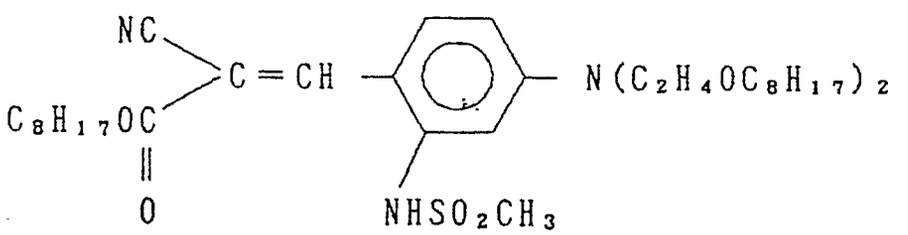


The dye compounds used in the present invention can be prepared easily in the following way. Typical examples are cited below, but other compounds can be prepared in the same way. Refer to A. Weissberger, The Chemistry of Heterocyclic Compound , Vol. 7, pages 117 to 140 in connection with the synthesis of 5-isoxazolones.

Synthesis Examples

The Values for λ_{max} and ϵ_{max} of the compounds prepared were measured in $CH_3CO_2C_2H_5$.

Preparation of Compound 1

A mixture of 22.4 grams of 3-tert-butyl-5-isoxazolone, 75.2 grams of 4-N,N-dodecylamino-2-methylbenzaldehyde, 200 ml of methyl alcohol and 20 ml of acetic acid was heated at 90° C for a period of 2 hours. After completion of the reaction, the mixture was filtered and cooled and the crystals which precipitated out were recovered by filtration.

Yield: 60 grams, m.p.: 50 to 51°C

$\lambda_{max}^{(ethyl\ acetate)}$ 479 nm

$\epsilon_{max}^{(ethyl\ acetate)}$ 5.64×10^4

Preparation of Compound 6

A mixture of 6.7 grams of 3-phenyl-5-isoxazolone, 19.6 grams of 4-N,N-dodecylamino-2-methylbenzaldehyde, 74 ml of ethyl alcohol and 7.4 ml of acetic acid was heated at 90° C for a period of 2 hours. After the reaction had been completed, the reaction mixture was filtered and cooled and the crystals which precipitated out were recovered by filtration.

Yield: 15 grams, m.p.: 70 to 71°C

$\lambda_{max}^{(ethyl\ acetate)}$ 486.1 nm

$\epsilon_{max}^{(ethyl\ acetate)}$ 6.32×10^4

Preparation of Compound 39

Dodecyl cyanoacetate (30.4 grams, 0.12 mol) and 28.4 grams (0.1 mol) of 4-formyl-N-ethyl-N-(2-methylsulfonylaminoethyl)-3-methylaniline were stirred in 120 ml of acetonitrile, 4.9 grams of ammonium acetate was added and the mixture was heated under reflux at 90° C for a period of about 2 hours. The reaction mixture was cooled after filtering off the solid materials and crystals precipitated out. These crystals were recovered by filtration, washed with a small quantity of acetonitrile and dried. Yield: 50.8 grams (97.8%). These crystals were recrystallized from acetonitrile and Compound 39 was obtained. Yield: 46.4 grams (89.2%).

Melting Point: 82 to 83°C

$\lambda_{max}^{(methanol)}$ 432 nm

$\epsilon_{max}^{(methanol)}$ 4.50×10^4

Preparation of Compound 49

Butyl cyanoacetate (7.8 grams, 0.055 mol) and 14.5 grams (0.05 mol) of 4-formyl-N,N-dihexylaniline were stirred in 80 ml of acetonitrile, 3.9 grams of ammonium acetate was added and the mixture was heated under reflux at 90° C for a period of about 3 hours. The filtrate was concentrated after filtering off the solid materials and Compound 49 was obtained using column chromatography.

Yield: 17.5 grams (85%) (Oil)

$\lambda_{max}^{(methanol)}$ 430 nm

$\varepsilon_{max}^{(methanol)}$ 5.28×10^4

The dyes of formula (1) and/or formula (2) are used in amounts of from 1 to 800 mg per square meter of light-sensitive material.

When the dyes represented by formula (1) and/or formula (2) are used as filter dyes, anti-halation dyes or color correcting dyes, they can be used in any amount which is effective, but they are preferably used in such a way that the optical density is within the range from 0.05 to 3.0. The addition may be made at any stage prior to coating.

The dyes of formula (1) or formula (3) can be more preferably used as anti-halation dyes or color correcting dyes. When the dyes are used for these purposes, they can be used in amounts of from 0.01 to 0.7 g, more preferably from 0.01 to 0.2 g, per square meter of light-sensitive material. The dyes of formula (2) or formula (4) can be more preferably used as filter dyes. When the dyes are used for the purpose, they can be used in amounts of from 0.01 to 0.7 g, preferably 0.02 to 0.2 g, per square meter of light-sensitive material.

The dyes of the present invention can be dispersed using a variety of known methods in emulsion layers or other hydrophilic colloid layers (for example, intermediate layers, protective layers, anti-halation layers and filter layers).

The dyes of formula (2) of formula (4} can be more preferably added in a light-insensitive emulsion layer or layers provided further than a green-sensitive emulsion layer from the support. The dyes of formula (1) or formula (3) can be more preferably added in a light-insensitive emulsion layer or layers provided between the support and a red-sensitive emulsion layer.

When used as color correcting dyes, the mol ratio of the dye of formula (1) for the dye of formula (2) is preferably not more than 1.

(1) Methods in which the dyes of the present invention are dissolved or dispersed directly in an emulsion layer or hydrophilic colloid layer and methods in which the dyes of the present invention are dissolved or dispersed in an aqueous solution or solvent and then used in an emulsion layer or hydrophilic colloid layer can be employed. They can also be added to an emulsion in the form of a solution obtained by dissolution in a suitable solvent such as methyl alcohol, ethyl alcohol, propyl alcohol, methylcellosolve, the halogenated alcohols disclosed in JP-A-48-9715 and U.S. Patent 3,756,830, acetone, water or pyridine, for example, or in a mixture of such solvents.

(2) Methods can also be employed in which a liquid obtained by dissolving the compounds in an oil, that is a high boiling point solvent which is substantially water-insoluble and has a boiling point of at least 160° C, is added to a hydrophilic colloid solution and dispersed.

A solvent such as those disclosed in U.S. Patent 2,322,027, for example, alkyl phthalates (for example, dibutyl phthalate, dioctyl phthalate), phosphate esters (for example, diphenyl phosphate, triphenyl phosphate, tricresyl phosphate, dioctyl butyl phosphate), succinates (for example, tributyl acetylsuccinate), benzoates (for example, octyl benzoate), alkylamides (for example, diethyllauryl amide), fatty acid esters (for example, dibutoxyethyl succinate, diethyl azelate) and trimesates (for example, tributyl trimesate) can be used for the high boiling point solvent. Furthermore, organic solvents having a boiling point from about 30° C to about 150° C, for example, lower alkyl acetates, such as ethyl acetate and butyl acetate, ethyl propionate, secondary butyl alcohol, methyl isobutyl ketone, β-ethoxyethyl acetate and methyl-cellosolve acetate, and solvents which are soluble in water, for example, alcohols, such as methanol and ethanol, can also be used.

The use ratio of the dye and high boiling point organic solvent is preferably from 10 to 1/10 (by weight).

(3) Methods can also be employed in which the dyes of the present invention and other additives are included as loaded polymer latex compositions in a photographic emulsion layer or other hydrophilic colloid layer.

Examples of such polymer latexes which can be used include polyurethanes, polymers obtained by polymerization from vinyl monomers (suitable vinyl monomers include acrylic acid esters (for example, methyl acrylate, ethyl acrylate, butyl acrylate, hexyl acrylate, octyl acrylate, dodecyl acrylate, glycidyl acrylate), α-substituted acrylic acid esters (for example, methyl methacrylate, butyl methacrylate, octyl methacrylate, glycidyl methacrylate), acrylamides (for example, butylacrylamide, hexylacrylamide), α-substituted acrylamides (for example, butylmethacrylamide, dibutylmethacrylamide), vinyl esters (for example, vinyl acetate, vinyl butyrate), vinyl halides (for example, vinyl chloride), vinylidene halides (for example, vinylidene chloride), vinyl ethers (for example, vinyl methyl ether, vinyl octyl ether), styrene, α-substituted styrenes (for example, α-methylstyrene), ring substituted styrenes (for example, hydroxystyrene, chlorostyrene, methylstyrene), ethylene, propylene, butylene, butadiene and acrylonitrile, and these may be used individually or in combinations of two or more, and other vinyl monomers, such as itaconic acid, acrylic acid, methacrylic acid, hydroxyalkyl acrylates, hydroxyalkyl methacrylates, sulfoalkyl acrylates, sulfoalkyl methacrylates and styrene sulfonic acid, can be included as other vinyl components).

These loadable polymer latexes can be prepared on the basis of the methods disclosed in U.S. Patent 4,358,533, JP-B-51-39853, JP-A-51-59943, JP-A-53-137131, JP-A-53-32552, JP-A-54-107941, JP-A-55-133465, JP-A-56-19043, JP-A-56-19047 and JP-A-58-149038. (The term "JP-B" as used herein signifies an "examined Japanese patent publication".)

The use ratio of dye and polymer latex is preferably from 10 to 1/10 (by weight).

(4) Methods can also be employed in which the compounds are dissolved using a surfactant.

Oligomers and polymers may be used as useful surfactants.

Details of these polymers have been disclosed on pages 19 to 27 of JP-A-60-158437.

(5) Methods can also be employed in which hydrophilic polymers are used in place of the high boiling solvents or jointly with the high boiling point solvents in (2) above. These methods have been disclosed, for example, in U.S. Patent 3,619,195 and West German Patent 1,957,467.

(6) Micro-encapsulation methods can also be employed using polymers which have carboxyl groups, sulfonic acid groups in side chains as disclosed in JP-A-59-113434.

Furthermore, hydrosols of oleophilic polymers as disclosed in JP-B-51-39835, for example can also be added to the hydrophilic colloidal dispersions obtained in the ways described above.

Gelatin is a typical hydrophilic colloid, but any of the other known hydrophilic colloids which are used for photographic purposes can be used.

Silver bromide, silver iodobromide, silver iodochlorobromide, silver chlorobromide or silver chloride can be used for the silver halide emulsion which is used in the present invention. The use of silver bromide, silver chlorobromide, silver iodobromide or silver iodochlorobromide is preferred.

The silver halide grains in the photographic emulsion layer may have a regular crystalline form, such asa cubic or octahedral form, an irregular crystalline form, such as a spherical or tabular form, or a crystalline form which is a composite of these crystalline forms. Use can also be made of mixtures of grains which have various crystalline forms.

The silver halide grains may be such that the interior and surface layer consist of different phases or they may be comprised of a uniform phase. Furthermore, the silver halide grains may be of the type with which the latent image is formed principally on the surface of the grains (for example, a negative type emulsion) or they may be of the type with which the latent image is formed principally within the grains (for example, internal latent image type emulsions and pre-fogged direct reversal type emulsions).

The silver halide emulsions used in the present invention may be such that tabular grains of thickness not more than 0.5 microns, and preferably not more than 0.3 microns, and of diameter preferably at least 0.6 microns and of which the average aspect ratio is at least 5 account for at least 50% of the total projected area. Furthermore, they may be monodisperse emulsions such that grains of grain size within the average grain size ±40% account for at least 95% by number of all of the grains.

The photographic emulsions used in the present invention can be prepared, for example, using the methods disclosed in P. Glafkides, Chimie et Physique Photographique , published by Paul Montel, (1966), in G.F. Duffin, Photographic Emulsion Chemistry , published by Focal Press, (1966), and in V.L. Zelikmann et al., Making and Coating Photographic Emulsion , published by Focal Press, (1964).

Furthermore, silver halide solvents, for example, ammonia, potassium thiocyanate, ammonium thiocyanate, thioether compounds (for example, those disclosed in U.S. Patents 3,271,157, 3,574,628, 3,704,130, 4,297,439 and 4,276,374), thione compounds (for example, those disclosed in U.S. patent 4,284,717, JP-A-53-144319 and JP-A-53-82408), and amine compounds (for example, those disclosed in JP-A-54-100717) can be used to control grain growth during the formation of the silver halide grains.

Cadmium salts, zinc salts, thallium salts, iridium salts or complex salts thereof, rhodium salts or complex salts thereof, and iron salts or complex salts thereof, for example, may be present during the

formation or physical ripening of the silver halide grains.

The silver halide emulsions are normally subjected to chemical sensitization. The methods described, for example, in H. Freiser, Die Grundlagen der Photographischen Prozesse mit Silverhalogeniden , pages 675 to 734, published by Akademishe Verlagsgeselshaft, (1968) can be used for this purpose.

Sulfur sensitization methods using active gelatin or compounds which contain sulfur which can react with silver (for example, thiosulfate, thioureas, mercapto compounds, rhodanines); reduction sensitization methods using reducing substances (for example, stannous salts, amines, hydrazine derivatives, formamidinesulfinic acids, silane compounds); and noble metal sensitization methods using noble metal compounds (for example, complex salts of the metals of group VIII of the periodic table, such as Pt, Ir or Pd, as well as gold) can be used, either individually or in combination, for this purpose.

Various compounds can be included in the emulsions used in the present invention with a view to preventing the occurrence of fogging during the manufacturing, storage or photographic processing of the light-sensitive materials or with a view to stabilizing photographic performance. Thus, many compounds can be employed which are known as anti-foggants or stabilizers, such as azoles, for example, benzothiazolium salts, nitroindazoles, triazoles, benzotriazoles and benzimidazoles (especially nitro or halogen substituted derivatives); heterocyclic mercapto compounds, for example, mercaptothiazoles, mercaptobenzothiazoles, mercaptobenzimidazoles, mercaptothiadiazoles, mercaptotetrazoles (especially 1-phenyl-5-mercaptotetrazole) and mercaptopyrimidines; heterocyclic mercapto compounds as described above but which have water solubilizing groups such as carboxyl groups and sulfo groups; thioketo compounds, for example, oxazolinethione; azaindenes, for example, tetraazaindenes (especially 4-hydroxy substituted 1,3,3a,7-tetraazaindenes); benzenethiosulfonic acids; and benzenesulfinic acid.

Ultraviolet absorbers, such as benzothiazoles may be used jointly in the light-sensitive materials of the present invention, and typical examples have been disclosed, for example, in Research Disclosure , No. 24239 (June, 1984).

Color couplers, such as cyan couplers, magenta couplers and yellow couplers can be included in the silver halide photographic emulsions of the present invention.

Thus, compounds which can form colors by oxidative coupling with the primary aromatic amine developing agents (for example, phenylenediamine derivatives and aminophenol derivatives) in a color development process can be included. For example, 5-pyrazolone couplers, pyrazolobenzimidazole couplers, cyanoacetylcoumarone couplers, open chain acylacetonitrile couplers and the pyrazolo[5,1-c][1,2,4]-triazoles disclosed in U.S. Patent 3,725,067 or the pyrazolo[5,1-b][1,2,4]triazoles disclosed in European Patent 119,860 can be used as magenta couplers, and acylacetamide couplers (for example, benzoylacetanilides and pivaloylacetanilides), for example, can be used as yellow couplers and naphthol couplers and phenol couplers, for example, can be used as cyan couplers, but couplers which are fast to humidity and temperature are preferably used, and typical examples include the phenol based couplers disclosed, for example, in U.S. patent 3,772,002, the 2,5-diacylaminophenol based couplers disclosed, for example, in U.S. Patent 4,463,086, JP-A-59-166956 and JP-A-58-133293, the phenol based couplers which have a phenylureido group in the 2-position and an acylamino group in the 5-position disclosed, for example, in U.S. Patent 4,333,999, and moreover the 5-position substituted naphthol based couplers and polymer couplers thereof disclosed in JP-A-60-237448, and Japanese Patent Application Nos. 59-264277 and 59-268135 (coresponding to JP-A-61-153640 and JP-A-61-145557, respectively). These couplers are preferably fast to difusion, having hydrophobic groups, known as ballast groups, within the molecule. The couplers may be of the four equivalent type or two equivalent type with respect to silver ion. Furthermore, colored couplers which have a color correcting effect and couplers which release development inhibitors during the course of development (so-called DIR couplers) can also be used.

In addition, colorless compound forming DIR coupling compounds of which the products of the coupling reaction are colorless but which release development inhibitors can also used instead of DIR couplers.

Poly(alkylene oxides) or ether, ester or amide derivatives thereof, thioether compounds, thiomorpholines, quaternary ammonium salt compounds, urethane derivatives, urea derivatives, imidazole derivatives and 3-pyrazolidones, for example, can be included in the photographic emulsions of the present invention with a view to increasing sensitivity, increasing contrast or accelerating development.

Known water soluble dyes (for example, oxonol dyes, hemi-oxonol dyes and merocyanine dyes) other than the dyes disclosed in the present invention can also be used jointly as filter dyes or anti-irradiation dyes, or for other purposes, in the silver halide photographic emulsions of the present invention. Furthermore, known cyanine dyes, merocyanine dyes and hemi-cyanine dyes can be used jointly as spectrally sensitizing dyes.

Various surfactants may be included in the photographic emulsions of the present invention for a variety of purposes, for example, as coating aids or anti-static agents, for improving slip properties, for emulsifica-

tion and dispersion purposes, for the prevention of sticking or for improving photographic performance (for example, for accelerating development, increasing contrast or increasing sensitivity).

Furthermore, actual disclosures have been made in Research Disclosure Vol. 176 (1978, XII), RD-17643), for example,in connection with discoloration inhibitors, hardening agents, anti-color fogging agents, ultraviolet absorbers, protective colloids, such as gelatin, and a variety of additives which can be used in the light-sensitive materials of the present invention.

The finished emulsion is coated on a suitable support, for example, on baryta paper, resin coated paper, synthetic paper, thiacetate film, poly(ethylene terephthalate) film or some other plastic film, or on a glass plate.

The silver halide photographic light-sensitive materials of the present invention may be, for example, color negative films, photographic light-sensitive materials for photomechanical process (for example, lith films or lith duplicating films), light-sensitive materials for cathode ray tube display purposes (for example, light-sensitive materials for X-ray recording purposes and materials for direct and indirect photographic purposes using a screen), light-sensitive materials for use in silver salt diffusion transfer processes, light-sensitive materials for use in color diffusion transfer processes, light-sensitive materials for use in dye transfer processes (imbibition transfer processes), emulsions for use in a silver dye bleach process, light-sensitive materials as used for recording print-out images, light development type printing (Direct print image) light-sensitive materials, light-sensitive materials for heat development purposes and light-sensitive materials for use with physical development.

The usual methods can be used for making the exposure by which the photographic image is obtained. Thus, any of the various known light sources, such as natural light (daylight), tungsten lamps, florescent lamps, mercury lamps, xenon arc lamps, carbon arc lamps, xenon flash lamps and the flying spot of a cathode ray tube can be used for making an exposure. The exposure time is normally from 1/1000 second to 1 second made using a camera, but of course exposures of duration less than 1/1000 second, for example, exposures of from 10^{-4} to 10^{-6} second made using a xenon strobe lamp or a cathode ray tube, can be used, and exposures of longer duration than 1 second can also be used. The spectral composition of the light which is used to make the exposure can be adjusted, as required, using colored filters. Laser light can also be used for making the exposure. Furthermore, exposures can also be made using the light released by phosphors which have been excited by means of electron beams, X-rays, γ-rays or α-rays, for example.

All of the known methods of processing and the known processing baths, such as those disclosed, for example, in Research Disclosure , Vol. 176, pages 28 to 30 (RD-17643) (December, 1978), can be used for the development processing of light-sensitive materials which have been formed in accordance with the present invention. The photographic processing may involve either processing in which a silver image is formed (black-and-white photographic processing) or processing in which a dye image is formed (color photographic processing), depending on the intended purpose. A processing temperature of from 18 ° C to 50 ° C is generally selected, but temperatures below 18 ° C or above 50 ° C can be used.

The silver halide photographic light-sensitive materials of the present invention have a dye layer which has an excellent filtering effect, anti-halation effect or light-sensitive emulsion sensitivity controlling effect. The dye layer in a silver halide photographic light-sensitive material of the present invention contains a dye which has the appropriate spectral absorption, which dyes a specific layer selectively and which does not diffuse into other layers.

Moreover, the silver halide photographic light-sensitive materials of the present invention have excellent ageing stability and excellent color reproduction.

The invention is described in more detail below by means of examples, but the invention is not limited by these examples.

EXAMPLE 1

Sample 101, a multi-layer color light-sensitive material comprising an undercoated cellulose triacetate film support having thereon the layers of which the compositions are indicated below, was prepared.

Composition of the Light-sensitive Layer

The coated amounts shown are the weight of silver in units of g/m^2 in the case of silver halides and

colloidal silver, the weight in units of g/m^2 in the case of couplers, additive and gelatin, and the number of mol per mol of silver halide in the same layer in the case of the sensitizing dyes.

First Layer (Anti-halation Layer)

Black colloidal silver	as silver	0.2
Gelatin		2.2

UV-1		0.1
UV-2		0.2
Cpd-1		0.05
Solv-1		0.01
Solv-2		0.01
Solv-3		0.08

Second Layer (Intermediate Layer)

Fine grain silver bromide (Corresponding sphere diameter 0.07 μm)	as silver	0.15
Gelatin		1.0
ExC-4		0.03
Cpd-2		0.2

Third Layer (First Red-Sensitive Emulsion Layer)

Silver iodobromide emulsion (AgI 8.5 mol%, high internal AgI type, corresponding sphere diameter 1.0 μm, coefficient of variation of the corresponding sphere diameter 25%, tabular grains, diameter/thickness ratio 3.0)	as silver	0.42
Silver iodobromide emulsion (AgI 4.0 mol%, high internal AgI type, corresponding sphere diameter 0.4 μm, coefficient of variation of the corresponding sphere diameter 22%, tetra-decahedral grains)	as silver	0.33
Gelatin		0.1
ExS-1		4.5×10^{-4} mol
ExS-2		1.5×10^{-4} mol

ExS-3	0.4×10^{-4} mol
ExC-1	0.40
ExC-2	0.11
ExC-3	0.009
ExC-4	0.023
Solv-1	0.24

Fourth Layer (Second Red-Sensitive Emulsion Layer)

Silver iodobromide emulsion (AgI 8.5 mol%, high internal AgI type, corresponding sphere diameter 1.0 μm, coefficient of variation of the corresponding sphere diameter 25%, tabular grains, diameter/thickness ratio 3.0) as silver	0.55
Gelatin	0.7
ExS-1	3×10^{-4} mol
ExS-2	1×10^{-4} mol
ExS-3	0.3×10^{-4} mol
ExC-1	0.10
ExC-2	0.05
ExC-4	0.025
Solv-1	0.20

Fifth Layer (Third Red-Sensitive Emulsion Layer)

Silver iodobromide emulsion (AgI 11.3 mol%, high internal AgI type, corresponding sphere diameter 1.4 μm, coefficient of variation of the corresponding sphere diameter 28%, tabular grains, diameter/thickness ratio 6.0)	as silver 1.29
Gelatin	0.6
ExS-1	2×10^{-4} mol
ExS-2	0.6×10^{-4} mol
ExS-3	0.2×10^{-4} mol
ExC-2	0.08
ExC-4	0.01
ExC-5	0.06
Solv-1	0.12
Solv-2	0.12

Sixth Layer (Intermediate Layer)

Gelatin	1.0
Cpd-4	0.1
Solv-1	0.1

Seventh Layer (First Green-Sensitive Emulsion Layer)

Silver iodobromide emulsion (AgI 8.5 mol%, high internal AgI type, corresponding sphere diameter 1.0 μm, coefficient of variation of the corresponding sphere diameter 25%, tabular grains, diameter/thickness ratio 3.0)	as silver 0.28

Silver iodobromide emulsion (AgI 4.0 mol%, high internal AgI type, corresponding sphere diameter 0.7 μm, coefficient of variation of the corresponding sphere diameter 38%, tabular grains, diameter/thickness ratio 2.0)	as silver 1.0
Gelatin	1.2
ExS-5	5×10^{-4} mol
ExS-6	2×10^{-4} mol
ExS-7	1×10^{-4} mol
ExM-1	0.50
ExM-2	0.10
ExM-5	0.03
Solv-1	0.2
Solv-4	0.03

Eighth Layer (Second Green-Sensitive Emulsion Layer)

Silver iodobromide emulsion (AgI 8.5 mol%, high internal AgI type, corresponding sphere diameter 1.0 μm, coefficient of variation of the corresponding sphere diameter 25%, tabular grains, diameter/thickness ratio 3.0)	as silver 0.47
Gelatin	0.35
ExS-5	3.5×10^{-4} mol
ExS-6	1.4×10^{-4} mol
ExS-7	0.7×10^{-4} mol
ExM-1	0.12
ExM-3	0.01

Solv-1	0.15
Solv-4	0.03

Ninth Layer (Intermediate Layer)

Gelatin	0.5

Tenth Layer (Third Green-Sensitive Emulsion Layer)

Silver iodobromide emulsion (AgI 11.3 mol%, high internal AgI type, corresponding sphere diameter 1.4 μm, coefficient of variation of the corresponding sphere diameter 28%, tabular grains, diameter/thickness ratio 6.0)	as silver 1.3
Gelatin	0.8
ExS-5	2×10^{-4} mol
ExS-6	0.8×10^{-4} mol
ExS-7	0.8×10^{-4} mol
ExM-3	0.01
ExM-4	0.04
ExC-4	0.005
Cpd-5	0.01
Solv-1	0.2

Eleventh Layer (Yellow Filter Layer)

Cpd-3	0.05
Gelatin	0.5
Solv-1	0.1

Twelfth Layer (Intermediate Layer)

Gelatin	0.5

Cpd-2		0.1

Thirteenth Layer (First Blue-Sensitive Emulsion Layer)

Silver iodobromide emulsion (AgI 10 mol%, high internal AgI type, corresponding sphere diameter 0.7 μm, coefficient of variation of the corresponding sphere diameter 14%, tetradecahedral grains)	as silver	0.1
Silver iodobromide emulsion (AgI 4.0 mol%, high internal AgI type, corresponding sphere diameter 0.4 μm, coefficient of variation of the corresponding sphere diameter 22%, tetradecahedral grains)	as silver	0.05
Gelatin		1.0
ExS-8		3×10^{-4} mol
ExY-1		0.6
ExY-2		0.02
Solv-1		0.15

Fourteenth Layer (Second Blue-Sensitive Emulsion Layer)

Silver iodobromide emulsion (AgI 19.0 mol%, high internal AgI type, corresponding sphere diameter 1.0 μm, coefficient of variation of the corresponding sphere diameter 16%, tetradecahedral grains)	as silver	0.19
Gelatin		0.3
ExS-8		2×10^{-4} mol
ExY-1		0.22
Solv-1		0.07

Fifteenth Layer (Intermediate Layer)

Fine grain silver iodobromide (AgI 2 mol%, uniform type, corresponding sphere diameter 0.13 μm)	as silver	0.2
Gelatin		0.36

Sixteenth Layer (Third Blue-Sensitive Emulsion Layer)

Silver iodobromide emulsion (AgI 14.0 mol%, high internal AgI type, corresponding sphere diameter 1.7 μm, coefficient of variation of the corresponding sphere diameter 28%, tabular grains, diameter/thickness ratio 5.0)	as silver	1.4
Gelatin		0.5
ExS-9		1.5×10^{-4} mol
ExY-1		0.2
Solv-1		0.07

Seventeenth Layer (First Protective Layer)

Gelatin	1.8
UV-1	0.1
UV-2	0.2
Solv-1	0.01
Solv-2	0.01

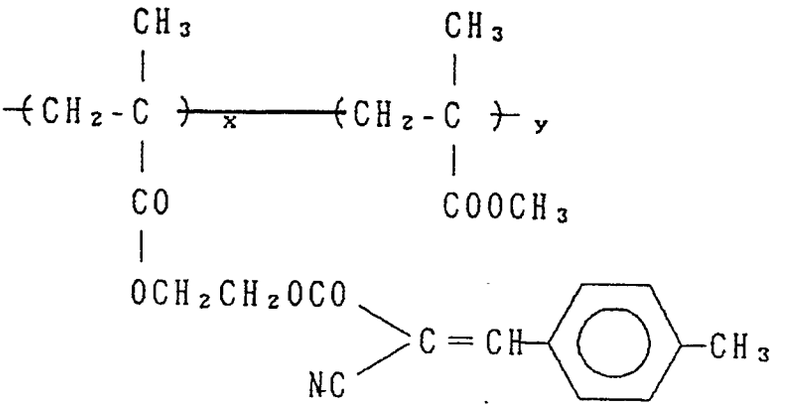
Eighteenth Layer (Second Protective Layer)

Fine grain silver chloride (corresponding sphere diameter 0.07 μm)	as silver	0.36
Gelatin		0.7

Poly(methyl methacrylate) particles (diameter 1.5 μm)	0.2
W-1	0.02
H-1	0.4
Cpd-6	1.0

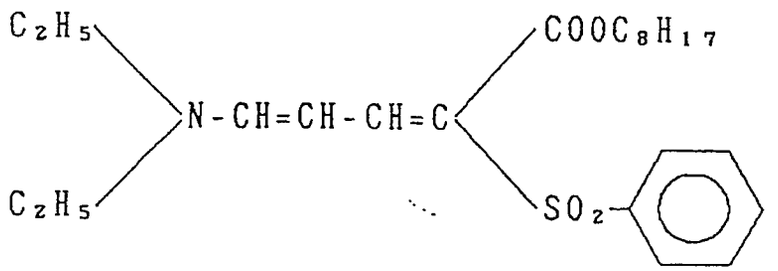
Apart from the components indicated above, B-1 (total 0.20 g/m^2), 1,2 benzisothiazolin-3-one (average about 200 ppm with respect to the gelatin), n-butyl p-hydroxybenzoate (1,000 ppm with respect to the gelatin) and 2-phenoxyethanol (10,000 ppm with respect to the gelatin) was added to each layer.

UV－1：

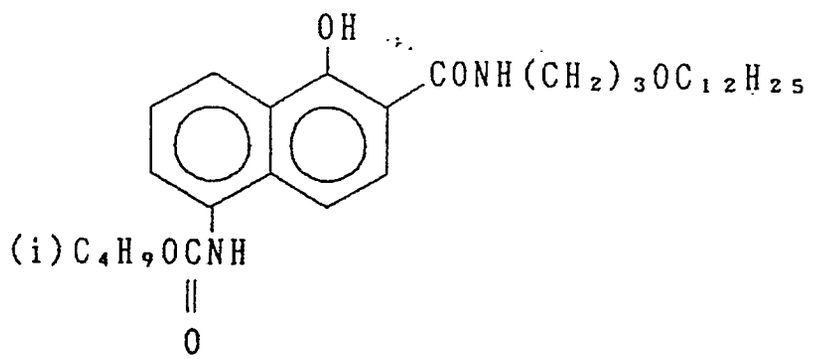


x/y=7/3 (weight ratio)

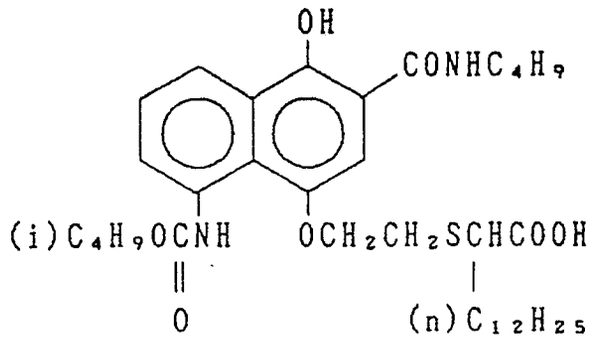
UV－2：



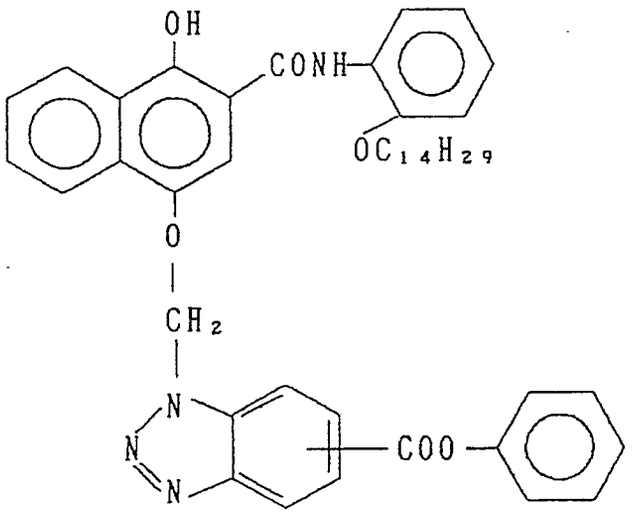
ExC－1



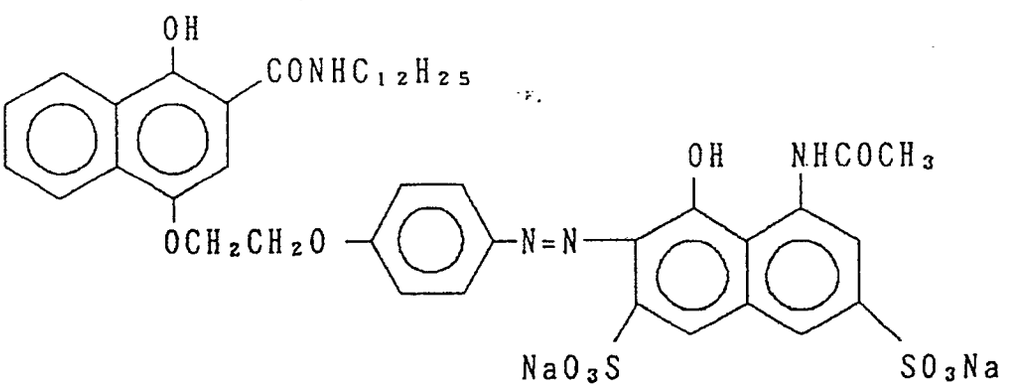
Ex C－2



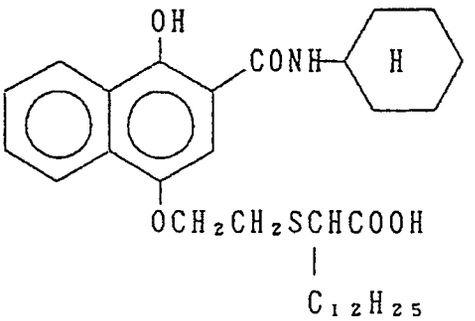
Ex C－3



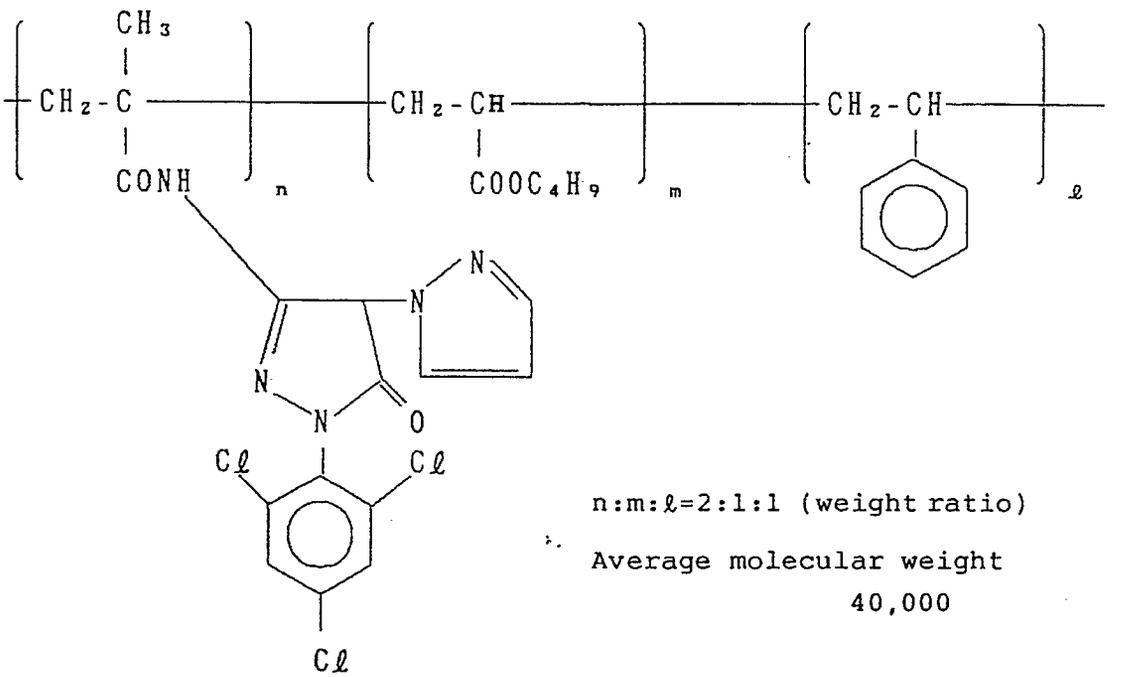
Ex C－4



Ex C－5



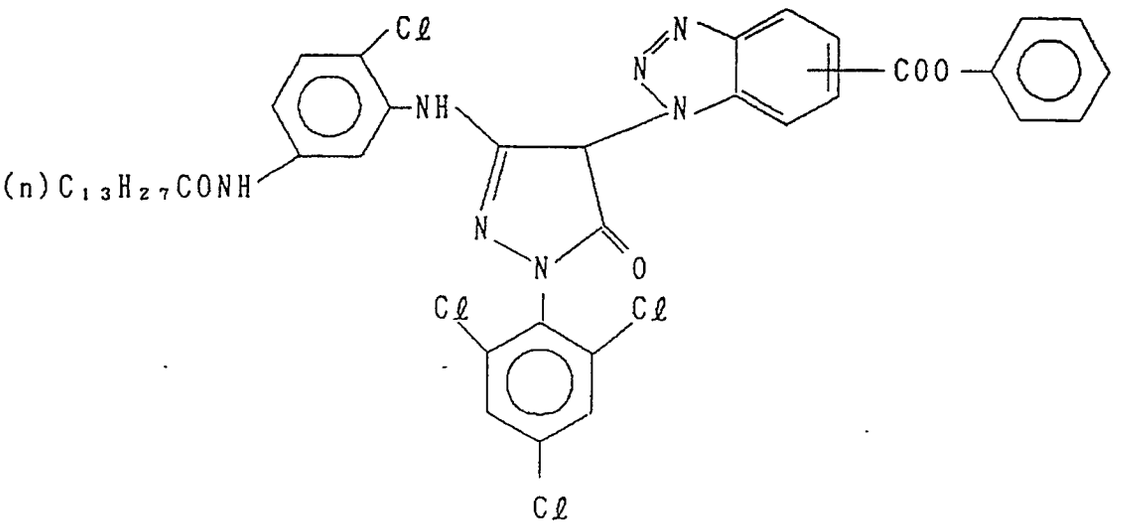
Ex M－1



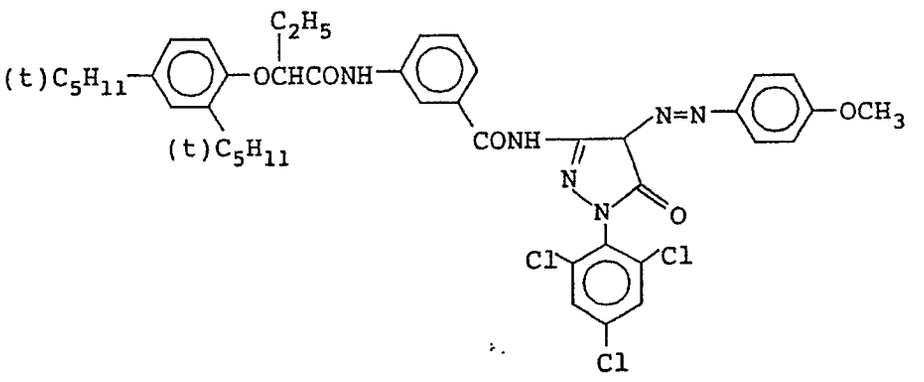
n:m:ℓ=2:1:1 (weight ratio)

Average molecular weight
40,000

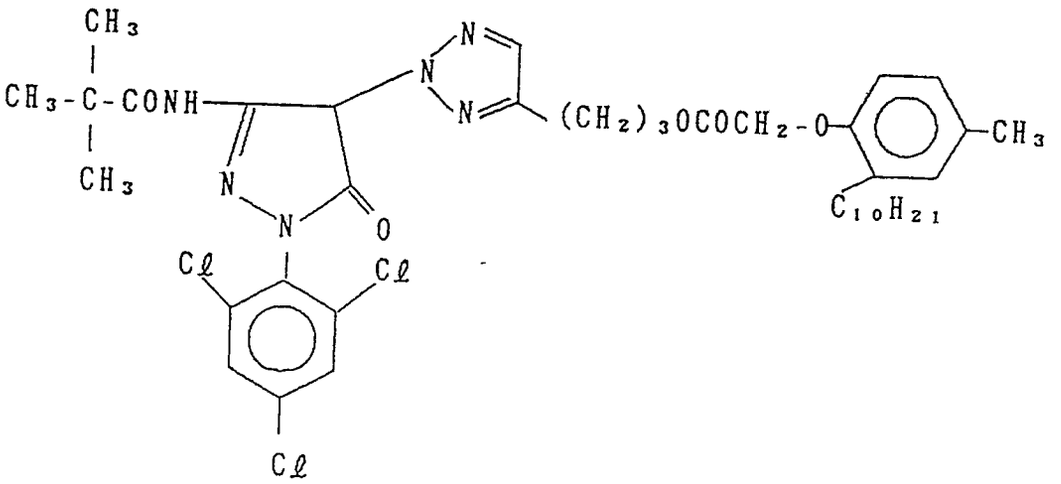
ExM-2



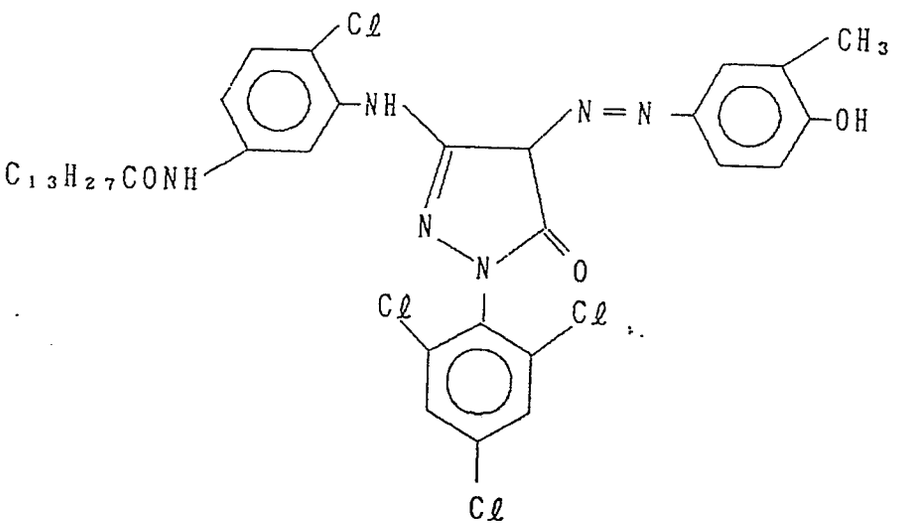
ExM-3



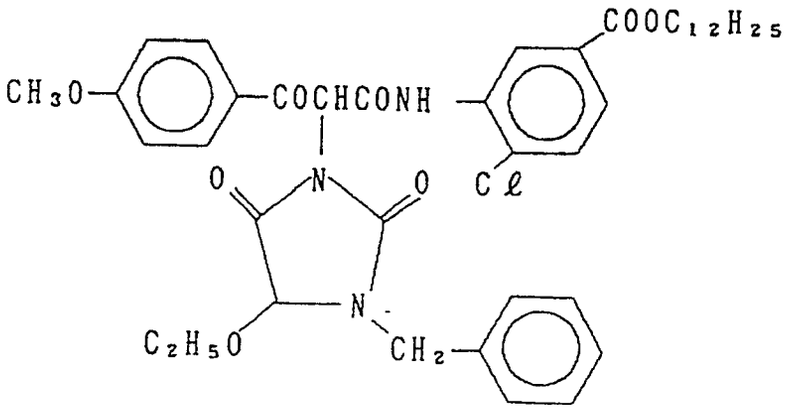
Ex M − 4



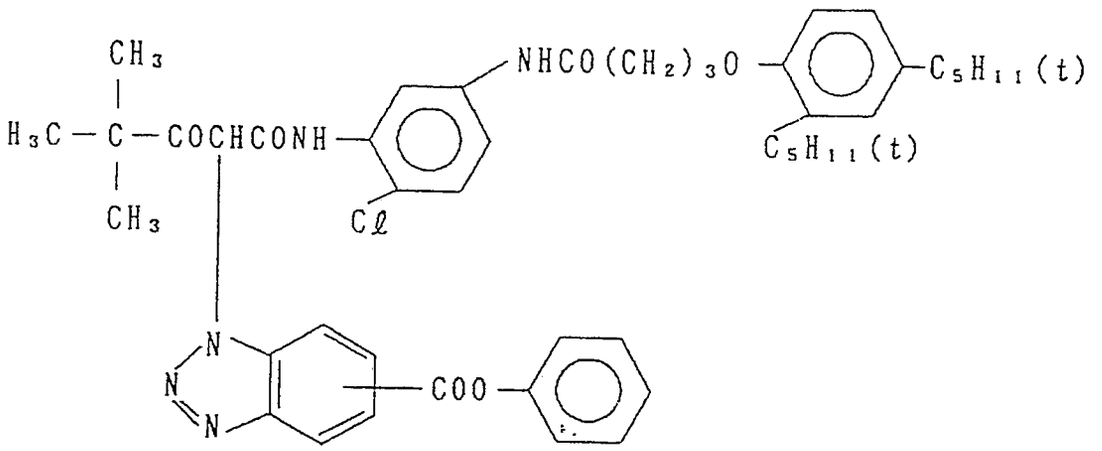
Ex M − 5



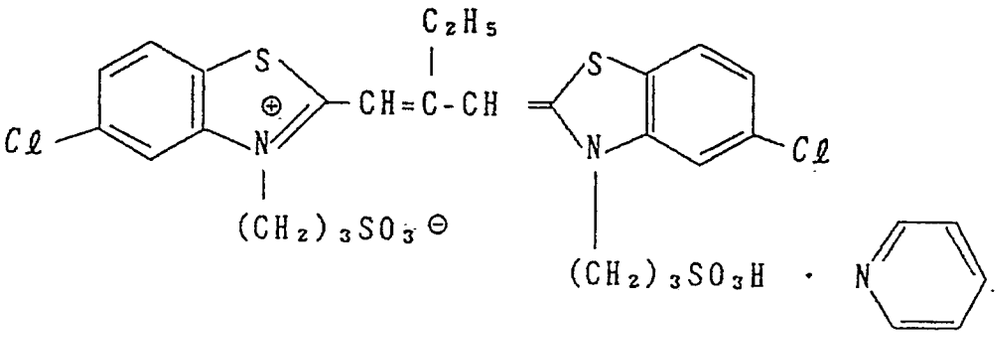
Ex Y－1



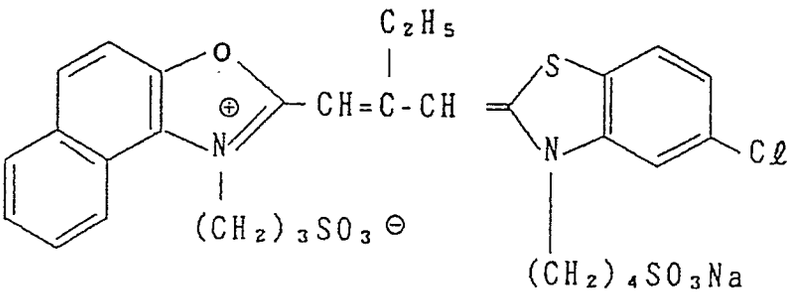
Ex Y－2



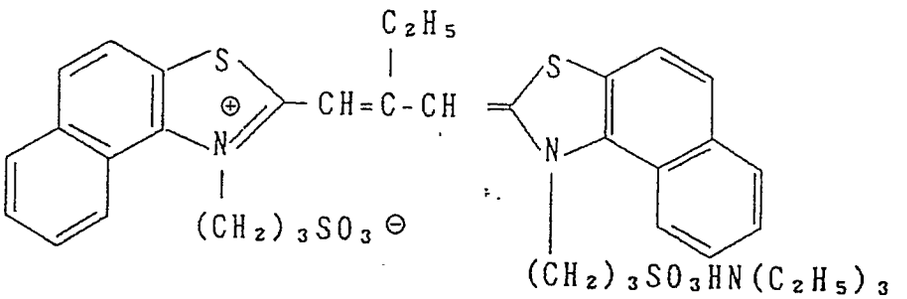
Ex S − 1



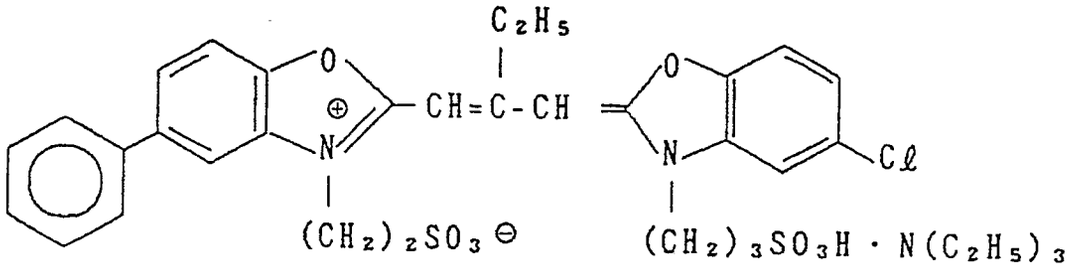
Ex S − 2



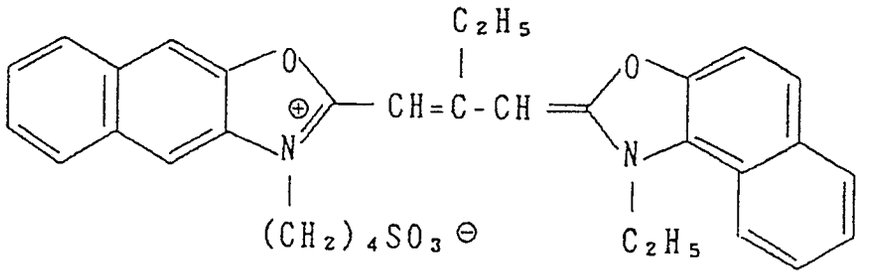
Ex S − 3



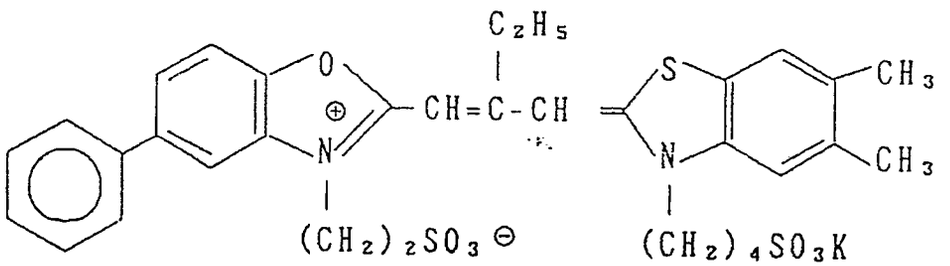
Ex S − 5



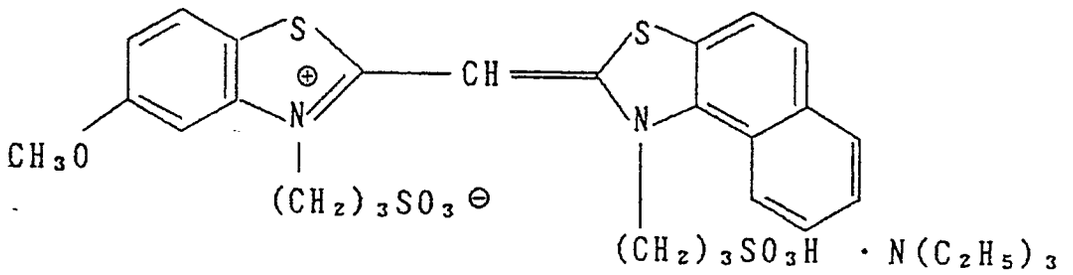
Ex S − 6



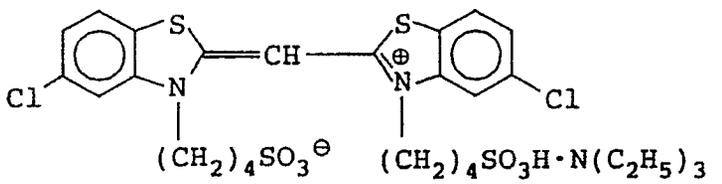
Ex S − 7



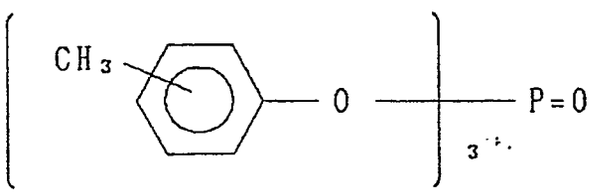
Ex S − 8



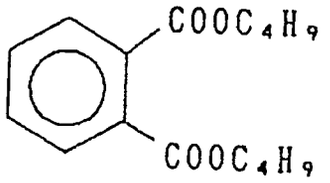
ExS-9



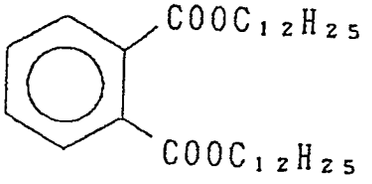
Solv − 1



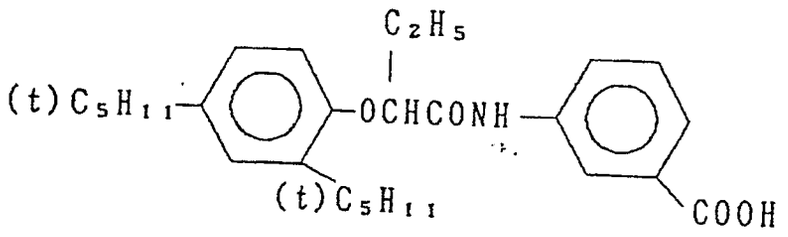
Solv-2



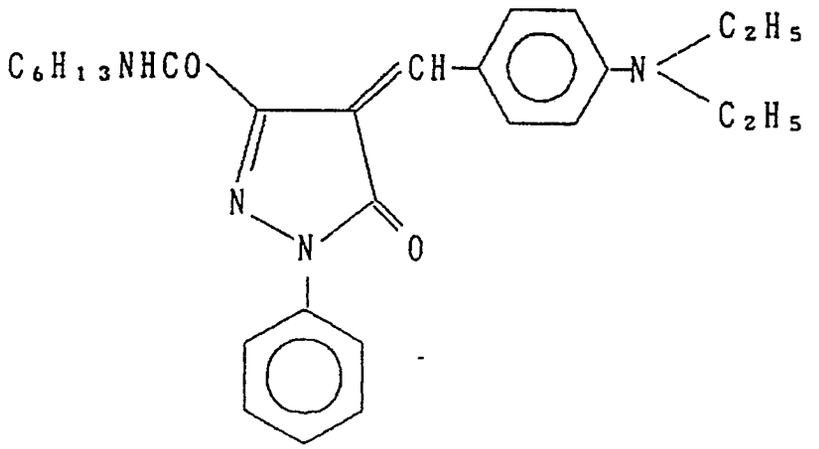
Solv-3



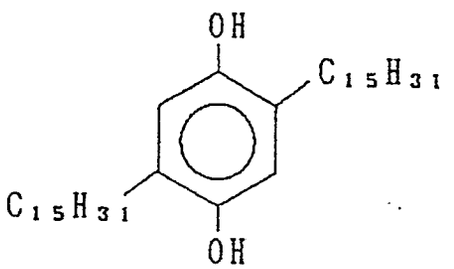
Solv-4



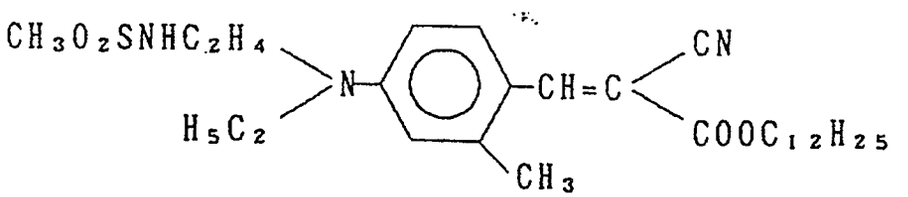
Cpd－1



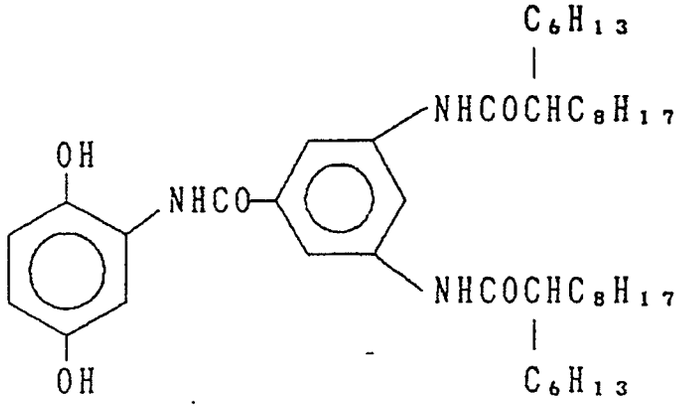
Cpd－2



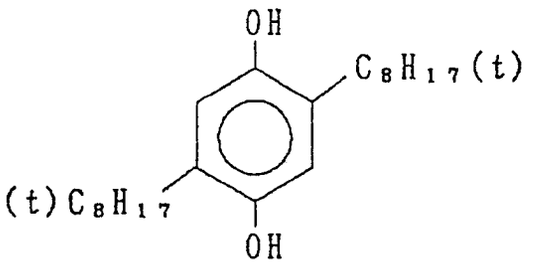
Cpd－3



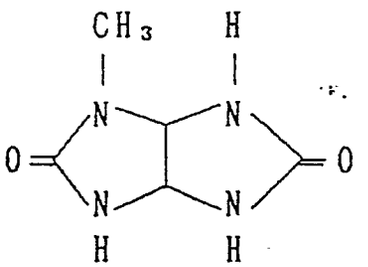
Cpd－4



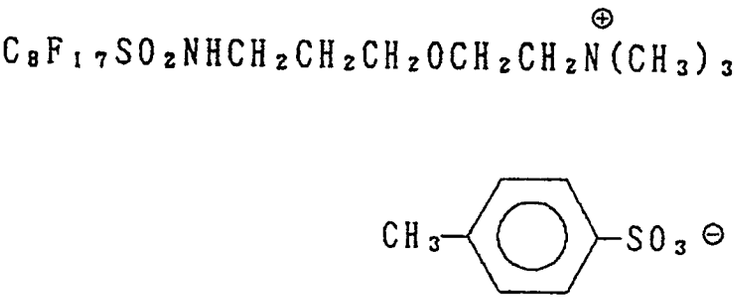
Cpd－5



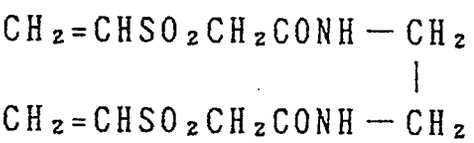
Cpd－6



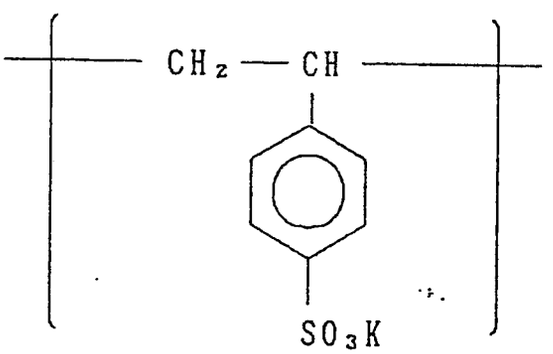
W-1



H-1

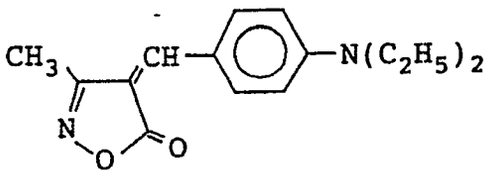


B-1

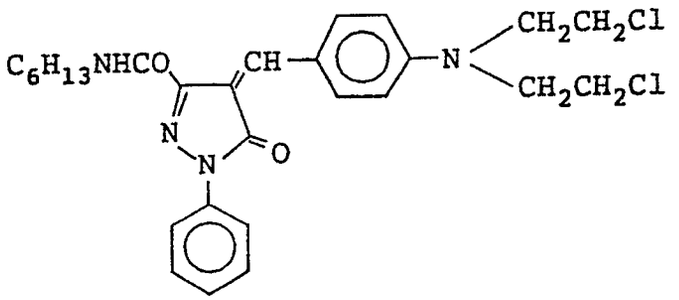


Samples 102 to 112 were prepared in the same way as sample 101 except that Cpd-1 in the first layer of sample 101 was replaced with Cpd-6, Cpd-7 and Cpd-8 indicated below, and compounds 1, 6, 8, 10, 14, 17, 20 and 21 of this present invention.

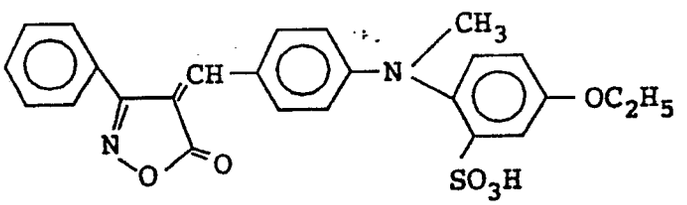
Cpd-6



Cpd-7



Cpd-8



The samples 101 to 112 obtained in this way were given a wedge exposure using white light and processed at 38° C in the way indicated below.

Processing	
1. Color Development	3 minutes 15 seconds
2. Bleaching	6 minutes 30 seconds
3. Water washing	3 minutes 15 seconds
4. Fixing	6 minutes 30 seconds
5. Water Washing	3 minutes 15 seconds
6. Stabilizing	3 minutes 15 seconds

The composition of the processing bath used in each process was as indicated below:

Color Development Bath	
Sodium nitrilotriacetate	1.0 g
Sodium sulfite	4.0 g
Sodium carbonate	30.0 g
Potassium bromide	1.4 g
Hydroxylamine sulfate	2.4 g
4-(N-Ethyl-N-β-hydroxyethylamino)-2-methylaniline sulfate	4.5 g
Water	to make 1.0 ℓ

Bleach Bath	
Ammonium bromide	160.0 g
Aqueous ammonia (28%)	25.0 ml
Sodium ethylenediaminetetraacetato ferrate	130.0 g
Glacial acetic acid	14.0 ml
Water	to make 1.0 ℓ

Fixer Bath	
Sodium tetrapolyphosphate	2.0 g
Sodium sulfite	4.0 g
Ammonium thiosulfate (70%)	175.0 ml
Sodium bisulfite	4.6 g
Water	to make 1.0 ℓ

Stabilizer Bath	
Formaldehyde	8.0 ml
Water	to make 1.0 ℓ

The photographic sensitivities of the green-sensitive layers were assessed by measuring the densities of the processed samples so obtained.

Moreover, samples 101 to 112 were stored for 10 days under conditions of 25° C, 60% RH or 50° C, 70% RH and then subjected to the aforementioned bleaching and subsequent processes without being exposed and density measurements were made to assess the changes in density.

The results obtained are shown in Table 1.

TABLE 1

Sample	Relative Green Sensitivity*	ΔD_B**	Dye	Relationship with the Invention
101	100	0.05	Cpd-1	Comparative Example
102	93	0.10	Cpd-6	"
103	93	0.15	Cpd-7	"
104	63	0.18	Cpd-8	"
105	107	0.01	1	Invention
106	107	0	6	"
107	107	0	8	"
108	107	0	10	"
109	107	0.01	14	"
110	107	0.01	17	"
111	107	0	20	"
112	107	0	21	"

*: Relative sensitivity taking the sensitivity for sample 101 to be 100

**: (Yellow density on aging at 25 ° C, 60% RH)-(Yellow density on aging at 50 ° C, 70% RH)

It is clear from Table 1 that with the samples of this present invention the green sensitivity was higher than that of the comparative examples and there was no change in density due to the aging of the material and these samples had excellent aging stability.

It is thought that dye migration is one of the reasons for the lowering of the green sensitivity and the change in density due to aging. The compounds of this present invention have excellent oil solubility and there is no migration of the dye during processing or during the long term storage of the light-sensitive material.

EXAMPLE 2

Sample 201, a multi-layer color light-sensitive material comprising a similar support to that used in Example 1 having thereon layers of which the compositions are indicated below, was prepared.

Composition of the Light-sensitive Layer

The coated amounts are indicated in the same way as in Example 1.

First Layer (Anti-halation Layer)	
Black colloidal silver	as silver 0.2
Gelatin	1.8
UV-1	0.1
UV-2	0.2
Solv-1	0.01
Solv-2	0.01

Second Layer (Intermediate Layer)

Same as the second layer in Example 1.

Third Layer (First Red-Sensitive Emulsion Layer)

Same as the third layer in Example 1.

Fourth Layer (Second Red-Sensitive Emulsion Layer)

Same as the fourth layer in Example 1.

Fifth Layer (Third Red-Sensitive Emulsion Layer)

Same as the fifth layer in Example 1.

Sixth Layer (Intermediate Layer)

Same as the sixth layer in Example 1.

Seventh Layer (First Green-Sensitive Emulsion Layer)

Same as the seventh layer in Example 1.

Eighth Layer (Second Green-Sensitive Emulsion Layer)

Same as the eighth layer in Example 1.

Ninth Layer (Intermediate Layer)

Same as the ninth layer in Example 1.

Tenth Layer (Third Green-Sensitive Emulsion Layer)

Same as the tenth layer in Example 1.

Eleventh Layer (Yellow Filter Layer)	
Yellow colloidal silver	0.04
Cpd-2	0.031
Solv-1	0.04
Solv-2	0.01
Gelatin	0.6

Twelfth Layer (First Blue-Sensitive Emulsion Layer)

Same as the thirteenth layer in Example 1.

Thirteenth Layer (Second Blue-Sensitive Emulsion Layer)

Same as the fourteenth layer in Example 1.

Fourteenth Layer (Intermediate Layer)

Same as the fifteenth layer in Example 1.

Fifteenth Layer (Third Blue-Sensitive Emulsion Layer)

Same as the sixteenth layer in Example 1.

Sixteenth Layer (First Protective Layer)

Same as the seventeenth layer in Example 1.

Seventeenth Layer (Second Protective Layer)

Same as the eighteenth layer in Example 1.

Apart from the components indicated above, B-1, 1,2-benzisothiazolin-3-one, n-butyl p-hydroxybenzoate and 2-phenoxyethanol were added to each layer in the same way as in Example 1.

The chemical structures of the additives were the same as in Example 1.

Next, sample 202 was prepared in the same way as sample 201 except that the eleventh layer of sample 201 was modified in the way indicated below, 0.05 g/m^2 of Cpd-10 was added to the first layer of sample 201 and the amount of Solv-1 in the first layer of sample 201 was changed from 0.01 g/m^2 to 0.10 g/m^2.

Eleventh Layer	
Cpd-9	0.05
Cpd-2	0.1
Solv-1	0.2
Gelatin	0.6

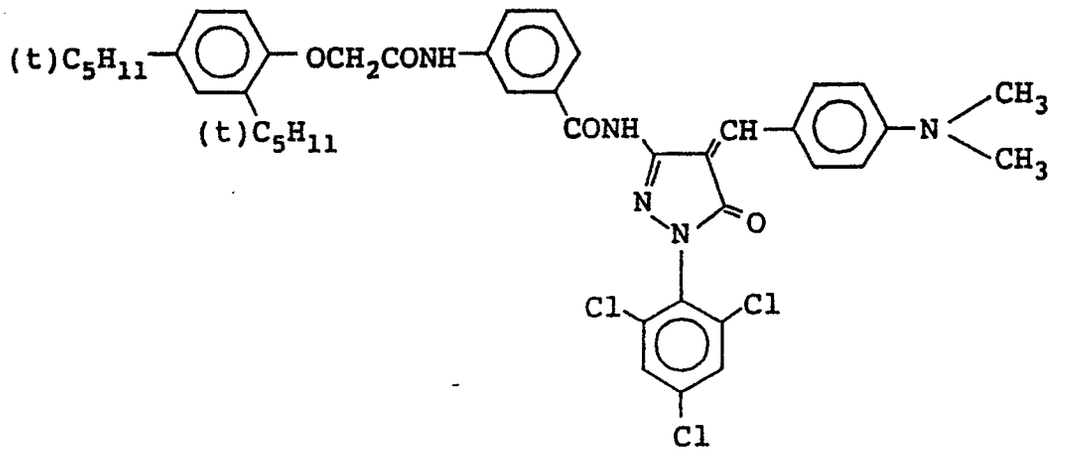
(Cpd-9 and Cpd-10 were used by emulsification and dispersion of a solution obtained by dissolving these compounds in a mixed solvent comprising ethyl acetate and a high boiling point organic solvent in the same way as the other oil soluble compounds used in this example.)

Furthermore, sample 203 was prepared in the same way as sample 202 except that Cpd-9 in the eleventh layer of sample 202 and Cpd-10 in the first layer of sample 202 were replaced by compound 44 and Cpd-11, respectively.

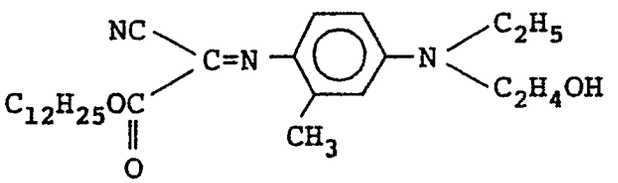
Furthermore, samples 204, 205 and 206 were prepared in the same way as sample 203 except that Cpd-11 in the first layer of sample 203 was replaced by compound 6, compound 32 and compound 5 of the present invention, respectively.

Moreover, samples 207 and 208 were prepared in the same way as sample 203 except that compound 44 in the eleventh layer of sample 203 was changed to compound 39, and Cpd-11 in the first layer of sample 203 was changed to compound 1 or compound 37, respectively.

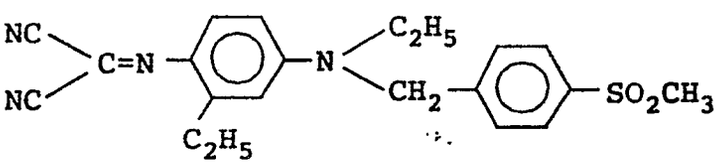
Cpd-9



Cpd-10



Cpd-11



Samples 201 to 208 obtained in this way were exposed and processed in the same way as described in Example 1.

Density measurements were carried out with the processed samples so obtained. Furthermore, samples 201 to 208 were stored for 1 month under an atmosphere of 60% RH at 40 °C and then (after aging) the samples were exposed and processed in the same way as before and density measurements were made.

The results obtained are shown in Table 2.

TABLE 2

Increase in Fog on Aging for 1 Month at 40 °C, 60% RH				
Sample	Relative Green Sensitivity*	Blue-Sensitive Layer ΔD_{min}**	Gren-Sensitive Layer ΔD_{min}**	Remarks
201	100	0.14	0.08	Comparative Example
202	105	0.13	0.08	"
203	120	0.19	0.10	"
204	123	0.12	0.06	Invention
205	122	0.12	0.06	"
206	123	0.11	0.05	"
207	123	0.12	0.05	"
208	122	0.11	0.05	"

*: Relative sensitivity taking the green sensitivity for sample 201 to be 100.
**: (Fog value after aging)-(Fog value before aging)

It is clear from Table 2 that in comparison to sample 201, the green-sensitive layer of sample 202 showed very little increase in sensitivity, while with sample 203 there was an increase in sensitivity when compared with sample 201 but the rise in fog level after aging was considerable. On the other hand, with the samples of the present invention there was a clear improvement in both sensitivity and the rise in fog level after aging.

EXAMPLE 3

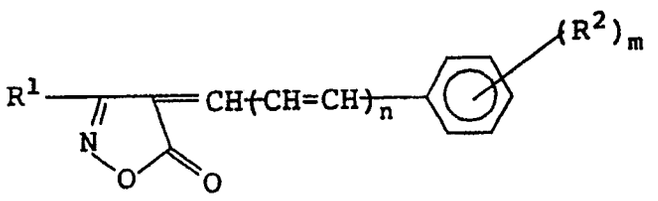
A Macbeth chart was photographed using samples 201, 202 and 207 prepared in Example 2 and, after processing in the way described in Example 2, the images were printed onto color paper using an auto-printer.

On printing under-conditions such that the gray patch part of the Macbeth chart was the proper gray with sample 201, there was a yellow cast with sample 202 and pronounced color displacement, while good color reproduction was obtained with sample 207 of the present invention.

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 light-sensitive material which comprises at least one dye which is insoluble in water and is represented by formula (1):

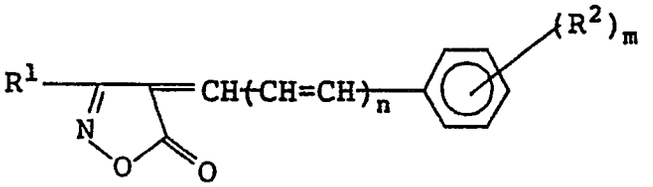


(1)

wherein R^1 represents an alkyl group, a cycloalkyl group, an aryl group, a heterocyclic group, a carboxyl group, an alkoxycarbonyl group, an aryloxycarbonyl group, a carbamoyl group or a cyano group; R^2 represents a hydrogen atom, a halogen atom, an alkyl group, an alkoxy group, a hydroxy group, an amino group, a carbamoyl group, a sulfamoyl group or an alkoxycarbonyl group; R^2 may form a five or six

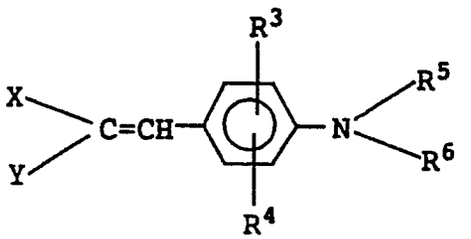
membered ring with the benzene ring; n represents 0 or 1, and m represents 1 to 5; with the proviso that at least one alkyl chain which has four or more carbon atoms is contained within R^1 and R^2; and where m is 2 or more, the R^2 groups may be the same or different.

2. A silver halide photographic light-sensitive material which comprises at least one dye which is insoluble in water and is represented by formula (1) and at least one dye which is insoluble in water and is represented by formula (2):



(1)

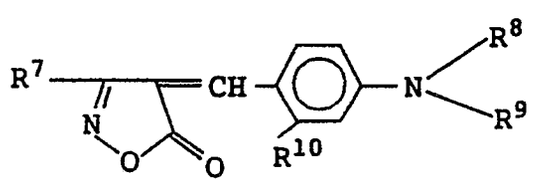
wherein R^1 represents an alkyl group, a cycloalkyl group, an aryl group, a heterocyclic group, a carboxyl group, an alkoxycarbonyl group, an aryloxycarbonyl group, a carbamoyl group or a cyano group; R^2 represents a hydrogen atom, a halogen atom, an alkyl group, an alkoxy group, a hydroxy group, an amino group, a carbamoyl group, a sulfamoyl group or an alkoxycarbonyl group; R^2 may form a five or six membered ring with the benzene ring; n represents 0 or 1, and m represents 1 to 5; with the proviso that at least one alkyl chain which has four or more carbon atoms is contained within R^1 and R^2; and where m is 2 or more the R^2 groups may be the same or different,



(2)

wherein X and Y may be the same or different, each representing 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, with the proviso that where the combination of X and Y is (cyano group, arylcarbonyl group), (cyan group, alkylcarbonyl group) or (cyano group, sulfonyl group) are excluded; R^3 and R^4 may be the same or different, each representing a hydrogen atom, a halogen atom, an alkyl group, an alkoxy group, a hydroxy group, a carboxyl group, an amino group, a carbamoyl group, a sulfamoyl group or an alkoxycarbonyl group; R^5 and R^6 may be the same or different, each representing a hydrogen atom, an alkyl group or an aryl group, and R^5 and R^6 may form a five or six membered ring; and R^3 or R^5, or R^4 and R^5, may be joined together to form a five or six membered ring.

3. The silver halide photographic light-sensitive material as in Claim 1, wherein said dye which is insoluble in water is represented by formula (3):



(3)

wherein R^7 represents an alkyl group; R^8 and R^9 may be the same or different, each representing an alkyl group, and a five or six membered ring may be formed by R^8 and R^9; R^{10} represents a hydrogen atom, a halogen atom, an alkyl group, an alkoxy group, a hydroxy group, an amino group, a carbamoyl group, a sulfamoyl group or an alkoxycarbonyl group; with the proviso that at least one of the groups R^7, R^8, R^9 and R^{10} contains an alkyl chain which has at least four carbon atoms.

4. The silver halide photographic light-sensitive material of Claim 2, wherein the mol ratio of the dye of formula (1) for the dye of formula (2) is not more than 1 when the dye of formula (1) is used as a color

correcting dye.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 90 11 4522

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
Y	DD-A-131177 (VEB FILMFABRIK WOLFEN) * page 1, line 1 - page 2, line 2; claim 2 *	1-4	G03C1/83 G03C1/12
Y	EP-A-0319999 (FUJI) * page 10 *formulae (17),(18)*	1-4	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

G03C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	05 SEPTEMBER 1990	MAGRIZOS S.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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