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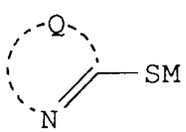
(54) **Silver halide photographic light-sensitive material.**

(57) A silver halide photographic light-sensitive material comprises a support and provided thereon, a silver halide emulsion layer containing spectrally sensitized silver halide grains having a silver chloride content of not less than 90 mol%, a cyclic compound having a 9- or more-membered ring containing a hetero atom, and at least one compound represented by the following formula (S):

Formula (S)



wherein Q represents an atomic group necessary to form 5- or 6-membered hetero cyclic ring, provided that said Q may form a condensed ring with a benzene ring; and M represents a hydrogen atom, an alkali metal atom, or an ammonium group.

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Field of the invention

The present invention relates to a silver halide photographic light-sensitive material, more particularly to a high-speed silver halide photographic light-sensitive material excellent in sensitivity fluctuation caused by long term storage of a raw product and improving fluctuation in sensitivity due to change of humidity on light exposure.

Background of the invention

Recently, in order to finish a large amount of prints in a short delivery time, light-sensitive materials for color photographic papers to be improved in terms of rapid processing have been demanded. As one of the methods for attaining this, a method to use silver chloride emulsions or silver bromochloride emulsion having a high silver chloride content for enhancing processing speed has been known. However, it has been known that silver chloride emulsions or silver bromochloride emulsion having a high silver chloride content have a shortcoming of low sensitivity.

As a method for enhancing sensitivity, it is known that a super sensitization method is useful. Super sensitization is described in Photographic Science and Engineering, Volume 13, pp. 13 - 17 (1969) and Volume 18, pp. 418 - 430 (1974) and The Theory of the Photographic Process 4th edition, page 259, published by MacMillan Inc., 1977. It is known that, by selecting suitable sensitizing dyes and super sensitizers, high sensitivity can be obtained.

Heretofore, many compounds such as stilbene, azaindene, mercaptoheterocycles, thiourea and condensed compounds between phenol and hexamethylenetetraamine have been known as a super sensitizer. For example, they are disclosed in USP. Nos. 2,875,058, 3,340,064, 3,457,078, 3,458,318, 3,615,632, 3,695,888 and 4,011,083 and Japanese Patent Publication Open to Public Inspection (hereinafter referred to as "Japanese Patent O.P.I. Publication") No. 203447/1986. However, it was discovered that, when a silver halide emulsion is subjected to super sensitization by the use of the above-mentioned conventional technology, increase in sensitivity is still insufficient, and that fluctuation in photographic sensitivity is noticeable after storage of raw products.

Storage stability of photographic light-sensitive materials is extremely critical for preventing deterioration in quality of the print finish. Therefore, the above-mentioned technologies are not practically desirable.

In Japanese Patent O.P.I.. Publication No. 100048/1990, technology to incorporate crown ethers and cyclodextrine into silver halide light-sensitive materials as a coagulation-destroying compound for magenta dyes is disclosed. However, the object of this technology is to improve stability of magenta dye, and no suggestion is given with regard to super sensitization effects of the above-mentioned compounds.

Japanese Patent O.P.I.. Publication No. 25833 discloses that tetrazole derivatives having a cyclic structure which serves as a chelating agent in a molecule provide super sensitization to silver bromide emulsions. However, there is no description in it about super sensitization effects on silver chloride or silver-chloride-rich silver bromochloride. According to the studies of the present inventors, it was proven that, even when tetrazole derivatives having a cyclic structure which serves as a chelating agent are used as a super sensitizing agent on silver-chloride-rich silver bromochloride, its sensitization effect is small and it has a remarkable sensitivity fluctuation against change in humidity when exposed to light.

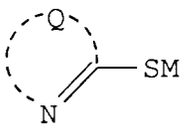
Summary of the Invention

An object of the present invention is to provide a silver halide photographic light-sensitive material, more particularly to a high-speed silver halide photographic light-sensitive material excellent in sensitivity fluctuation caused by long term storage of a raw product wherein fluctuation in sensitivity due to change of humidity when exposed to light has been modified.

Detailed Description of the Invention

The above object of the invention can be attained by a silver halide photographic light-sensitive material comprising a support and provided thereon, a silver halide emulsion layer containing spectrally sensitized silver halide grains having a silver chloride content of not less than 90 mol%, a cyclic compound comprising a 9- or more-membered ring containing a hetero atom, and at least one of compounds represented by the following formula (S):

Formula (S)



wherein Q represents an atomic group necessary to form 5- or 6-membered hetero cyclic ring, provided that said Q may form a condensed ring with a benzene ring; and M represents a hydrogen atom, an alkali metal atom, or an ammonium group.

A preferred embodiment of the above-mentioned cyclic compound has an aromatic ring and an ether bond or has an aliphatic ring and an ether bond. The number of the aforesaid aliphatic ring is 0 to 4. The aforesaid cyclic compound preferably comprises two or more aromatic rings and an ether bond. The aforesaid cyclic compound is more preferably a compound represented by the following Formula (1) . The aforesaid silver halide emulsion layer preferably has a maximum spectral sensitivity in the wavelength region of not less than 600 nm.

Hereunder, the present invention will be explained in detail.

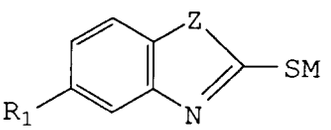
At first, compounds represented by Formula (S) will be explained.

In Formula (S), as 5-membered heterocycles represented by Q, for example, an imidazole ring, a tetrazole ring, a thiazole ring, an oxazole ring, a selenazole ring, a benzoimidazole ring, a naphthothiazole, a benzoselenazole ring, a naphthoselenazole ring and a benzoxazole ring are cited. As 6-membered heterocycles represented by Q, a pyridine ring, a pyrimidine ring and a quinoline ring are cited. The above-mentioned 5-membered or 6-membered rings may contain a substituent.

In Formula (S), as alkaline metal atoms represented by M, a sodium atom and a potassium atom are cited.

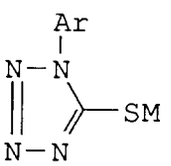
The mercapto compounds represented by Formula (S) preferably includes those represented by the following Formulas (S-1), (S-2), (S-3) and (S-4).

Formula (S-1)

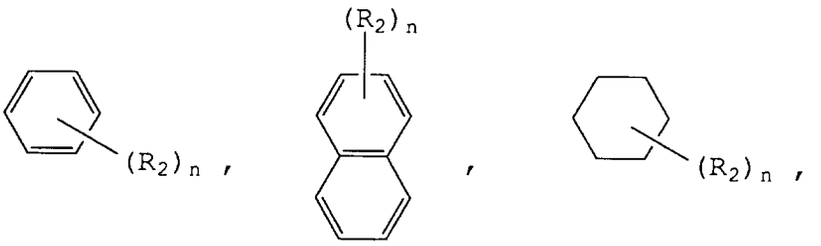


wherein R_1 represents a hydrogen atom, an alkyl group, an alkoxy group, an aryl group, a halogen atom, a carboxyl group or its salts, a sulfo group or its salts or an amino group; Z represents -NH-, -O- or -S-; M is the same as M in Formula (S).

Formula (S-2)



wherein Ar represents a group represented by the following chemical structure:



wherein R_2 represents an alkyl group, an alkoxy group, a carboxyl group or its salts, a sulfo group or its salts, a hydroxyl group, an amino group, an acylamino group, a carbamoyl group or a sulfonamide group; n represents 0 to 2; M is the same as M in Formula (S).

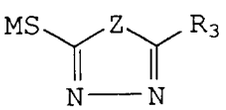
In Formulas (S-1) and (S-2), as alkyl groups represented by R_1 and R_2, for example, a methyl group, an ethyl group and a butyl group are cited. As alkoxy groups, for example, a methoxy group and an ethoxy group are cited. As salts of a carboxyl group or a sulfo group, a sodium salt and an ammonium salt are cited.

In Formula (S-1), as aryl groups represented by R_1, for example, a phenyl group and a naphtyl group are cited. As halogen atoms, for example, a chlorine atom and a bromine atom are cited.

In Formula (S-2), as acylamino groups represented by R_2, for example, a methylcarbonylamino group and a benzoylamino group are cited. As carbamoyl groups, for example, an ethylcarbamoyl group, a phenylcarbamoyl group are cited. As sulfonamide groups, for example, a methylsulfoamido group and a phenylsulfoamido group are cited.

The above-mentioned alkyl groups, alkoxy groups, aryl groups, amino groups, acylamino groups, carbamoyl groups and sulfonamide groups include those having a substituent.

Formula (S-3)



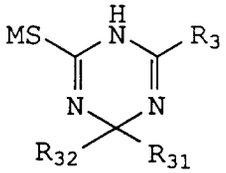
wherein Z represents $-NR_3-$, an oxygen atom or a sulfur atom; R_3 represents a hydrogen atom, an alkyl group, an aryl group, an alkenyl group, a cycloalkyl group, $-SR_{31}-$, $-NR_{32}(R_{33})-$, $-NHCOR_{34}$, $-NHSO_2R_{35}$ or a heterocyclic group; R_{31} represents a hydrogen atom, an alkyl group, an alkenyl group, a cycloalkyl group, an aryl group, $-COR_{34}$ or $-SO_2R_{35}$; R_{32} and R_{33} independently represent a hydrogen atom, an alkyl group or an aryl group; R_{34} and R_{35} independently represent an alkyl group or an aryl group; M is the same as M in Formula (S).

In Formula (S-3), as alkyl groups represented by R_3, R_{31}, R_{32}, R_{33}, R_{34} and R_{35}, a methyl group, a benzyl group, an ethyl group and a propyl group are cited. In addition, as aryl groups, a phenyl group and a naphtyl group are cited.

As alkenyl groups represented by R_3 and R_{31}, for example, a propenyl group is cited. As cycloalkyl groups, for example, a cyclohexyl group is cited. In addition, as heterocycles represented by R_3, a furyl group and a pyrridinyl group are cited.

Alkyl groups and aryl groups represented by the above-mentioned R_3, R_{32}, R_{33}, R_{34} and R_{35}, alkenyl groups and cycloalkyl groups represented by R_3 and R_{31} and heterocycles represented by R_3 also include those having a substituent.

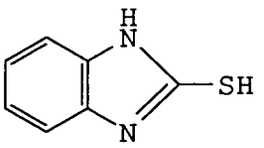
Formula (S-4)



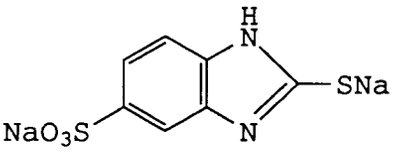
wherein R_3 and M independently represent the same group as R_3 and M in Formula (S-3).

Hereunder, examples of compounds represented by Formula (S) will be shown. However, the present invention is not limited thereto.

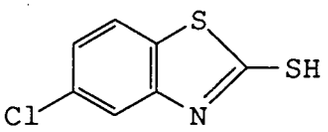
S-1-1



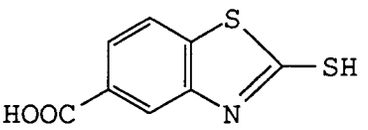
S-1-2



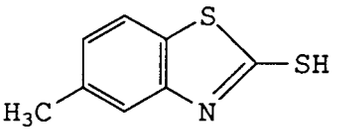
S-1-3



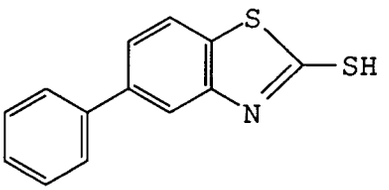
S-1-4



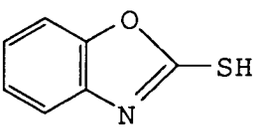
S-1-5



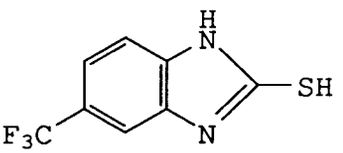
S-1-6



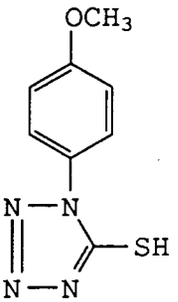
S-1-7



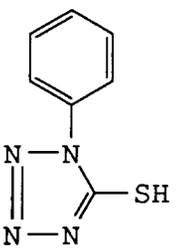
S-1-8



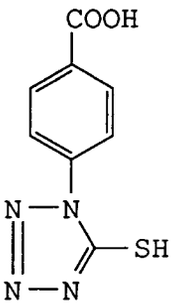
S-2-1



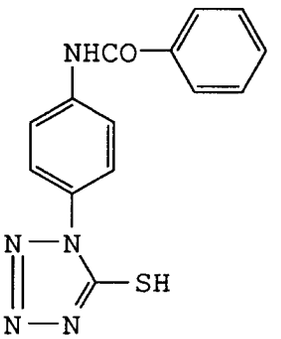
S-2-2



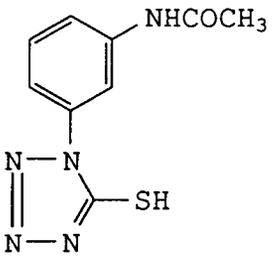
S-2-3



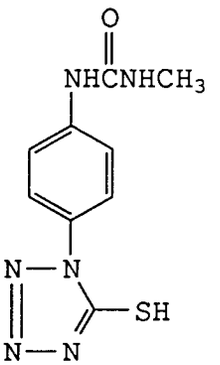
S-2-4



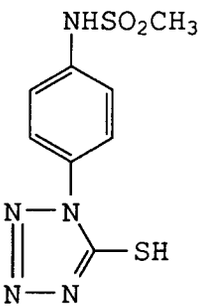
S-2-5



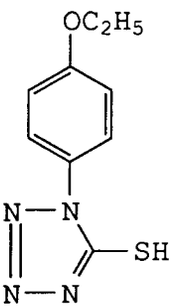
S-2-6

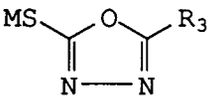


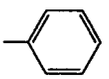
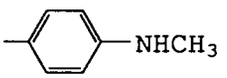
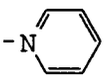
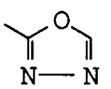
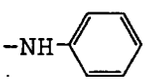
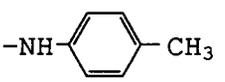
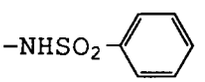
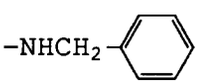
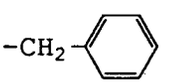
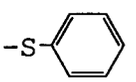
S-2-7

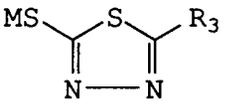


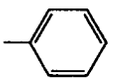
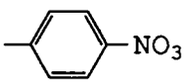
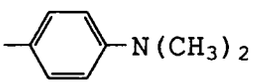
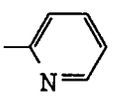
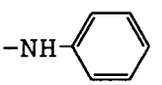
S-2-8

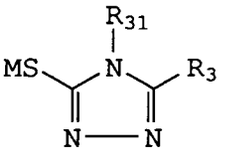


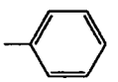
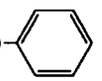
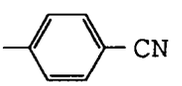
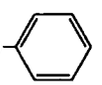
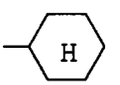
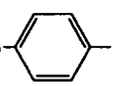
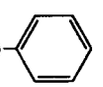
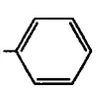


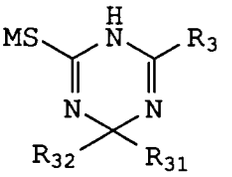
No. of the illustrated compound	R_3	M
S-3-1	$-C_2H_5$	-H
S-3-2	$-CH_2-CH=CH_2$	-H
S-3-3	$-CH=CH-CH_2-CH_3$	-H
S-3-4	$-C_7H_{15}$	-H
S-3-5	$-C_9H_{19}$	-Na
S-3-6		-H
S-3-7	$-C_4H_9(t)$	-H
S-3-8		-H
S-3-9		-H
S-3-10		-H
S-3-11		-H
S-3-12		-H
S-3-13	$-NHCOCH_3$	-H
S-3-14		-H
S-3-15	$-N(CH_3)_2$	-H
S-3-16		-H
S-3-17		-H
S-3-18	$-S-SH_3$	-H
S-3-19		-H
S-3-20	-SH	-H

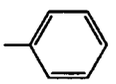
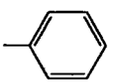
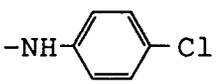
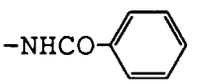
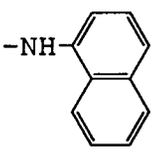
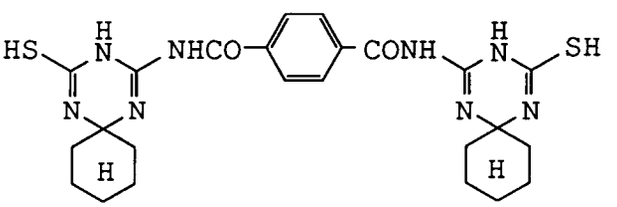


No. of the illustrated compound	R_3	M
S-3-21	-H	-H
S-3-22	$-C_2H_5$	-H
S-3-23	$-C_4H_9(t)$	-H
S-3-24	$-C_6H_{13}$	-H
S-3-25		-H
S-3-26		-H
S-3-27		-H
S-3-28		-H
S-3-29		-H
S-3-30	$-NH_2-N(CH_3)_2$	-H
S-3-31	$-CH_2CH-CH_2$	-H
S-3-32	-SH	-H
S-3-33	$-NHCOC_2H_5$	-H



No. of the illustrated compound	R_3	R_{31}	M
S-3-34	$-C_2H_5$	-H	-H
S-3-35	$-CH_3$	$-CH_3$	-H
S-3-36	$-CH_3$		-H
S-3-37	$-NHCOCH_3$	$-CH_3$	-H
S-3-38	-NHCO- 	-CO- 	-H
S-3-39	$-NHCOCH_3$	$-COCH_3$	-H
S-3-40	$-NHCOCH_3$	$-CH_2$- 	-H
S-3-41	$-NHCOC_2H_5$		Na
S-3-42	-NHCO- 		H
S-3-43	$-NHSO_2CH_3$	-H	H
S-3-44	-NHCO- 	$-CH_3$	Na
S-3-45	-NHCO- 	$-CH_2CH=CH_2$	H
S-3-46	-NHCO- 	$-CH_2CH_2O$- 	-H



No. of the illustrated compound	R_3	R_{31}	R_{32}	M
S-4-1	$-C_2H_5$	$-CH_3$	$-CH_3$	-H
S-4-2		$-CH_3$	$-CH_3$	-H
S-4-3	$-NH_2$	-H		-H
S-4-4		-H	$-C_4H_9$	-H
S-4-5	$-NHCOCH_3$	$-CH_3$	$-CH_3$	-H
S-4-6		$-CH_3$	$-CH_3$	-H
S-4-7		$-CH_3$	$-C_3H_7(i)$	-H
S-4-8				

Compounds represented by the above-mentioned Formula (S) include those described in Japanese Patent Publication No. 28496/1965, Japanese Patent O.P.I. Publication No. 89034/1975, Journal of Chemical Society (J. Chem. Soc.)49, 1748 (1927) and 4237 (1952), Journal of Organic Chemistry (J. Org. Chem.) 39, 2469 (1965), U.S.P. No. 2,824,001, Journal of Chemical Society, 1723 (1951), Japanese Patent O.P.I. Publication No. 111846/1981, U.S.P. No. 1,275,701 and U.S.P. No. 3,266,897 and 2,403,927. They can be synthesized according to methods described therein.

When compounds represented by Formula (S) of the present invention (hereinafter referred to as compounds (S)) are added to silver halide emulsion layers of the present invention, the compounds may be dissolved in water or an organic solvent which can arbitrarily mixed with water (for example, methanol and ethanol) before being added. Compounds (S) may be used independently or may be used in combination with other compounds represented by Formula (S), other stabilizers except for compounds represented by Formula (S) or anti-foggants.

The above-mentioned compound (S) may arbitrarily be added at any time either before silver halide grains are formed, during silver halide grains are formed, between completion of forming of silver halide grains and the starting of chemical ripening, during chemical ripening, when chemical ripening is completed or between completion of chemical ripening and the time of coating. All amount of the compound may be added either at a time, or in several times.

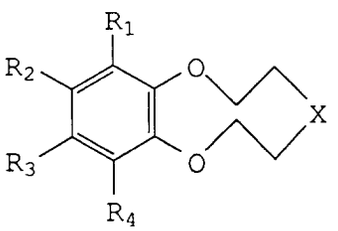
The above-mentioned compound (S) may be added either directly to a silver halide emulsion or to a coating solution for a nonsensitive hydrophilic colloidal layer which adjoins a silver halide emulsion layer so that they may be continued in a silver halide emulsion layer of the present invention though the diffusion in the course of multi-layer coating.

Though there is no limit to the amount of adding, it is normally be 1×10^{-6} mol to 1×10^{-1} mol and preferably 1×10^{-5} mol to 1×10^{-2} mol per mol of silver halide.

Next, the super sensitizer of the present invention will be explained.

The supersensitizers of the present invention are a 9- or more-membered cyclic compound. The cyclic compound is preferable to be one having an aliphatic group ring and/or an aromatic group ring and an ether linkage in view of giving significant effects of the present invention. In addition, the number of an aliphatic ring forming the aforesaid cyclic compound is preferred to be 4 or less. The macrocyclic compound represented by the following Formula (1) is more preferred.

Formula (1)

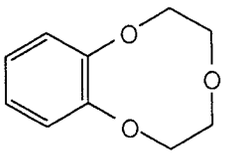


wherein R_1, R_2, R_3, and R_4 independently represent a hydrogen atom, an alkyl group, an alkoxy group, an aryl group, an aryloxy group, an alkenyl group, an alkenyloxy group, an acylamino group, a halogen atom, an alkylthio group, an arylthio group, an alkoxycarbonyl group, an acyloxy group, an acyl group or a sulfonamido group, provided that two of R_1 to R_4 may combine to form a 5- or 6-membered ring; and X represents a divalent group containing an oxygen atom or a nitrogen atom.

Typical compounds include crown ethers. Since the below-mentioned Pedersen synthesized them in 1967 and reported their specific characteristics, many compounds have been synthesized. They are described in detail in C. J. Pedersen, Journal of American chemical Society, vol. 86 (2495), 7017 - 7036 (1967), G.W. Gokel, S.H, Korzeniowski, "Macrocyclic polyether synthesis", Springer-Verlag. (1982), "Chemistry of crown ether" edited by Oda, Shono and Tabuse, Kagaku Dojin (1978), "Host-Guest" edited by Tabuse, Kyoritsu Shuppan (1979) and "Organic synthetic chemistry" edited by Sasaki and Koga, vol. 45 (6), pp. 571 - 582 (1987).

Hereunder, practical examples of the macrocyclic compound containing a hetero-atom used in the present invention are illustrated. However, the present invention is not limited thereto.

S-1



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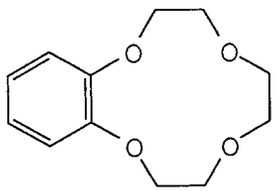

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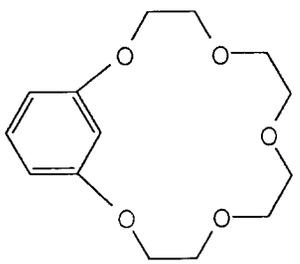

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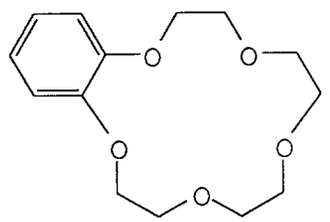

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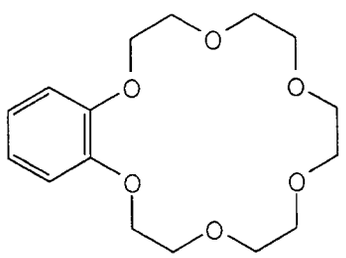
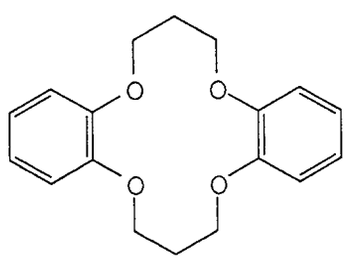
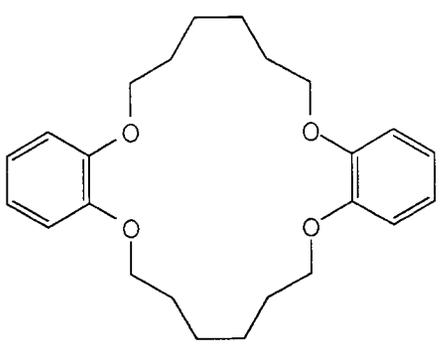


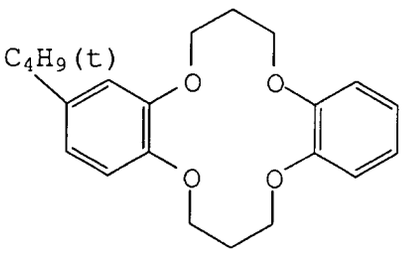
S-6



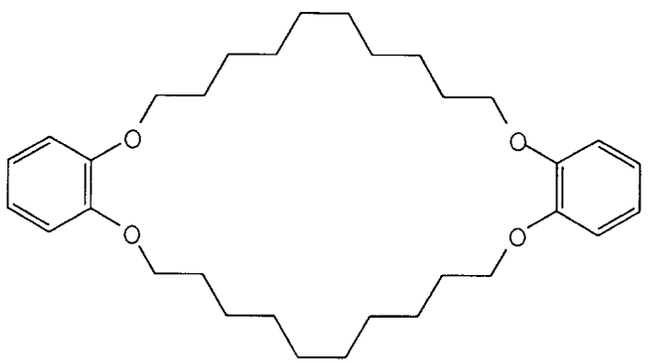
S-7



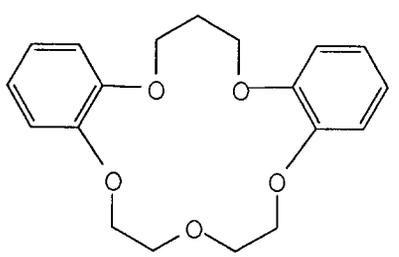
S-8



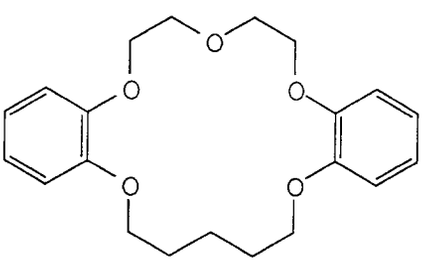
S-9



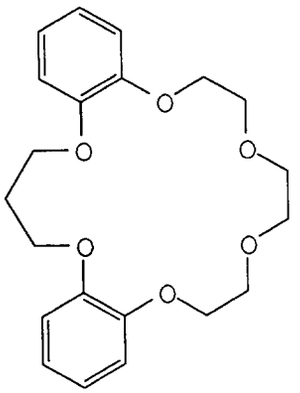
S-10



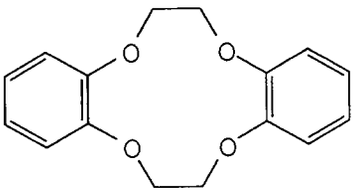
S-11



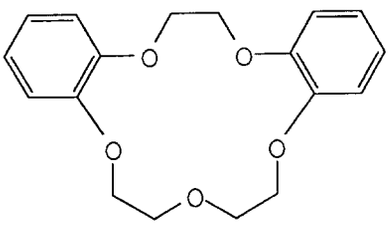
S-12



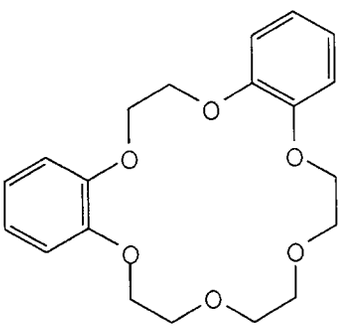
S-13



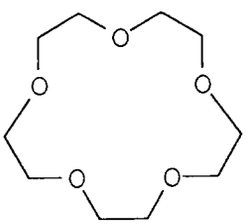
S-14



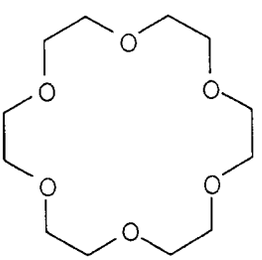
S-15



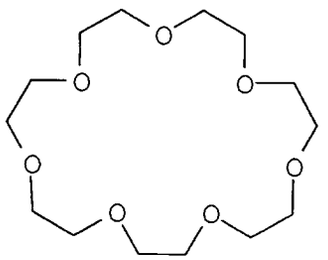
S-16



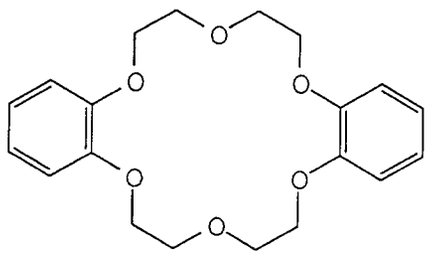
S-17



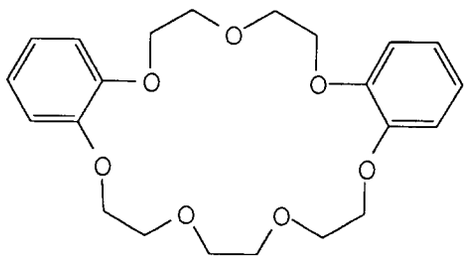
S-18



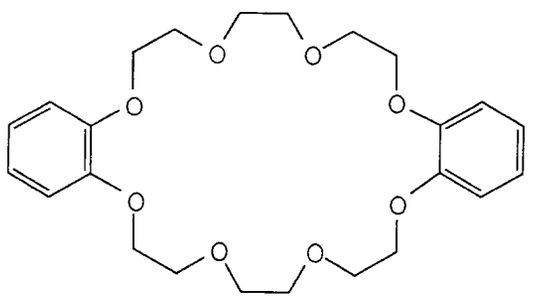
S-19



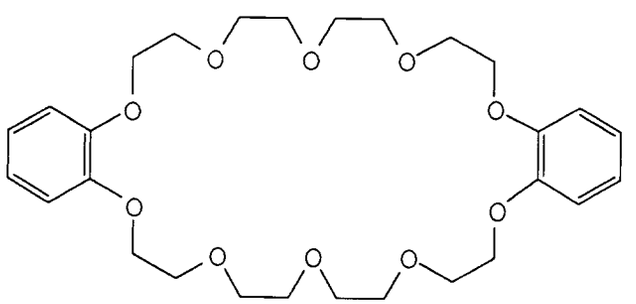
S-20



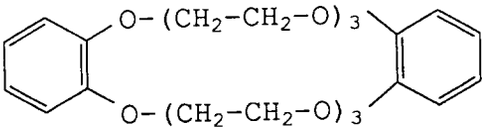
S-21



S-22



S-23



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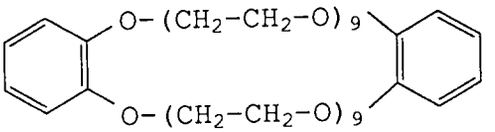
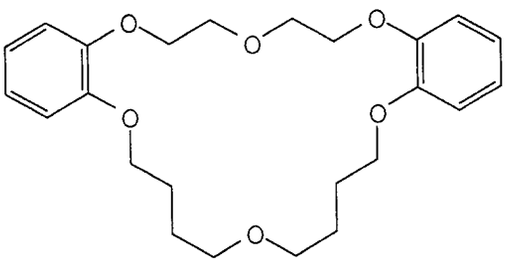


S-25



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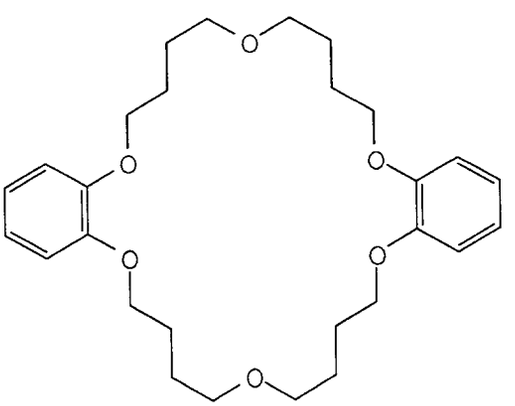

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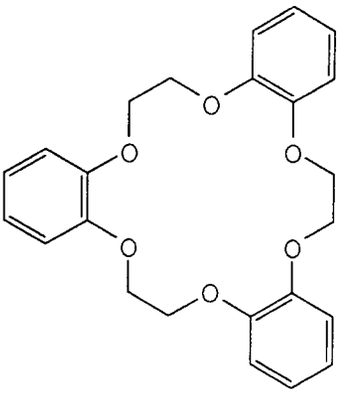
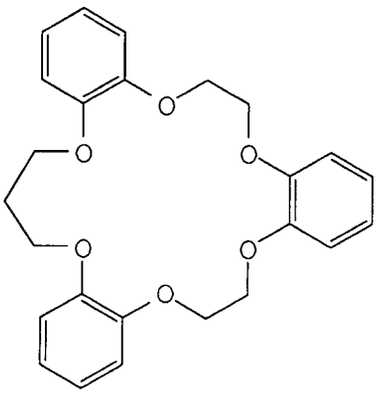


S-28



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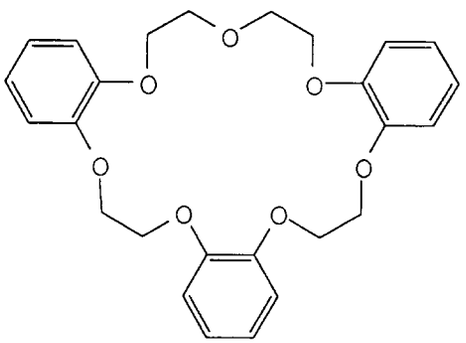

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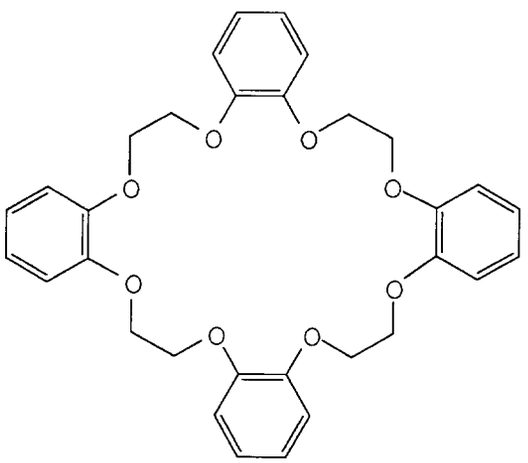

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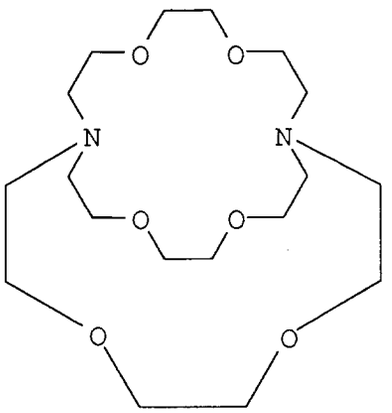

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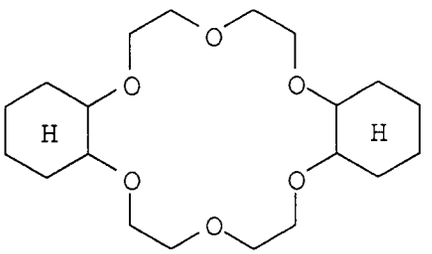

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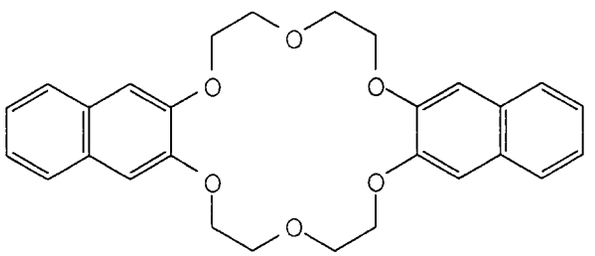

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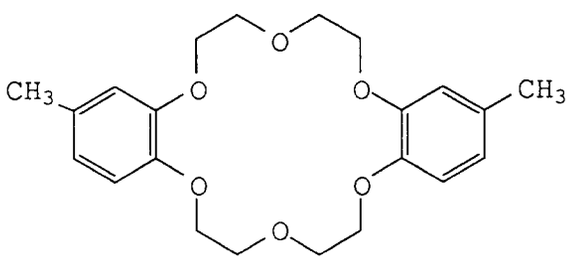

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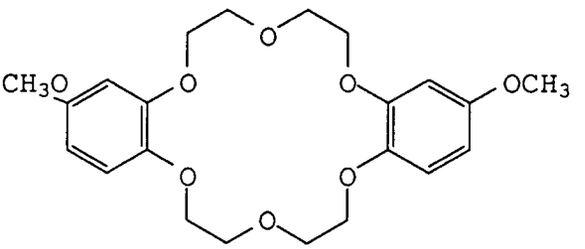
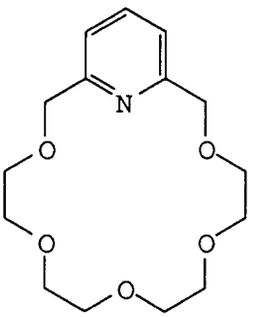


S-36



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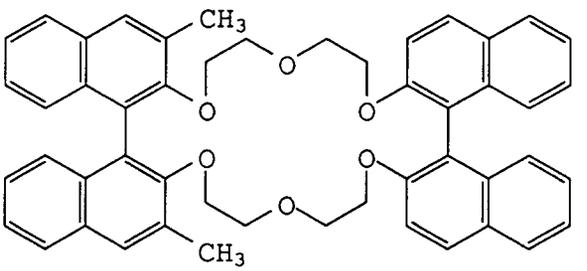
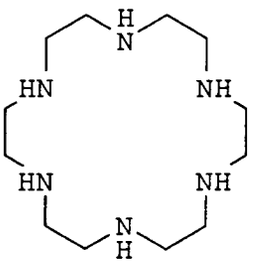
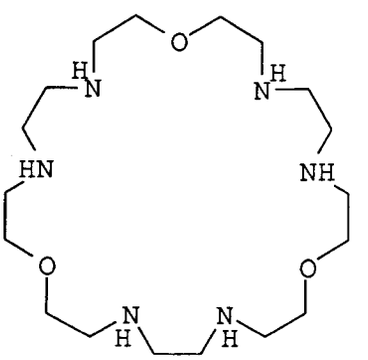


S-38



S-39

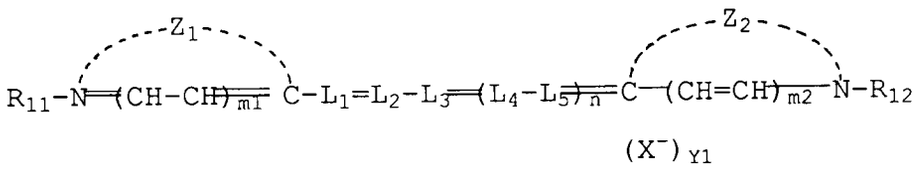


The macrocyclic compound of the present invention may be added to hydrophilic colloid containing silver halide grains after being dissolved into water or hydrophilic organic solvents such as methanol, ethanol and fluorinated alcohol. With regard to addition timing, any time is allowed provided that it is before the coating of emulsions. However, it is preferred to be added before completion of chemical sensitization. The amount of adding the macrocyclic compound of the present invention is different depending upon the

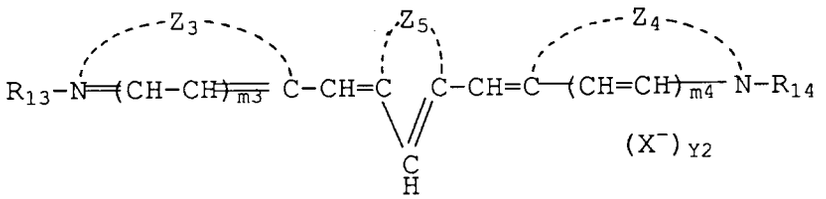
kind of them. However, it is ordinarily in the range of 1×10^{-6} to 1×10^{-1} mol and preferably 5×10^{-6} to 1×10^{-2} mol per mol of silver halide.

The super sensitizer of the present invention is so effective in terms of the effects of the present invention to red sensitive sensitizing dyes as to be desirable. They are especially useful to cyanine dyes represented by formulas (2) and (3), of the red sensitive sensitizing dyes.

Formula (2)



Formula (3)



wherein R_{11}, R_{12}, R_{13} and R_{14} independently represent an alkyl group, an alkenyl group or an aryl group; L_1, L_2, L_3, L_4 and L_5 independently represent a methine group; Z_1, Z_2, Z_3 and Z_4 independently represent an atomic group necessary for forming a 5- or 6-membered heterocyclic ring; Z_5 represents an atomic group necessary for forming a 6-membered ring; m_1, m_2, m_3 and m_4 independently represent 0 or 1; n represents 0 or 1; x^- represents an acid anion; Y_1 and Y_2 independently represent 0 or 1, provided that Y_1 and Y_2 independently represent 0 when the compound forms an inner salt.

In sensitizing dyes used in the present invention, alkyl groups represented by R_1, R_2, R_3 and R_4 in formulas (2) or (3) may be branched. In addition, sensitizing dyes having 10 or less carbons are more preferable. They may have a substituent. As a substituent, a sulfo group, an aryl group, a carboxy group, an amine (primary, secondary and tertiary) group, an alkoxy group, an aryloxy group, a hydroxy group, an alkoxycarbonyl group, an acyloxy group, an acyl group, an aminocarbonyl group or a cyan group or a halogen atom can be cited. Practical examples of alkyl groups are a methyl group, an ethyl group, a propyl group, a butyl group, a pentyl group, a hexyl group, a heptyl group, a sulfoethyl group, a sulfopropyl group, a sulfobutyl group, a benzyl group, a phenethyl group, a carboxyethyl group, a carboxymethyl group, a dimethylaminopropyl group, a methoxyethyl group, a phenoxypropyl group, a methylsulfonylethyl group, a p-t-butylphenoxyethyl group, a cyclohexyl group, an octyl group, a decyl group, a carbamoylethyl group, a sulfophenethyl group, a sulfobenzyl group, a 2-hydroxy-3-sulfopropyl group, an ethoxycarbonylethyl group, a 2,3-disulfopropoxypropyl group, a sulfopropoxyethoxyethyl group, a trifluoroethyl group, a carboxybenzyl group, a cyanopropyl group, a p-carboxyphenethyl group, an ethoxycarbanylmethyl group, a pivaloylpropyl group, a propyonylethyl group, an anisyl group, an acetoxyethyl group, a benzoyloxypropyl group, a chloroethyl group, a morphorinoethyl group, an acetylaminoethyl group, an N-ethylaminocarbonylpropyl group and a cyanoethyl group are cited.

As alkenyl groups, those having 10 or less carbons are preferable. For example, an allyl group, a 2-butenyl group and a 2-propenyl group are cited.

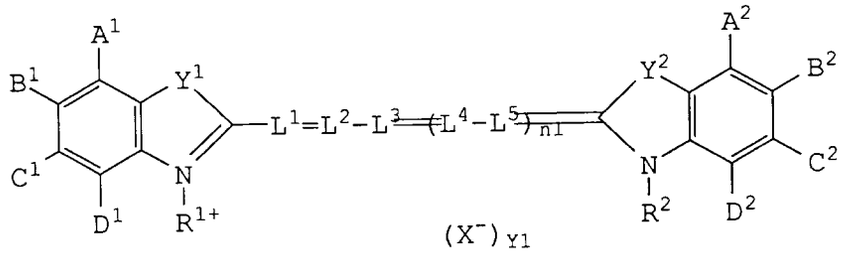
In addition, as aryl groups, a phenyl group, a carboxyphenyl group and a sulfonyl group are cited.

A methine group represented by L_1, L_2, L_3, L_4 and L_6 in formula (2) or (3) may have a substituent. When it has a substituent, it is represented by a formula ($-CR_5-$). As a group represented by R_5, straight-chained or branched chained alkyl groups (for example, a methyl group, an ethyl group, a propyl group, a butyl group, a carboxyl group and a benzyl group), alkoxy groups (for example, a methoxy group and an ethoxy group) and aryl groups (for example, a phenyl group and a tolyl group) are cited.

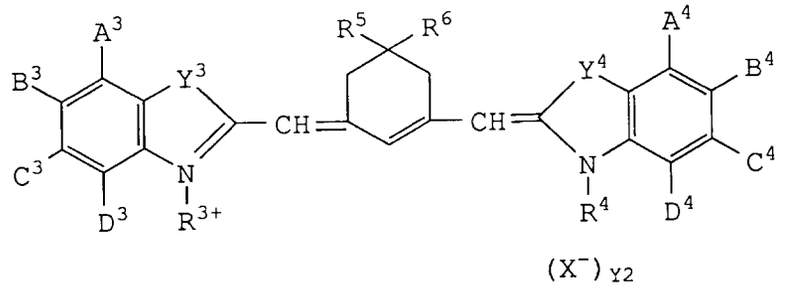
As anions represented by X^- in formulas (2) and (3), a chloride ion, bromide ion, iodide ion, perchloroxide ion, fluorinated borate ion, p-toluenesulfonic acid ion, ethylsulfonic acid ion, methylsulfonic acid ion and nitrate ion are cited.

In addition, of the sensitizing dyes represented by the above-mentioned formula (2) or (3), especially useful sensitizing dyes can be represented by the following formulas (4) and (5).

Formula (4)



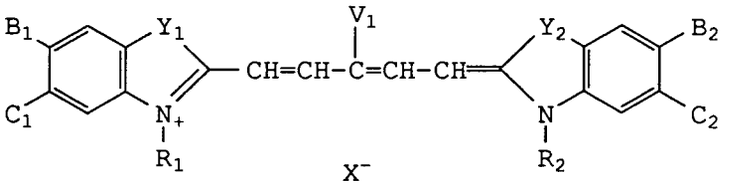
Formula (5)



wherein Y^1, Y^2, Y^3 and Y^4 independently represent an oxygen atom, a sulfur atom or a selenium atom; A^1, A^2, A^3, A^4, B^1, B^2, B^3, B^4, C^1, C^2, C^3, C^4, D^1, D^2, D^3 and D^4 independently represent a hydrogen atom, a halogen atom, an alkyl group, an alkoxy group, a phenyl group, a cyano group, a nitro group or an alkoxycarbonyl group, provided that at least one combination of A^1 and B^1, B^1 and C^1, C^1 and D^1, A^2 and B^2, B^2 and C^2, C^2 and D^2, A^3 and B^2, B^3 and C^3, C^3 and D^3, A^4 and B^4, B^4 and C^4 and C^4 and D^4 may be bound together to form a benzene ring; R^5 and R^6 independently represent a lower alkyl group; R^1, R^2, R^3, R^4, L^1, L^2, L^3, L^4, L^5, X^-, n^1, Y^1 and Y^2 are the same as R_1, R_2, R_3, R_4, L_1, L_2, L_3, L_4, L_5, X^-, n^1, Y_1 and Y_2 in the above-mentioned formula (2) or (3).

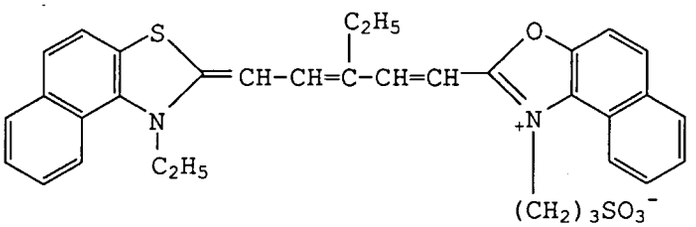
As alkyl groups represented by A^1, A^2, A^3, A^4, B^1, B^2, B^3, B^4, C^1, C^2, C^3, C^4, D^1, D^2, D^3 and D^4 in formula (4) or (5), straight-chained or branched-chained lower alkyl groups having 1 to 5 carbons (for example, a methyl group, an ethyl group, a propyl group, a butyl group and a trifluoromethyl group) are cited. As alkoxy groups represented by them, straight-chained or branched-chained alkoxy groups having 1 to 5 carbons (for example, a methoxy group and an ethoxy group) are cited. As halogen atoms represented by them, fluorine, chlorine, bromine or iodine are cited. As phenyl groups, a phenyl group not having a substituent, a hydroxyphenyl group and a carboxyphenyl group are cited. As alkoxycarbonyl groups, a methoxycarbonyl group and an ethoxycarbonyl group are cited. In addition, n^1 represents 0 or 1, provided that 1 is preferable.

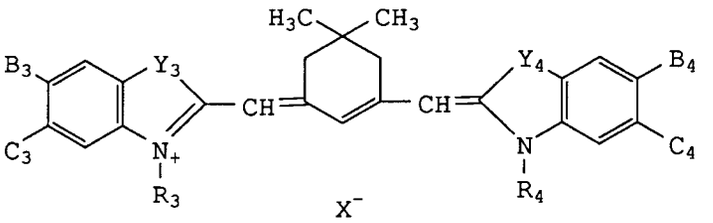
Next, practical examples of red sensitive sensitizing dyes of the present invention are illustrated. However, the present invention is not limited thereto.



Illustrated compound No.	Y_1	Y_2	B_1	C_1	B_2	C_2	R_1	R_2	V_1	X^-
I-1	Se	Se	H	H	H	H	C_2H_5	C_2H_5	H	I
I-2	S	S	H	H	H	H	C_2H_5	C_2H_5	H	I
I-3	Se	Se	H	H	H	H	$(CH_2)_2OCH_3$	$(CH_2)_2OCH_3$	H	Br
I-4	Se	S	H	H	H	H	$(CH_2)_3SO_3H$	C_2H_5	H	-
I-5	S	S	H	OCH_3	H	H	C_2H_5	C_2H_4OH	C_2H_5	Br
I-6	S	S	C_2H_5	H	C_2H_5	H	C_5H_{11}	C_5H_{11}	C_2H_5	Br
I-7	S	S	C_2H_5	H	C_2H_5	H	C_5H_{11}	C_5H_{11}	C_4H_9	Br
I-8	S	S	OCH_3	OCH_3	OCH_3	OCH_3	C_2H_5	C_2H_5	CH_3	I

1-9

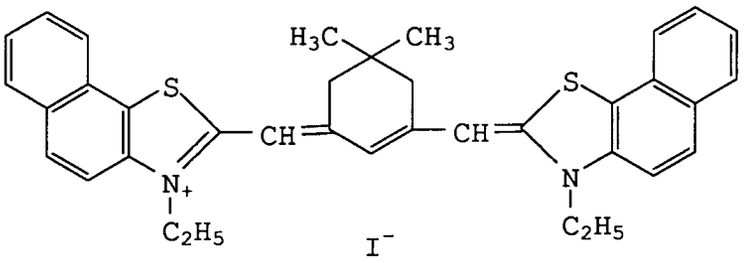




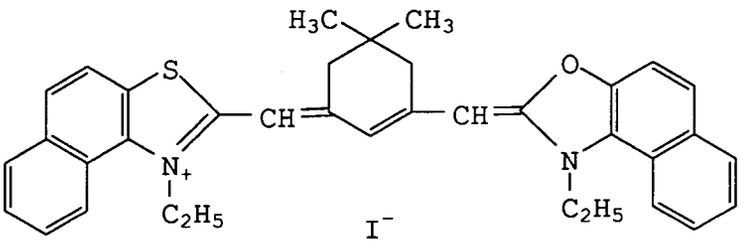
Illustrated compound No.	Y_3	Y_4	B_3	C_3	B_4	C_4	R_3	R_4	X^-
II-1	S	S	H	H	H	H	C_2H_5	C_2H_5	Br
II-2	S	S	CH_3	H	H	H	C_2H_5	C_2H_5	Br
II-3	S	S	CH_3	H	CH_3	H	C_2H_5	C_2H_5	Br
II-4	S	S	H	H	H	H	C_2H_5	C_3H_7	Br
II-5	S	S	H	H	H	H	C_2H_5	C_4H_9	Br
II-6	S	S	H	H	H	H	C_2H_5	C_5H_{11}	Br
II-7	S	S	H	H	H	H	C_2H_5	C_7H_{15}	Br
II-8	S	S	H	H	H	H	C_2H_5	$C_{10}H_{21}$	Br
II-9	S	S	H	H	H	H	C_3H_7	C_3H_7	Br
II-10	S	S	H	H	H	H	C_4H_9	C_4H_9	PTS$^-$*
II-11	S	S	H	H	H	H	C_5H_{11}	C_5H_{11}	Br
II-12	S	S	H	H	H	H	C_7H_{15}	C_7H_{15}	Br
II-13	S	S	CH_3	H	H	H	C_2H_5	C_5H_{11}	Br
II-14	S	S	CH_3	H	CH_3	H	C_2H_5	C_5H_{11}	Br
II-15	S	S	OCH_3	H	H	H	C_2H_5	C_2H_5	Br
II-16	S	S	OCH_3	H	H	H	C_2H_5	C_5H_{11}	Br
II-17	S	S	CH_3	CH_3	CH_3	CH_3	C_2H_5	C_2H_5	Br
II-18	S	S	$C_3H_{7(i)}$	H	$C_3H_{7(i)}$	H	C_2H_5	C_2H_5	Br
II-19	S	S	H	H	H	H	C_2H_5	$(CH_2)_3SO_3^-$	-
II-20	S	S	CH_3	H	CH_3	H	C_2H_5	$(CH_2)_4SO_3^-$	-
II-21	S	S	CH_3	H	CH_3	H	$(CH_2)_3SO_3HN(C_2H_5)_3$	$(CH_2)_3SO_3^-$	-
II-22	S	O	H	H	H	H	C_2H_5	C_2H_5	Br
II-23	S	O	CH_3	H	CH_3	H	C_2H_5	C_5H_{11}	Br
II-24	Se	Se	H	H	H	H	C_2H_5	C_2H_5	Br
II-25	Se	Se	CH_3	H	CH_3	H	C_2H_5	C_2H_5	Br

(*PTS: Paratoluene sulfonic acid)

II-26



II-27



The above-mentioned red sensitive sensitizing dyes can easily be synthesized by a method described in The Chemistry of Heterocyclic Compounds written by F.M. Harmer, Volume 18 and The Cyanine Dyes and Related Compounds, New York, 1964 published by A. Weissherger ed. Interscience Co., Ltd.).

There is no limitation to the amount of adding the abovementioned red sensitive sensitizing dyes. However, it is preferred to add 2×10^{-8} to 1×10^{-2} mol per mol of silver halide.

Any blue sensitive sensitizing dyes and green sensitive sensitizing dyes can be used for the present invention. As blue sensitive sensitizing dyes, BS-1 through 8 described on pp. 108 and 109 of Japanese Patent O.P.I. Publication No. 251840/1991 are preferable. As green sensitive sensitizing dyes, GS-1 through 5 described on page 110 of aforesaid patent application are preferable.

In the silver halide photographic light-sensitive material of the present invention, the silver halide grain emulsion of the present invention comprises either silver bromochloride grains or silver chloride grains substantially not containing silver iodide wherein 90 mol% or more of them are composed of silver chloride. When the above-mentioned emulsion does not substantially contain silver iodide, the content of silver iodide is 0.5 mol% or less, preferably 0.1 mol% or less, more preferably zero. With regard to silver chloride content, preferred is 95 mol% or more, more preferred is 98 mol% or more and most preferred is 99 mol% or more.

When the silver halide grains of the present invention is composed of silver bromochloride containing silver bromide, they may be core/shell grains having different components inside the grains or grains having a localized phase of silver bromide on the surface thereof or inside thereof. However, the preferred is silver halide grains having uniform components thoroughly from the inside of the grains to the surface thereof.

The average grain size (the grain size is defined to be the diameter of a circle equivalent to the projected area of the grain, and the average grain size is the average thereof) of silver halide grains contained in silver halide emulsions used in the present invention is preferred to be 0.1 to 2 μm.

In addition, the variation coefficient (which means the standard deflection of the grain size distribution divided by the average grain size) of grain size distribution is preferred to be 20% or less and more preferred to be 15% or less (so called "mono-dispersed emulsion"). Here, in order to obtain broad latitude, the above-mentioned mono-dispersed emulsions are preferably blended to be used, or they are preferably coated multiply. The form of silver halide grains contained in the photographic emulsion may be regulatory crystal-form such as a cubic, tetradechedral or octahedral, anomalous crystal such as spherical and tabular. Or it may be hybrid thereof.

In addition, it may be a mixed one having various crystal forms. In the present invention, of them, those having the above-mentioned regulatory form by 50% or more are preferred, and those having the above-mentioned regulatory form by 90% or more are more preferable.

Other than the above, emulsions having an average aspect ratio (diameter in conversion of circle/thickness) of 5 or more and 8 or more preferably wherein tabular grains exceed 50% of the total grains in terms of a projected area are preferably used.

To silver halide emulsions of the present invention, impurity of various kinds of multi-value metal ion may be added during the course of forming the grains of the emulsions or physical ripening. Examples of compounds used are salts of cadmium, zinc, lead, copper and thallium or salts or complex salts of iron, ruthenium, rhodium, paradium, osmium, iridium and platinum that are elements from the VIII group. Especially, the elements of the above-mentioned VIII group can preferably used. The added amount of these compounds i varied depending upon the purpose. However, it is preferred to be 10^{-10} to 10^{-3} mol per mol of silver halide.

As an apparatus and a method for preparing silver halide emulsions, various conventional ones known in the field can be used.

The silver halide emulsions of the present invention may be prepared through any of those including an acid process, a neutral process and an ammonia process. Aforesaid grains may be grown directly, or may be grown after producing seed grains. A method for producing seed grains and a method for growing them may be the same or different.

In addition, as a method to cause soluble silver salt and a soluble halogenated salt to react, any of a normal precipitation method, a reverse precipitation method, a double-jet method and combination thereof are allowed. Of them, those obtained through a double-jet method is desirable. In addition, as one type of a double-jet method, pAg-controlled double jet method described in Japanese Patent O.P.I. Publication No. 48521/1979 can also be used.

In addition, an apparatus disclosed in Japanese Patent O.P.I. Publication Nos. 92523/1982 and 92524/1982 wherein water-soluble silver salt and water-soluble halogenated compound salt aqueous solution is fed from an addition device placed in an initial solution for reaction, an apparatus disclosed in German Patent No. 2921164 wherein the concentration of water-soluble silver salt and water-soluble halogenated compound salt aqueous solution is continuously changed for adding, or an apparatus disclosed in Japanese Patent Publication No. 501776/1981 wherein grains are formed while the distance between each silver halide grain is kept constant by taking an initial solution outside of a reactor and concentrating it by the use of a ultra filtration method may be used.

In addition, if necessary, silver halide solvents such as thioether may be used. In addition, compounds having a mercapto group and compounds such as nitrogen-containing heterocycles or sensitizing dyes may be used by adding during formation of silver halide grains or after completion of forming grains.

The silver halide emulsions of the present invention may be sensitized by the use of sensitizing methods using gold compounds and sensitizing methods using chalcogen sensitizers in combination.

As chalcogen sensitizers applicable to the silver halide emulsions of the present invention, sulfur sensitizers, selenium sensitizers and tellurium sensitizers can be used. Among them, sulfur sensitizers are desirable. As sulfur sensitizers, thiosulfate, allylthiocarbamidothiourea, allylisothiacyanate, cystine, p-toluenethiosulfonate salt and rhodanine are cited.

The gold sensitizers applicable to the silver halide emulsions of the present invention can be added in the form of gold chloride, silver chloride, gold sulfide, gold thiosulfate and various gold complex. As compounds to be used therein, dimethylrhodanine, thiocyanate, mercaptotetrazole and mercaptotriazole are cited.

The added amount of gold compounds is different depending upon the kind of silver halide emulsion, kind of compounds used and ripening conditions. Ordinarily, it is 1×10^{-8} mol per mol of silver halide.

For the silver halide emulsions of the present invention, conventional anti-foggants and stabilizers can be used for preventing fog which occurs during preparation step of a silver halide photographic light-sensitive material, for reducing fluctuation in properties during storage and preventing fog which occurs when being developed. As an example of compounds used for such purposes, compounds represented by formula (II) described in the lower column on page 7 of Japanese Patent O.P.I.. Publication No. 146036/1990 are cited. Practical examples thereof are compounds (IIa-1) through (IIa-8) and (II-b) through (IIb-7) and 1-(3-methoxyphenyl)-5-mercaptotetrazole are cited. These compounds are added, depending upon their purposes, in a preparation step, in a chemical sensitization step, at the end of chemical sensitization step and in a preparation step for a coating solution.

To the silver halide photographic light-sensitive materials of the present invention, dyes having absorption ability for various wavelength can be used for preventing irradiation and halation.

For couplers used in the silver halide photographic light-sensitive materials of the present invention, there can be used any compounds which can form a coupling substance having a spectral absorption maximum wavelength in a wavelength region longer than 340 nm through a coupling reaction with an

oxidized product of a color developing agent. The typical ones are yellow couplers having spectral absorption maximum wavelength in the wavelength region of 350 to 500 nm, magenta couplers having spectral absorption maximum wavelength in the wavelength region of 500 to 600 nm and cyan couplers having spectral absorption maximum wavelength in the wavelength region of 600 to 750 nm.

As yellow couplers which can be preferably used for the silver halide photographic light-sensitive materials of the present invention, couplers represented by formula (Y-I) described on page 8 of Japanese Patent O.P.I. Publication No. 114154/1992 are cited. Practically, YC-1 through YC-9 described on pages 9 through 11 of aforesaid application can be cited. Of them, YC-8 and YC-9 which are described on page 11 of aforesaid application can reproduce preferred yellow color tone.

As magenta couplers which can be preferably used for the silver halide photographic light-sensitive materials of the present invention, couplers represented by formula (M-I) and (M-II) described on page 12 of Japanese Patent O.P.I. Publication No. 114154/1992 are cited. Practically, MC-1 through MC-11 described on pages 13 through 16 of aforesaid application can be cited. Of them, MC-8 and MC-11 which are described on pages 15 to 16 of aforesaid application are so preferred as to be excellent in color reproduction for a range from blue through violet and red and also excellent in description ability for details.

As cyan couplers preferably applicable to the silver halide photographic light-sensitive materials of the present invention, couplers represented by formula (C-I) and (C-II) described on page 17 of Japanese Patent O.P.I. Publication No. 114154/1992 are cited. Practically, compounds CC-1 through CC-9 described from page 18 to page 21 of aforesaid Application are cited.

When an oil-in-water emulsification dispersion method is used for adding couplers used for the silver halide photographic light-sensitive materials of the present invention, it is ordinary to dissolve the coupler with water-insoluble and high boiling organic solvents having a boiling point of 150 °C and, if necessary, with low boiling and/or water-soluble organic solvents in combination, and then, to emulsify and disperse into a hydrophilic binder such as a gelatin aqueous solution using surfactants. As dispersing means, an stirrer, a homogenizer, a colloid mill, a flow jet mixer and a supersonic disperser can be used. After completing the dispersion, or during the course of dispersion, a step for removing low-boiling organic solvents may be added. As high-boiling organic solvents which can be used for dissolving couplers for dispersion, phthalic acid ester such as dioctylphthalate and phosphoric acid ester such as tricresyl-phosphate are preferably used.

In addition, in place of a method to use high-boiling organic solvents, methods to dissolve low-boiling and/or water-soluble organic solvents if necessary and to emulsify and disperse aforesaid solution into, using surfactants, a hydrophilic binder such as a gelatin aqueous solution by means of various dispersing means. In such cases, as a polymer insoluble in water and soluble in organic solvents, poly(N-t-butylacrylamido) can be cited.

In order to shift the absorption wavelength of coloring dyes, a compound (d-11) described on page 33 of Japanese Patent O.P.I. Publication No. 114154/1992 and a compound (A'-1) described on page 35 of aforesaid specification. In addition, compounds described in USP. No. 4774187 which release a fluorescent dye can be used.

For the silver halide photographic light-sensitive materials of the present invention, it is advantageous to use gelatin as a binder. In addition, other gelatins, gelatin derivatives, graft polymers between gelatin and other polymers, proteins other than gelatin, sugar derivatives, cellulose derivatives and hydrophilic colloid such as synthetic hydrophilic polymers including monopolymers or copolymers can also be used if necessary.

In the present invention, hardeners for a binder may be used. As hardeners, vinylsulfon type hardeners and chlorotriazine type hardeners are preferably used. As vinylsulfone type hardeners, compounds described on the 13th line at the upper right column on page 25 to the 2nd line at the upper right column on page 26 in Japanese Patent O.P.I. Publication No. 249054/1986 can preferably be used. In addition, compound H-12 described on page 26 of aforesaid specification. As chlorotriazine type hardeners, compounds described from the 1st line at the lower left column on page 3 to he 4th line from the bottom at the lower right column on page 3 in Japanese Patent O.P.I. Publication No. 245153/1986 are preferably used. A compound represented by XII-1 described on page 4 of the latter is more preferable. These hardeners are preferably used in combination of other compounds and can be added to any layer of the material. The content of the hardener is preferably 0.1 to 10% by weight of a binder used.

In the present invention, it is preferred to use an anti-mildew agent in either of layers. As anti-mildew agents, compounds represented by a formula described on page 9 in Japanese Patent O.P.I. Publication No. 157646/1991 are preferred. As examples of practical compounds, compound Nos. 9 through 22 described from page 69 to page 70 in aforesaid specification are cited. Of them, the especially preferred compound is a compound represented by No. 9.

As reflection supports of the present invention, papers laminated with white-pigment-containing polyethylene, baryta papers, vinylchloride sheet, polypropylene containing a white pigment and a polyethylenephthalate support can be used.

Of them, supports laminated with polyorefin resin layer containing white pigments are preferable.

As white pigments to be used for the reflection supports of the present invention, inorganic and/or organic white pigments can be used. The preferred are inorganic white pigments. For example, sulfate of alkaline earth metals such as barium sulfate, carbonate salts of alkaline earth metals such as calcium carbonate, silicas such as fine silicate and synthetic silicate, calcium silicate, alumina, alumina hydrate, titanium oxide, zinc oxide, talc and clay are cited. The preferred white pigments are barium sulfate and titanium oxide.

The amount of white pigment contained in the water-proof resin layer on the surface of the reflection support of the present invention is preferable to be not less than 10% by weight, more preferable to be not less than 13% by weight and especially preferable to be not less than 15% by weight in terms of the content amount in the water-proof resin layer. The degree of dispersion of white pigment in the water-proof resin layer on a paper support of the present invention can be measured by means of a method described in Japanese Patent O.P.I. Publication No. 28640/1990. When measured by means of this method, the degree of dispersion of white pigment is preferable to be not more than 0.20, more preferable to be not more than 0.15 and especially more preferable to be not more than 0.10 in terms of fluctuation coefficient described in the aforesaid specification.

After the surface of the support is provided with corona discharge, UV ray irradiation and firing treatment if necessary, a light-sensitive materials may be coated directly or through subbing layers (one or two or more subbing layer in order to improve adhesivity, anti-static property stability in sizing, anti-abrasion property, stiffness, anti-halation property, abrasion property and/or other properties of the surface of the support.)

When a light-sensitive materials using silver halide emulsions is coated, a thickener may be used. As coating methods, an extrusion coating method and a curtain coating method is especially advantageous because they can coat 2 or more layers concurrently.

Color developing agents which are used in color developers in the present invention include aminophenol type and p-phenylenediamine type derivatives which are commonly used in various color photographic processes.

To color developers applicable to the processing of light-sensitive materials of the invention, conventional developer component compounds in addition to the above-mentioned primary aromatic amine type color developing agents can be added.

pH value of the color developers are ordinarily 9 or more and preferably about 10 to 13.

The temperature of color developer is ordinarily 15 °C or more, and normally 20 °C to 50 °C.

The temperature of rapid processing is preferably 30 °C or more. Time for developing is ordinarily from 10 seconds to 4 minutes. For rapid processing, it is preferable to be in the range from 10 seconds to 1 minute. When furthermore rapid processing is required, it is preferable to be in the range from 10 seconds to 30 seconds. However, the effects of the present invention can be offered more effectively in such a rapid processing.

In addition, when the light-sensitive material of the present invention is subjected to running processing wherein a replenisher for the color developing agent is consecutively replenished, the replenished amount of the color developer is preferably 20 - 150 ml, more preferably 20 - 120 ml and especially more preferably 20 - 100 ml per 1 m^2. However, the effects of the present invention can be offered more effectively in such a running processing with low replenishing. To the light-sensitive materials of the present invention, bleach-fixing processing is provided after subjecting to color developing.

After subjecting to bleach-fixing processing, the light-sensitive material is subjected to a washing process or a stabilizing process or a combination process thereof.

Examples

Hereunder, practical examples of the present invention are shown. However, the present invention is not limited thereto.

Example 1

To 1,000 ml of 2% aqueous gelatin solution kept at 40 °C, there were added simultaneously Aqueous solution A containing 2.91 g of sodium chloride and 29.8 mg of potassium bromide and Aqueous solution B

containing 8.5 g of silver nitrate spending 30 minutes while pAg was controlled to 6.5 and pH was controlled to 3.0. In addition, Aqueous solution C containing 55.3 g of sodium chloride, 565 mg of potassium bromide, 0.024 mg of potassium hexachloroiridium acid and 8.44 mg of potassium hexacyanoferric and Aqueous solution D containing 161 g of silver nitrate were concurrently added spending 120 minutes while pAg was controlled to 7.3 and pH was controlled to 5.5.

Here, pAg was controlled by means of a method described in Japanese Patent O.P.I. Publication No. 45437/1984. In addition, pH was controlled by the use of an aqueous solution of sulfuric acid or sodium hydroxide.

After the addition was completed, the solution was subjected to desalting by the use of a 10% aqueous solution of Demol N produced by Kao Atlas Co., Ltd. and 30% aqueous solution of magnesium sulfate. Then, the desalted emulsion was mixed with an aqueous gelatin solution to prepare a mono-dispersed cubic emulsion having an average grain size of 0.40 μm, fluctuation coefficient (standard deviation of the grain size/the average grain size) of 0.07 and a silver chloride content of 99.9 mol%. The above-mentioned emulsion was subjected to the most suitable chemical sensitization employing sodium thiosulfate and chloroaurate. In addition, a sensitizing dye, supersensitizer and inhibitor as shown in Table 1 were added thereto for spectral sensitization in an amount of 4×10^{-5} mol, 2×10^{-3} mol, and 6×10^{-4} mol per mol of silver halide, respectively. Thus, Em-1 through Em-12 were obtained.

Next, cyan couplers CC-1 and CC-2 were dissolved in a mixed solution of dioctylphthalate (DOP) and ethyl acetate together with anti-stain agent HQ-1 and dye image stabilizer ST-1. Then, the resulting mixture was emulsified and dispersed in 8% aqueous gelatin solution containing Alkanol B (produced by Du Pont).

The resulting emulsified and dispersed solution was independently mixed with the above-mentioned emulsions Em-1 through Em-12 so that coating solutions were prepared. The coating solutions were independently coated on a paper support laminated with polyethylene on both surfaces to prepare Samples 101 through 112. As a protective layer, gelatin was coated. In a protective layer, 2,4-dichloro-6-hydroxy-s-sodium triazine (H-1) was added.

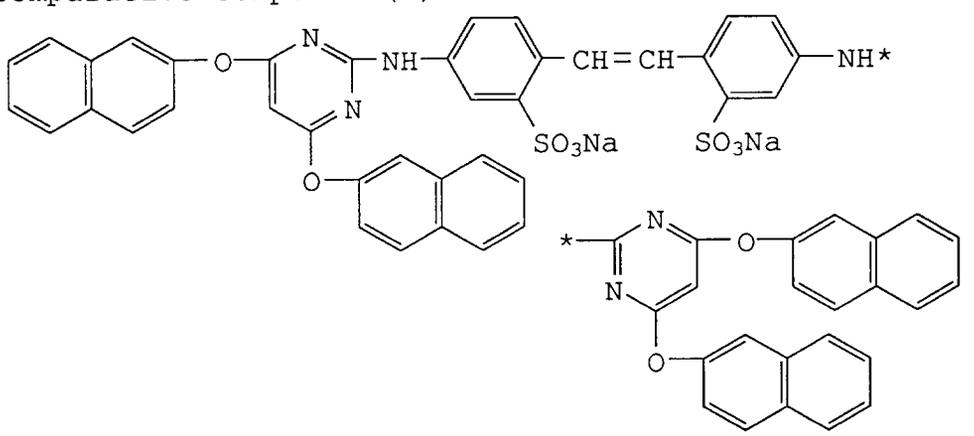
The coated layers are shown in Table 1

		Amount added (g/m^2)
Protective layer	Gelatin	1.0
Red sensitive layer	Silver bromochloride emulsion (Em-1 through Em-12) Cyan coupler (CC-1) Cyan coupler (CC-2) Dye image stabilizer (ST-1) Anti-stain agent (HQ-1) DOP Gelatin	0.3 in terms of silver 0.3 0.1 0.2 0.01 0.2 1.0
Support	Polyethylene-laminated paper	

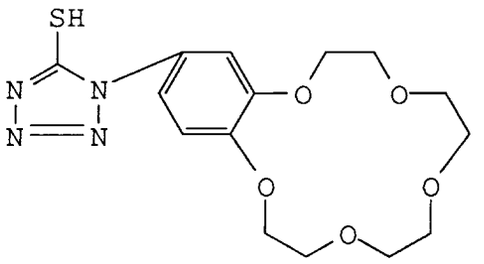
Table 1

Sample No.	Em. No..	Sensitizing dye	Super sensitizer	Inhibitor	Note
101	Em-1	II-1	Compound(A)	Compound(X)	Comparative
102	Em-2	II-1	Compound(B)	Compound(X)	Comparative
105	Em-5	II-1	S-5	S-2-5	Invention
106	Em-6	II-1	S-10	S-2-5	Invention
107	Em-7	II-1	S-19	S-2-5	Invention
108	Em-8	II-1	S-27	S-2-5	Invention
109	Em-9	II-1	S-30	S-2-5	Invention
110	Em-10	II-1	S-19	S-2-6	Invention
111	Em-11	II-1	S-19	S-1-1	Invention
112	Em-12	II-1	S-19	S-3-22	Invention

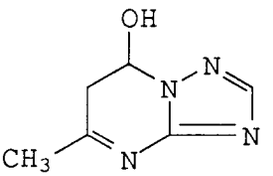
Comparative compound (A)



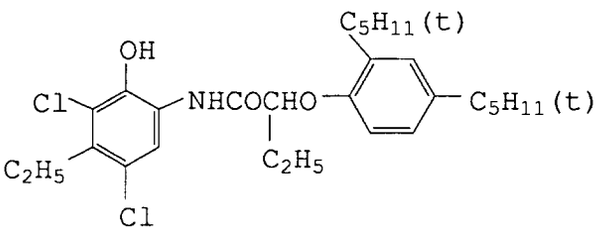
Compound B



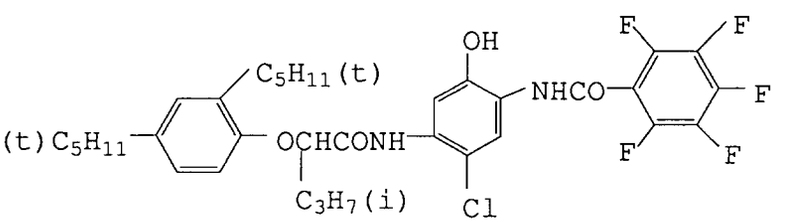
Compound X



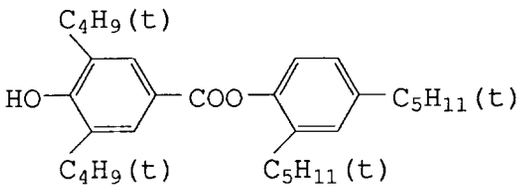
CC-1



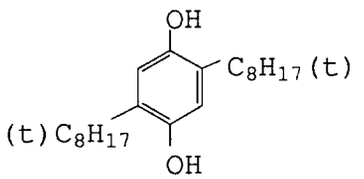
CC-2



ST-1



HQ-1



The resulting samples were subjected to evaluation using in the following manner.

(Evaluation of relative sensitivity)

Each sample was subjected to optical wedge exposure to light through a red filter for 0.5 second, and was subjected to the following development. The density of the resulting sample was measured by the use of an optical densitometer (Model PDA-65 produced by Konica Corporation). Then, the sensitivity of each sample was compared and relative sensitivity was calculated.

(Evaluation on storage stability)

One day after coating, each sample was stored for 3 months under the conditions of 25 °C and 60% RH. Then, the resulting sample was subjected to exposure and processing in the same manner as in above, and the sensitivity was compared with that of the above.

In comparison of sensitivity, the sensitivity of the sample aged one day after being coated was defined to be 100, and the sensitivity of the sample stored for 3 months was represented by a relative sensitivity.

(Evaluation on the variation in sensitivity caused by change of humidity in exposing to light)

By changing the ambient humidity to 15% RH or to 80% RH while keeping the ambient temperature at 25 °C when exposed to light, variation in sensitivity caused by change of ambient humidity in exposure to light was tested. In comparison of sensitivity, the sensitivity in the case of the humidity of 15% RH was defined to be 100, and the sensitivity for the humidity of 80% RH was represented in terms of a relative sensitivity.

Processing conditions used for evalution were as follows:

Processing step	Temperature	Time
Color developing	35.0 ± 0.3 °C	45 seconds
Bleach-fixing	35.0 ± 0.5 °C	45 seconds
Stabilizing	30 - 34 °C	90 seconds
Drying	60 - 80 °C	60 seconds

(Color developing solution)	
Pure water	800 ml
Triethanolamine	10 g
N,N-diethylhydroxylamine	5 g
Potassium bromide	0.02 g
Potassium chloride	2 g
Potassium sulfite	0.3 g
1-hydroxyethylidene-1,1-diphosphate	1.0 g
Ethylenediamine tetraacetate	1.0 g
Disodium catechol-3.5-diphosphate	1.0 g
N-ethyl-N-β-methanesulfonamidoethyl-3-methyl-4-aminoaniline sulfate	4.5 g
Fluorescent brightening agent (4,4'-diaminostylbenesulfonate derivative)	1.0 g
Potassium carbonate	27 g
Water was added to make 1 ℓ in total and pH was regulated to 10.10.	

(Bleach-fixer)	
Ethylenediamine tetraacetate ferric ammonium dehydrate	60 g
Ethylenediamine tetraacetate	3 g
Ammonium thiosulfate (70% aqueous solution)	100 ml
Ammonium sulfite (40% aqueous solution)	27.5 ml
Water was added to make 1 ℓ in total, and pH was regulated to potassium carbonate or glacial acetic acid to 5.7.	

(Stabilizer)	
5-chloro-2-methyl-4-isothiazoline-3-on	1.0 g
Ethylene glycol	1.0 g
1-hydroxyethylidene 1,1-diphosphate	2.0 g
Ethylenediamine tetraacetate	1.0 g
Ammonium hydroxide (20% aqueous solution)	3.0 g
Fluorescent brightening agent (4,4'-diaminostylbenesulfonate derivative)	1.5 g
Water was added to make 1 ℓ in total, and pH was regulated to 7.0 with sulfuric acid or potassium hydroxide.	

Table 2 shows the results of the evaluation.

Table 2

Sample No.	Sensitivity	Stability *1	Variation in *2 sensitivity against humidity
101 (Comparative)	100	82	111
102 (Comparative)	83	85	116
103 (Comparative)	107	92	125
104 (Comparative)	101	82	110
105 (Invention)	126	96	106
106 (Invention)	134	97	105
107 (Invention)	138	97	105
108 (Invention)	130	97	106
109 (Invention)	124	96	106
110 (Invention)	128	96	105
111 (Invention)	130	95	106
112 (Invention)	132	96	105

*1 Stability : The nearer to 100 the value is, the stability becomes more excellent.
*2 Variation in sensitivity against humidity : The nearer to 100 the value is, the stability becomes more excellent.

From the results shown in Table 2, the remarkable effects of the present invention is understood apparently. Namely, Samples (101 and 102) not using supersensitizers of the present invention show remarkable decrease of sensitivity after being stored, and also show great variation in sensitivity due to the change of humidity when exposed to light. This sensitivity variation cannot be improved even when the inhibitors of the present invention are used (104). In the case of Sample No. 103 which uses the supersensitizer of the present invention but does not use the inhibitor of the present invention, though storage stability is improved, sensitivity variation due to the change of humidity is deteriorated to the contrary. On the other hand, it can be understood that samples using the supersensitizers of the present invention and the inhibitors of the present invention (sample Nos. 105 through 112) are highly sensitive and are excellent in storage stability and less in sensitivity variation.

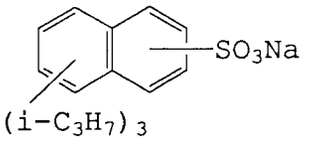
Example 2

On both sides of paper pulp having a weight of 180 g/m^2, there was laminated high density polyethylene to prepare a paper support. However, on a side on which emulsion layers are coated, a fused polyethylene provided with surface treatment containing dispersed anatase type titanium oxide in an amount of 15 weight% was laminated to prepare a reflection support. On this reflection support, each layer having the following composition was coated to prepare a multi-layer silver halide photographic light-sensitive material Sample 201. The coating solution was prepared as follow:

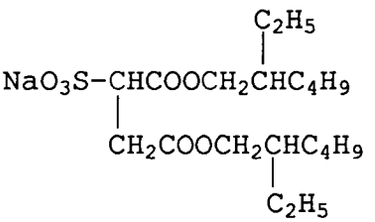
To 26.7 g of yellow coupler (Y-1), 0.67 g of additive (HQ-1) and 6.67 g of high boiling organic solvent (DNP), 60 ml of ethyl acetate was added and dissolved. The solution was emulsified and dispersed into 220 ml of a 10% aqueous gelatin solution containing 9.5 ml of 15% surfactant (SU-1) by the use of a supersonic homogenizer to prepare yellow coupler dispersant. This dispersant was mixed with blue sensitive silver halide emulsion (EM-B) to prepare a coating solution for the first layer. The 2nd layer through the 7th layer were prepared in the same manner as in the above-mentioned coating solution for the 1st layer. In addition, as a hardener, (H-2) was added to the 2nd layer and the 4th layer, and (H-2) was added to the 7th layer. As a coating aid, surfactants SU-2 and SU-3 were added.

The layer structure is as follows:

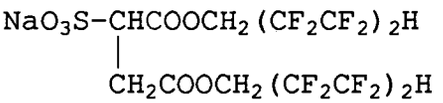
SU-1



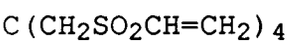
SU-2



SU-3



H-2



Y-1

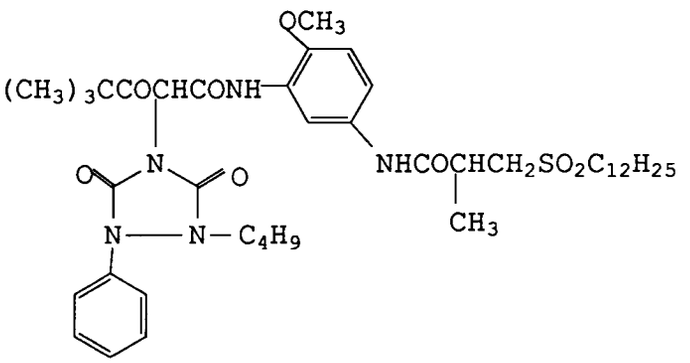


Table 3

Layer	Structure	Added amount (g/m^2)
7th layer (Protective layer)	Gelatin	1.00
	Anti-stain agent (HQ-2)	0.002
	Anti-stain agent (HQ-3)	0.002
	Anti-stain agent (HQ-4)	0.004
	Anti-stain agent (HQ-5)	0.02
	Compounds B, C, D and E	2×10^{-5} respectively
	DIDP	0.005
	Silicone dioxide	0.003
	Anti-mildew agent (F-1)	0.002
6th layer (UV absorbing layer)	Gelatin	0.40
	AI-2	0.02
	AI-4	0.01
	UV absorber (UV-1)	0.10
	UV absorber (UV-2)	0.04
	UV absorber (UV-3)	0.16
	UV absorber (UV-5)	0.04
	Compound E	4×10^{-4}
	DNP	0.20
	Compound F and G	2×10^{-4} respectively
	PVP	0.03
5th layer (Red sensitive layer)	Gelatin	1.30
	Red sensitive silver bromochloride emulsion (see Table 5)	0.21
	Cyan coupler (C-1)	0.10
	Cyan coupler (C-2)	0.28
	Dye image stabilizer (ST-1)	0.20
	Anti-stain agent (HQ-1)	0.01
	HBS-1	0.20
	DOP	0.20

Table 4

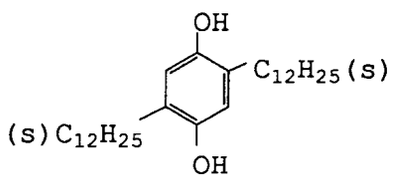
Layer	Structure	Added amount (g/m^2)
4th layer (UV absorbing layer)	Gelatin	0.94
	UV absorber (UV-1)	0.28
	UV absorber (UV-2)	0.09
	UV absorber (UV-3)	0.38
	Compounds F and G	4×10^{-4} respectively
	Anti-stain agent (HQ-5)	0.10
	Compound E	1×10^{-3}
	DNP	0.40
3rd layer (Green sensitive layer)	Gelatin	1.40
	AI-1	0.01
	Green sensitive silver bromochloride emulsion (Em-G)	0.17
	Magenta coupler (M-1)	0.23
	Dye image stabilizer (ST-3)	0.20
	Dye image stabilizer (ST-4)	0.17
	DIDP	0.13
	DBP	0.13
2nd layer (Intermediate layer)	Gelatin	1.20
	AI-3	0.01
	Anti-stain agent (HQ-2)	0.03
	Anti-stain agent (HQ-3)	0.03
	Anti-stain agent (HQ-4)	0.05
	Anti-stain agent (HQ-5)	0.23
	Compounds B, C, D and E	3×10^{-4} respectively
	DIDP	0.06
	Fluorescent brightening agent (W-1)	0.10
	Anti-mildew agent (F-1)	0.02

Table 4 (cont'd)

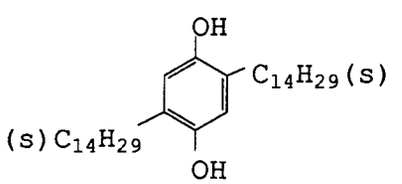
Layer	Structure	Added amount (g/m^2)
1st layer (Blue sensitive layer)	Gelatin	1.20
	Blue sensitive silver bromochloride emulsion (Em-B)	0.26
	Yellow coupler (Y-1)	0.80
	Dye image stabilizer (ST-1)	0.30
	Dye image stabilizer (ST-2)	0.20
	Anti-stain agent (HQ-1)	0.02
	Compound A	2×10^{-4}
	DNP	0.20
Support	Paper laminated with polyethylene (containing minute colorant)	

The added amount of the silver halide emulsion is illustrated in terms of silver.

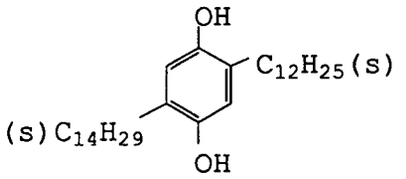
HQ-2



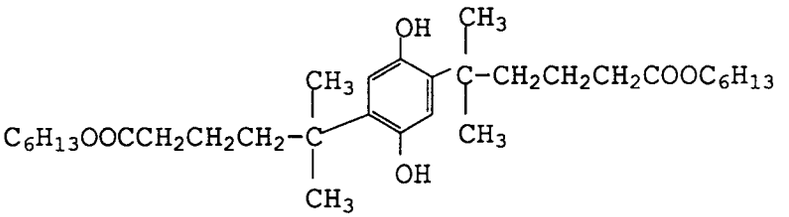
HQ-3



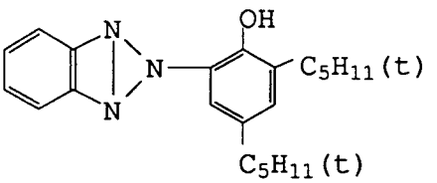
HQ-4



HQ-5



UV-1



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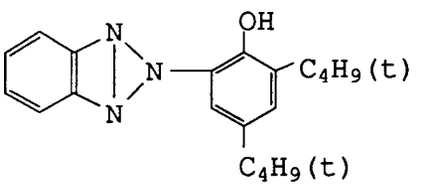
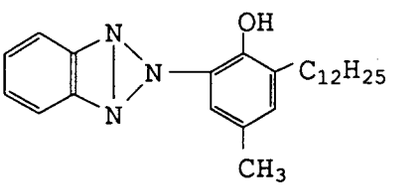
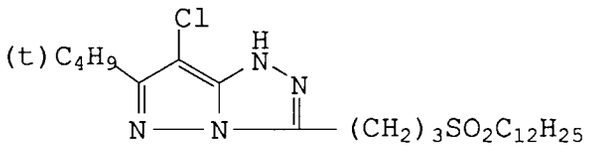


UV-3



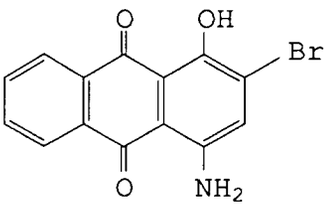
DBP : Dibutylphthalate
DOP : Dioctylphthalate
DNP : Dinonylphthalate
DIDP : Diisodecylphthalate
PVP : Polyvinylpyrrolidone

M-1

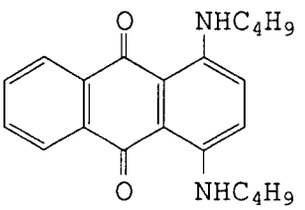


Compounds A, B, C, D and E represent quinone compounds of HQ-1, 2, 3, 4 and 5, respectively.

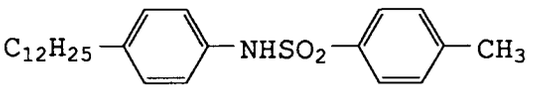
Compound F



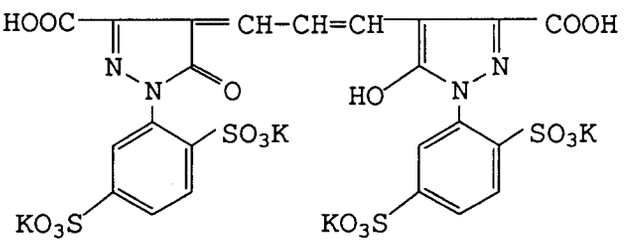
Compound G



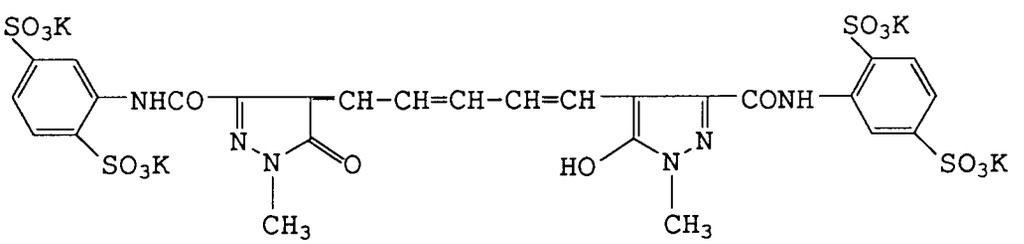
HBS-1



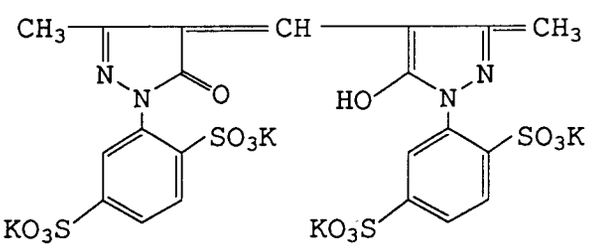
AI-1



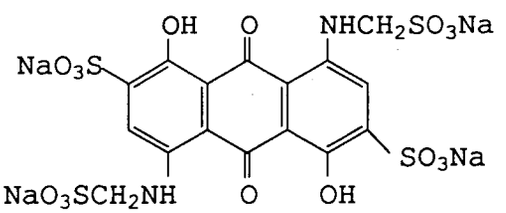
AI-2



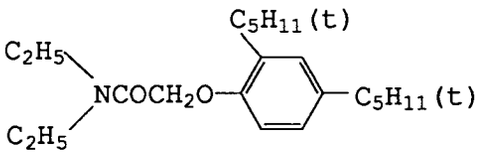
AI-3



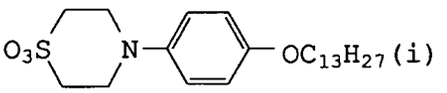
AI-4



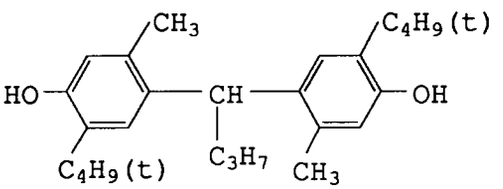
ST-2



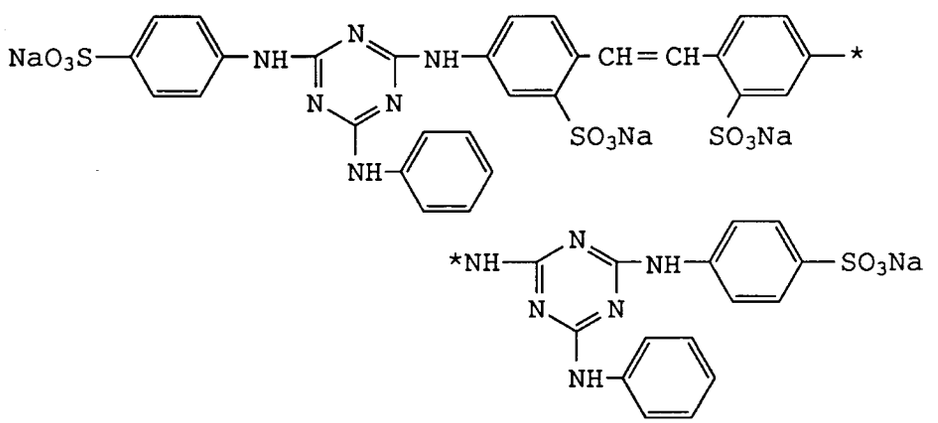
ST-3



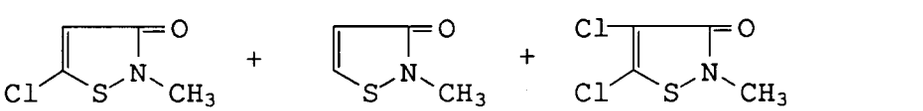
ST-4



W-1



F-1



(50%) (46%) (4%) mol ratio

(Preparation method of EM-B)

To 1,000 ml of a 2% aqueous gelatin solution kept at 40 °C, 2.90 g of sodium chloride, Aqueous solution A containing 59.5 mg of potassium bromide and Aqueous solution B containing 8.5 g of silver

nitrate were concurrently added spending 30 minutes while pAg was controlled to 6.5 and pH was controlled to 3.0. In addition, Aqueous solution C containing 55.0 g of sodium chloride, 1.13 g of potassium bromide, 0.005 mg of potassium iridium (IV) hexachloride and 3 mg of potassium hexacyano ferric trihydrate and Aqueous solution D containing 161 g of silver nitrate were concurrently added while pAg as controlled to 7.3 and pH was controlled to 5.5.

After the addition was completed, the solution was subjected to desalting by the use of a 10% aqueous solution of Demol N produced by Kao Atlas Co., Ltd. and a 30% aqueous solution of magnesium sulfate. Then, the resulting solution was mixed with an aqueous gelatin solution to prepare a mono-dispersed cubic emulsion having an average grain size of 0.70 μm, fluctuation coefficient (standard deviation of the grain size/the average grain size) of 0.09 and silver chloride content of 99 mol%.

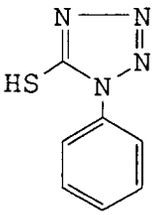
The above-mentioned emulsion was subjected to the most suitable sensitization employing sodium thiosulfate, chloroaurate, STAB-2, STAB-3 and sensitization dyes (BS-1 and BS-2) at 65 °C so that a blue sensitive silver halide emulsion EM-B was prepared.

(Preparation method of EM-G)

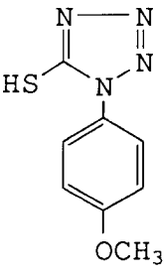
To 1,000 ml of a 2% aqueous gelatin solution kept at 40 °C, 2.91 g of sodium chloride, Aqueous solution A containing 29.8 mg of potassium bromide and Aqueous solution B containing 8.5 g of silver nitrate were concurrently added spending 30 minutes while pAg was controlled to 6.5 and pH was controlled to 3.0. In addition, Aqueous solution C containing 55.3 g of sodium chloride, 565 mg of potassium bromide, 0.024 mg of potassium iridium (IV) hexachloride acid and 8.44 mg of potassium hexacyano ferric trihydrate and Aqueous solution D containing 161 g of silver nitrate were concurrently added spending 120 minutes while pAg as controlled to 7.3 and pH was controlled to 5.5.

After the addition was completed, the solution was subjected to desalting by the use of a 10% aqueous solution of Demol N produced by Kao Atlas Co., Ltd. and a 30% aqueous solution of magnesium sulfate. Then, the resulting solution was mixed with an aqueous gelatin to prepare a mono-dispersed cubic emulsion having an average grain size of 0.40 μm, fluctuation coefficient (standard deviation of the grain sizes/the average grain size) of 0.07 and silver chloride content of 99.9 mol%. The above-mentioned emulsion was subjected to the most suitable sensitization employing sodium thiosulfate, chloroaurate, the below-mentioned compound (STAB-1) and a sensitization dye (GS-1) at 65 °C so that a green sensitive silver halide emulsion EM-G was prepared.

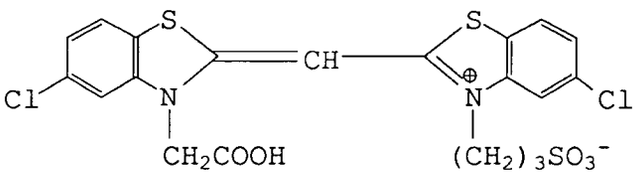
STAB-2



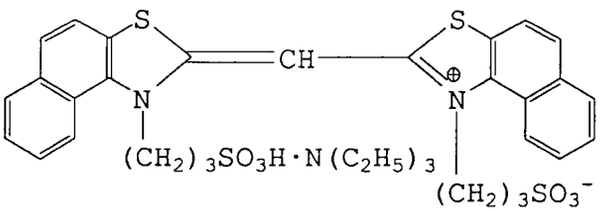
STAB-3



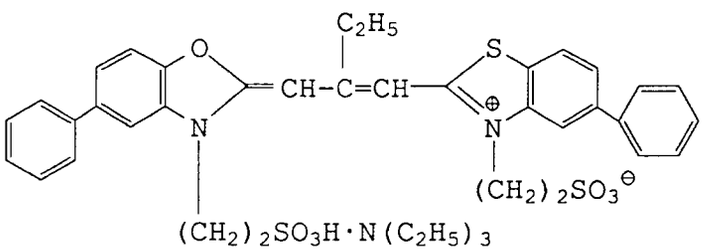
BS-1



BS-2



GS-1



Light-sensitive materials were prepared in the same manner as in the sample obtained as above, except that the emulsion of the red sensitive layer as shown in Table 5 was replaced. They were defined to be Samples 201 through 212.

The sensitivity and the sensitivity variation due to the change in humidity of samples obtained in the above-mentioned manner were evaluated in the same manner as in Example 1. Table 5 shows the results regarding the red sensitive layer. Development processing was conducted in the following steps.

(Processing step)			
Processing step	Processing temperature	Time	Amount of replenishing
Color developing	38.0 ± 0.3 °C	27 seconds	81 ml/m^2
Bleach-fixing	35.0 ± 0.5 °C	27 seconds	54 ml/m^2
Stabilizing	30 - 34 °C	90 seconds	150 ml/m^2
Drying	60 - 80 °C	30 seconds	

The following shows a composition of a color developing solution.

(Tank solution for a color developing solution)	
Pure water	800 ml
Diethylene glycol	10 g
Potassium bromide	0.01 g
Potassium chloride	3.5 g
Potassium sulfite	0.25 g
N-ethyl-N-(βmethanesulfonamidoethyl)-3-methyl-4-aminoaniline sulfate	6.5 g
N,N-diethylhydroxylamine	3.5 g
Disulfonateethylhydroxylamine	3.5 g
Triethanolamine	10.0 g
Diethylenetriamine pentaacetate sodium salt	2.0 g
Fluorescent brightening agent (4,4'-diaminostylbenzsulfonate derivative)	2.0 g
Potassium carbonate	30 g
Water was added to make 1 ℓ in total and pH was regulated to 10.10.	

(Replenisher for a color developing solution)	
Pure water	880 ml
Diethyleneglycol	10 g
Potassium sulfite	0.5 g
N-ethyl-N-(βmethanesulfonamidoethyl)-3-methyl-4-aminoaniline sulfate	10.5 g
N,N-diethylhydroxylamine	6.0 g
Disulfonateethylhydroxylamine	6.0 g
Triethanolamine	10.0 g
Diethylenetriamine pentaacetate sodium salt	2.0 g
Fluorescent brightening agent (4,4'-diaminostylbenzsulfonate derivative)	2.5 g
Potassium carbonate	30 g
Water was added to make 1 ℓ in total and pH was regulated to 10.60.	

	Replenishing solution for bleach-fixer	Tank solution for bleach-fixer
Diethylenetriamine pentaacetate ferric ammonium dehydrate	100 g	50 g
Diethylenetriamine pentaacetate	3 g	3 g
Ammonium thiosulfate (70% aqueous solution)	200 ml	100 ml
5-amino-1,3,4-thiadiazole-2-thiol	2.0 g	1.0 g
Ammonium sulfite (40% aqueous solution)	50 ml	25 ml
	pH 6.5	7.0
Water was added to make 1 l in total, and pH was regulated with aqueous ammonium or glacial acetic acid.		

(Tank solution and a replenisher for a stabilizer)	
Orthophenylphenol	1.0 g
5-chloro-2-methyl-4-isothiazoline-3-0n	0.02 g
2-methyl-4-isothiazoline-3-on	0.02 g
Diethyleneglycol	1.0 g
Fluorescent brightening agent (Thinopal SFP)	2.0 g
1-hydroxyethilidene-1,1-diphosphate	1.8 g
PVP (Polyvinylpyrroridone)	1.0 g
Aqueous ammonia (25% aqueous solution of ammonium hydroxide)	2.5 g
Ethylenediamine tetraacetate	1.0 g
Ammonium sulfite (40% aqueous solution)	10 ml
Water was added to make 1 l in total, and pH was regulated to 7.5 with sulfuric acid or aqueous ammonia.	

The stabilizing solution was replenished by means of a multi-step counter-flow system with 3 tanks.

Color papers prepared in the above-mentioned manner were subjected to running processing using processing solutions prepared in the above-mentioned manner. After incorporating the above-mentioned color developer, the tank solution for bleach-fixing and the tank solution for stabilizing in the automatic processing machine, the above-mentioned color paper samples were subjected to running processing while replenishing the above-mentioned color developer, bleach-fixer and stabilizer.

Table 6 shows the results thereof.

Table 5

Sample No.	Emulsion of the red sensitive layer	*1 Sensitivity	Stability	Variation in sensitivity against humidity
201 (Comparative)	Em-1	100	82	112
202 (Comparative)	Em-2	83	85	112
203 (Comparative)	Em-3	107	92	126
204 (Comparative)	Em-4	101	82	112
205 (Invention)	Em-5	126	96	106
206 (Invention)	Em-6	134	97	106
207 (Invention)	Em-7	138	97	105
208 (Invention)	Em-8	130	97	106
209 (Invention)	Em-9	124	96	106
210 (Invention)	Em-10	128	96	107
211 (Invention)	Em-11	130	95	107
212 (Invention)	Em-12	132	96	107

*1 The more the value is, the higher sensitivity is.

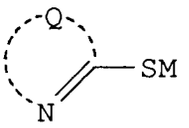
As is seen from the results shown in Table 5, the multilayered silver halide photographic light sensitive material of the invention comprising the super sensitizer and inhibitor of the invention in combination also shows the effects of the invention that exhibit high sensitivity, excellent storage stability and less sensitivity fluctuation due to the change of humidity at exposure.

It can be understood that, of the super sensitizers of the present invention, the macrocyclic compound having an aromatic group ring offers great sensitization effect, and that the macrocyclic compound having 2 aromatic group rings is preferable and offers greater sensitization effect.

Claims

1. A silver halide photographic light-sensitive material comprising a support and provided thereon, a silver halide emulsion layer containing spectrally sensitized silver halide grains having a silver chloride content of not less than 90 mol%, a cyclic compound having a 9- or more-membered ring containing a hetero atom, and at least one compound represented by the following formula (S):

Formula (S)



wherein Q represents an atomic group necessary to form 5- or 6-membered hetero cyclic ring, provided that said Q may form a condensed ring with a benzene ring; and M represents a hydrogen atom, an alkali metal atom, or an ammonium group.

2. The material of claim 1, wherein said silver halide grains have a silver chloride content of not less than 98 mol%.

3. The material of claim 1, wherein said silver halide grains have a silver chloride content of not less than 99 mol%.

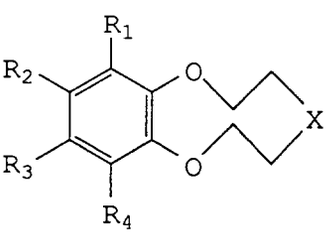
4. The material of claim 1, wherein said cyclic compound has a saturated ring containing an ether bond.

5. The material of claim 1, wherein said cyclic compound has an aromatic ring and an ether bond.

6. The material of claim 1, wherein said cyclic compound has two or more aromatic rings and an ether bond.

7. The material of claim 1, wherein said cyclic compound is a compound represented by the following Formula (1):

Formula (1)

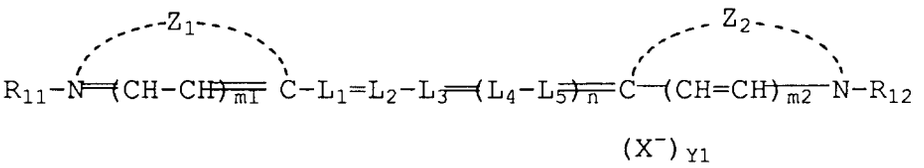


wherein R_1, R_2, R_3, and R_4 independently represent a hydrogen atom, an alkyl group, an alkoxy group, an aryl group, an aryloxy group, an alkenyl group, an alkenyloxy group, an acylamino group, a halogen atom, an alkylthio group, an arylthio group, an alkoxycarbonyl group, an acyloxy group, an acyl group or a sulfonamido group, provided that two of R_1 to R_4 may combine to form a 5- or 6-membered ring; and X represents a divalent group containing an oxygen atom or a nitrogen atom.

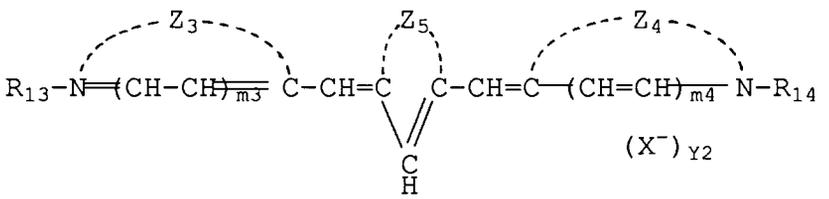
8. The material of claim 1, wherein said silver halide emulsion layer has a maximum spectral sensitivity in the wavelength region of not less than 600 nm.

9. The material of claim 1, wherein said silver halide emulsion layer further contains in an amount of 2×10^{-8} to 1×10^{-2} mol per mol of silver a red-sensitive sensitizing dye represented by the following Formula (2) or (3):

Formula (2)



Formula (3)



wherein R_{11}, R_{12}, R_{13}, and R_{14} independently represent an alkyl group, an alkenyl group or an aryl group; L_1, L_2, L_3, L_4 and L_5 independently represent a methine group; Z_1, z_2, z_3, and Z_4 independently represent an atomic group necessary to form a 5-or 6-membered ring; m_1, m_2, m_3, and m_4 independently represent 0 or 1; n represents 0 or 1; X^- represents an anion; and Y_1 and Y_2 independently represent 0 or 1.

10. The material of claim 9, wherein said silver halide emulsion layer has a maximum spectral sensitivity in the wavelength region of not less than 600 nm.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 93 11 8944

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	EP-A-0 509 810 (KONICA) * page 2, line 50 - page 17, line 20 * * page 21, line 26 - line 27 * * page 22, line 23 - line 26 * ---	1-10	G03C1/28 G03C7/392
Y	EP-A-0 476 602 (KONICA) * page 11, line 47 - page 21, line 48 * * page 32, line 39 - line 50 * * page 33, line 18 - line 27 * -----	1-10	

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	25 January 1994	Magrizos, S

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

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