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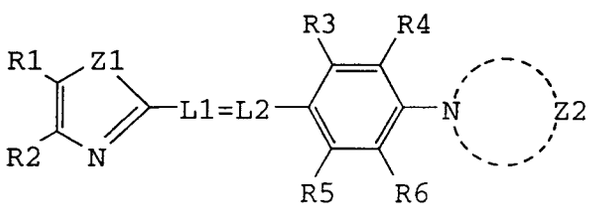
(54) Silver halide light-sensitive photographic material.

(57) A silver halide photographic light-sensitive material improved in latent image stability is provided, comprising a support having thereon a silver halide emulsion layer which contains a compound represented by the following formula.



EP 0 611 109 A1

Field of the Invention

The present invention is relates to a silver halide light-sensitive photographic material and, especially, to a silver halide light-sensitive photographic material which comprises silver halide emulsion containing silver halide grains of which storage stability is improved by incorporating therein a specific novel compound.

Background of the Invention

Recently, the improvement in the preservation stability of the silver halide light-sensitive photographic materials has been a strong demand as well as the demand for high sensitivity and low fog.

In the image-forming technology using silver halide light-sensitive photographic materials, it is well known that two steps are necessary to form an image. That is; (a) a step of imagewise exposing a silver halide light-sensitive photographic material to light to form a latent image; and (b) a step of developing thus imagewise exposed photographic material to convert the formed latent image into a silver image or a dye image.

Concerning these processes, for instance, there is a detailed description in "The Theory of the Photographic Process", by James.

The formation of latent image is a microscopic change of state in silver halide crystal by exposure and the latent image itself is essentially unstable.

Therefore, the latent image is liable to be decayed or intensified with the lapse of time between exposure and development.

The decay of latent image is called, in the field of photographic industry, "latent-image fading" and the latter is called "latent image progression".

Generally, the behavior of the latent image depends strongly upon the storage condition of the exposed light-sensitive material and, for example, the latent-image fading or the latent image intensification is remarkable in the preservation under high temperature. On the other hand, the latent-image fading hardly be caused when the light-sensitive material is stored under low temperature.

One method to solve this problem is to carry out development process immediately after imagewise exposure. Another method is simply to store the exposed photographic material under cool condition.

These are the simplest methods from chemical point of view, but they are not necessarily welcomed to the customer.

In fact, for example, it is often the case that the imagewise exposed photographic material is left as it is for a period of several months without undergoing development.

In the case of multi-layered color photographic materials, the latent image fading or the latent image intensification causes imbalanced photographic behavior between layers, which results in imbalanced color balance and deteriorates color reproduction.

In order to prevent the latent image intensification, various attempts have been made. For example, there have been proposed a method of using a hardener which is capable of releasing an acid to lower pH of the emulsion layer, disclosed in Japanese Patent Publication No. 51-9 109(1976); a method of adding a rhodium compound and an iridium compound at the time of preparing of emulsion, which is disclosed in Japanese Patent O.P.I.Publication No. 48-6875(1973); a method of adding a heterocyclic mercapto compound to a silver halide emulsion prepared by using a rhodium compound, which is disclosed in Japanese Patent Publication No.57-23250(1982); a method of adding a hydroxy-aza-indorizine compound and a nitrogen-containing heterocyclic compound having a mercapto group to a silver halide emulsion containing a rhodium compound disclosed in Japanese Patent O.P.I. Publication No. 53-127714(1988).

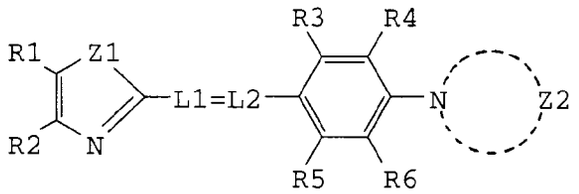
However, these conventional methods were not necessarily satisfactory in view of its specific manner of preparation or insufficient effects, etc.

Summary of the Invention

The object of the present invention is, therefore, to provide a silver halide light-sensitive photographic material comprising a silver halide emulsion of which preservation stability and, especially, anti-latent- image fading property is improved.

The object of the present invention was found to be achieved by a silver halide light-sensitive photographic material which comprises a compound represented by the following formula [I].

Formula [I]



wherein R1 and R2 independently represent a hydrogen atom, an alkyl group, an alkenyl group, an alkynyl group, an aryl group or a heterocyclic group; Z1 represents an oxygen atom, a selenium atom, a sulfur atom, a telurium atom, an organic group represented by -N(R7)- or -C(R8) (R9)-, provided that R1 and R2 may be bonded to each other to form a ring; R7, R8, and R9 independently represent a hydrogen atom, an alkyl group, an alkenyl group, an alkynyl group, an aryl group, and a heterocyclic group; R3, R4 , R5, and R6 independently represent a hydrogen atom or a substituent; Z2 represents a group of non-metal atoms necessary to form a 5- membered or 6- membered heterocyclic ring; and each of L1 and L2 represents a methine group.

The alkyl group represented by R1 and R2 is, for example, methyl group, ethyl group, propyl group, isopropyl group, n-butyl group, tert.-butyl group, n-pentyl group, a cyclopentyl group, n-hexyl group, a cyclohexyl group, n-octyl group, or n-dodecyl group. These alkyl groups may further be substituted by, for example, a halogen atom such as chlorine atom, bromine atom, fluorine atom, etc.; an alkoxy group, such as methoxy group, ethoxy group, 1,1-dimethylethoxy group, n-hexyloxy group, n-dodecyloxy group, etc.; an aryloxy group such as phenoxy group, naphthoxy group; an aryl group such as phenyl group, naphthyl group; an alkoxycarbonyl group such as methoxycarbonyl group, ethoxycarbonyl group, n-butoxycarbonyl group, 2-ethylhexyloxycarbonyl group, etc.; an aryloxy carbonyl group such as phenoxycarbonyl group, naphthoxycarbonyl group, etc.; an alkenyl group such as vinyl group, allyl group, etc.; a heterocyclic group such as 2-pyridyl group, 3-pyridyl group, 4-pyridyl group, morphoryl group, pyperizyl group, pyperazyl group, furyl group; an alkynyl group such as propynyl group; an amino group such as amino group, N,N-di-methyl amino group, anilino group; hydroxy group, cyano group, sulfo group, carboxyl group, and a sulfonamide group such as methylsulfonylamino group, ethylsulfonylamino group, n-butylsulfonylamino group, n-octylsulfonylamino group, phenylsulfonylamino group, etc.

The alkenyl group represented by R1 and R2 is, for example, a vinyl group or an allyl group. These groups can further be substituted by the alkyl group represented by R1 and R2, and the groups as mentioned as the substituent for the alkyl group.

The alkynyl group is, for example, propagyl group. The alkynyl group may be substituted by the alkyl group represented by R1 and R2, and the groups as mentioned as the substituent for the alkyl group.

The aryl group represented by R1 and R2 is, for example, a phenyl group, or a naphthyl group and these groups may also be substituted by the alkyl group represented by R1 and R2, and the groups mentioned as the substituent for the alkyl group.

The heterocyclic group represented by R1 and R2 is, for example, a pyridyl group such as 2-pyridyl group, 3-pyridyl group, 4-pyridyl group, etc., a thiazolyl group, an oxazolyl group, an imidazolyl group, a furyl group, a pyrollyl group, a pyrradinyl group, a pyrimidinyl group, a pyridazinyl group, a selenazolyl group, a sulforanyl, a pyperizinyl group, a pyrazolyl group, or a tetrazolyl group and these groups may be substituted by the alkyl group represented by R1 and R2 and the groups mentioned as the substituent for the alkyl group.

The substituent represented by R3, R4, R5 and R6 is, for example, an alkyl group such as methyl group, ethyl group, n-propyl 1 group, iso-propyl group, tert.-butyl group, n-pentyl group, cyclopentyl group, n-hexyl group, cyclohexyl group, n-octyl group, or n-dodecyl group; an alkenyl group such as vinyl group, or allyl group; an alkynyl group such as propargyl group; an aryl group such as a phenyl group, naphthyl group, etc.; a heterocyclic group such as a pyridyl group, a thiazolyl group, an oxazolyl group, an imidazolyl group, a furyl group, a pyrrolyl group, a pyrradinyl group, a pyrimidinyl group, a pyridazinyl group, a selenazolyl group, a sulforanyl group, a pyperidinyl group, a pyrazolyl group, tetrazolyl group, etc.; a halogen atom such as chlorine atom, bromine atom, fluorine atom, etc.; an alkoxy group such as methoxy group, ethoxy group, propyloxy group, n-pentyloxy group, cyclopentyloxy group, n-hexyloxy group, cyclohexyloxy group, n-octyloxy group, n-dodecyloxy group, etc.; an alkoxycarbonyl group such as methoxycarbonyl group, ethylethoxycabonyl group, n-butyloxycarbonyl group, n-octyloxycarbonyl group, n-dodecyloxycabonyl group, etc.; an aryloxycarbonyl group such as phenyloxycarbonyl group, naphthoxycarbonyl group, etc.; a sulfonamide group such as methylsulfonylamino group, ethylsulfonylamino group, n-butylsulfonylamino group, n-hexylsulfonylamino group, cyclohexylsulfonylamino group, n-octylsulfonylamino group, n-dodecylsulfonylamino group, phenylsulfonylamino

group, etc.; a sulfamoyl group such as aminosulfonyl group, methylaminosulfonyl group, dimethylaminosulfonyl group, n-butylaminosulfony group, n-hexylaminosulfonyl group, cyclohexylaminosulfonyl group, n-octylaminosulfonyl group, n-dodecylaminosulfonyl group, phenylaminosulfonyl group, naphthylaminosulfonyl group, 2-pyridylaminosulfonyl group, etc.; a ureido group such as methylureido group, ethylureido group, pentylureido group, cyclohexylureido group, n-octylureido group, n-dodecylureido group, phenylureido group, naphthylureido group, 2-pyridylaminoureido group, etc.; an acyl group such as acetyl group, ethylcarbonyl group, propylcarbonyl group, n-pentylcarbonyl group, cyclohexylcarbonyl group, n-octylcarbonyl group, 2-ethylhexylcarbonyl group, n-dodecylcarbonyl group, phenylcarbonyl group, naphthoxycarbonyl group, pyridylcarbonyl group, etc.; a carbamoyl group such as aminocarbonyl group, methylaminocarbonyl group, dimethylaminocarbonyl group, propylcarbonylamino group, n-pentylcarbonylamino group, cyclohexylcarbonylamino group, n-octylcarbonylamino group, 2-ethylhexylcarbonylamino group, n-dodecylcarbonylamino group, phenylcarbonylamino group, naphthylcarbonylamino group, etc.; a sulfonyl group such as methylsulfonyl group, ethylsulfonyl group, n-butylsulfonyl group, cyclohexylsulfonyl group, 2-ethylhexylsulfonyl group, dodecylsulfonyl group, phenylsulfonyl group, naphthylsulfonyl group, 2-pyridylsulfonyl group, etc.; an amino group such as amino group, ethylamino group, dimethylamino group, n-butylamino group, cyclopentylamino group, 2-ethylhexylamino group, n-dodecylamino group, anilino group, naphthylamino group, 2-pyridylamino group, etc.; a cyano group; a nitro group; a carboxyl group; and a hydroxyl group. These groups may be substituted by the alkyl group represented by R1 and the groups as mentioned for the substituent for the alkyl group.

The ring which can be formed with R1 and R2 is, for example, a benzene ring, a naphthalene ring, a thiophen ring, a pyridine ring, a furane ring, a pyrimidine ring, a cyclohexane ring, a pyrane ring, a pyrrole ring, a pyradine ring, an indole ring, etc. These groups may be substituted by the alkyl group represented by R1 and the groups as mentioned for the substituent for the alkyl group.

The methine group represented by substituted L1 and L2 can have a substituent. The substituent is, for example, an alkyl group such as methyl group, ethyl group, propyl group, etc.; an aryl group such as phenyl group, etc.; an alkoxy group such as methoxy group, ethoxy group, etc.; an aryloxy group such as phenoxy group, etc.; a halogen atom such as chlorine atom, bromine atom, etc.

The 5-membered or 6-membered ring is, for example, a morphorine ring, a pyperidine ring, a pyperadine ring, a pyrroridine ring, etc. and these groups may be substituted by the alkyl group represented by R1 and R2, and the groups as mentioned for the substituent for the alkyl group.

Specific examples of the compounds of the present invention are given below, but the scope of the present invention is not limited by these.

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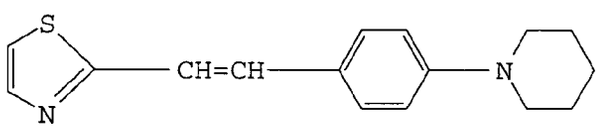

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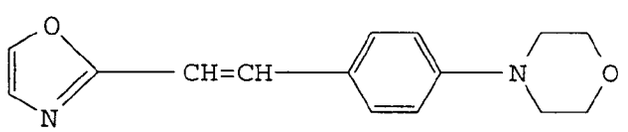

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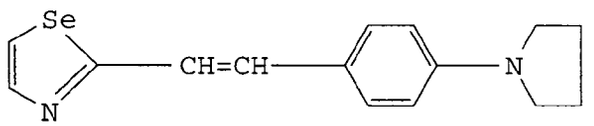

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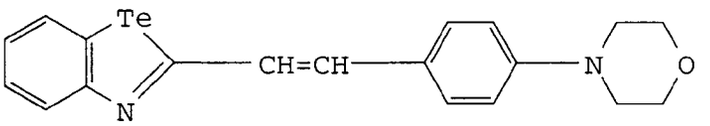

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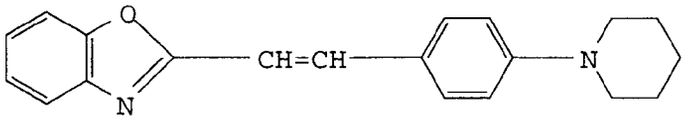

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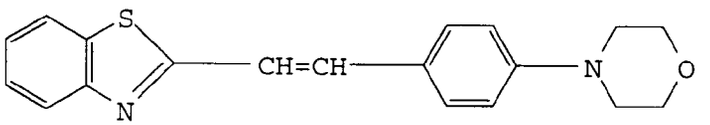

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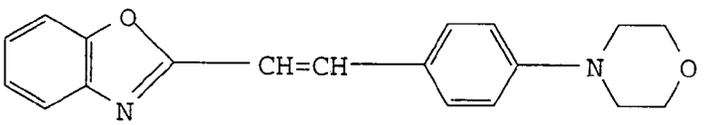

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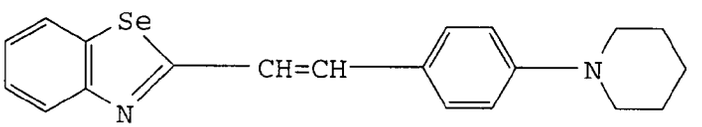

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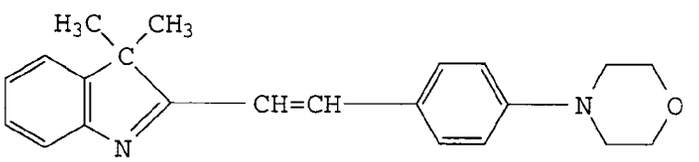

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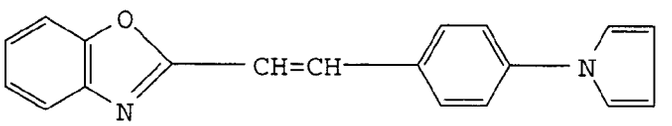

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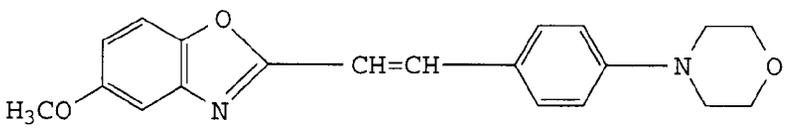

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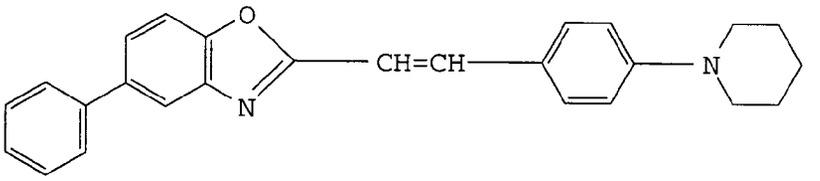

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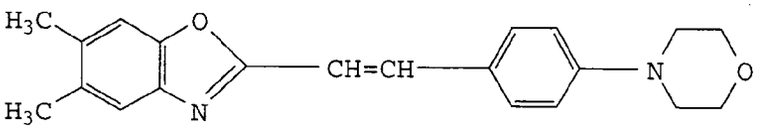

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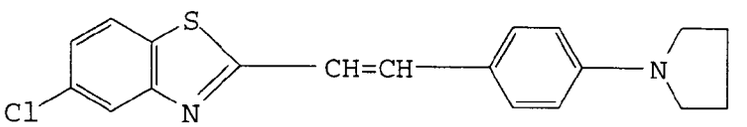

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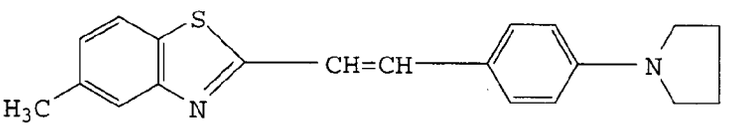

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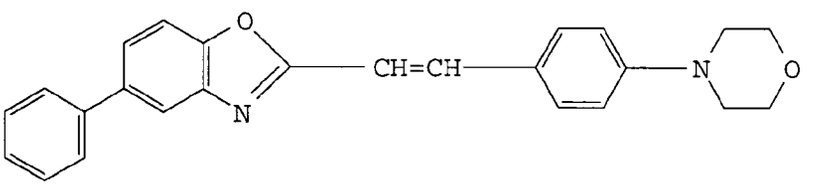

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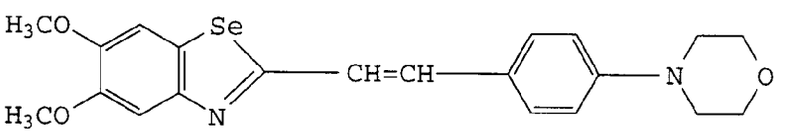

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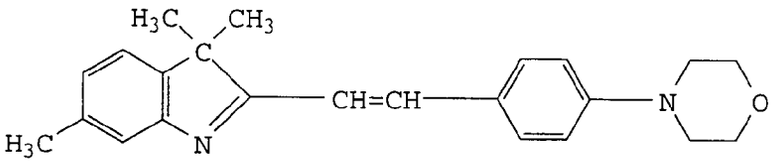

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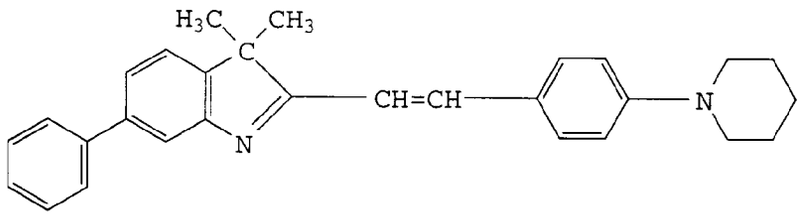

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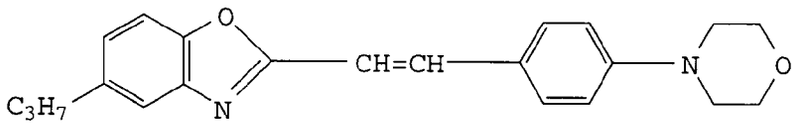

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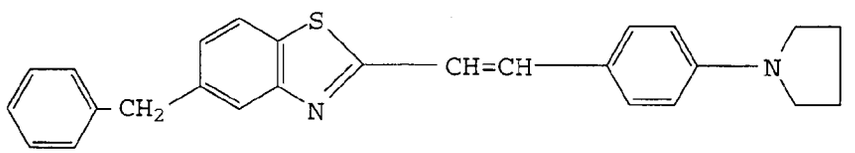

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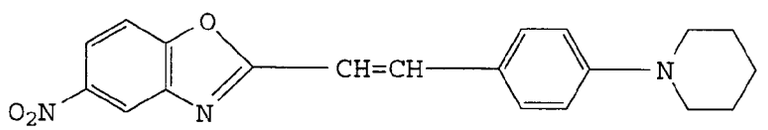

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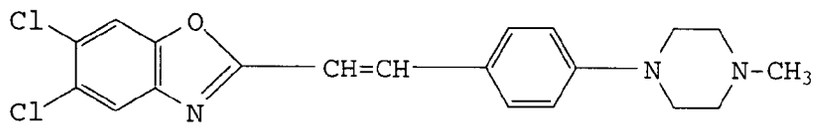

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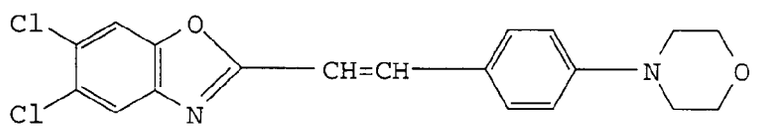

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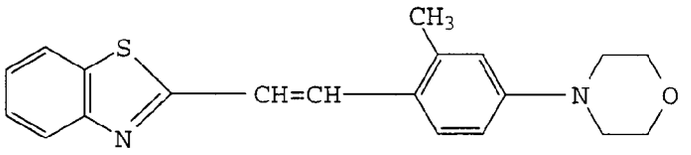

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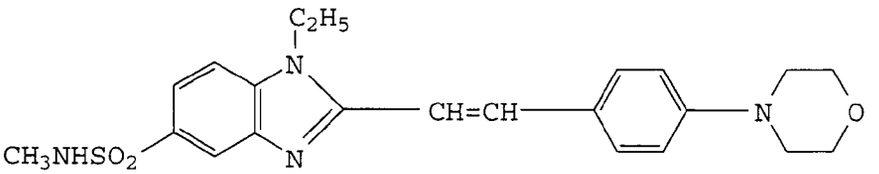

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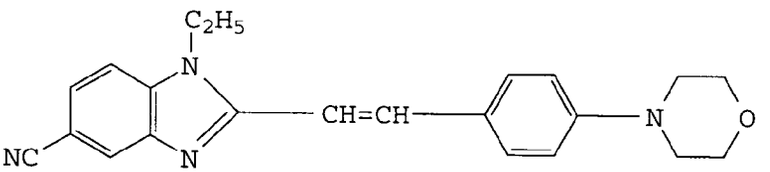

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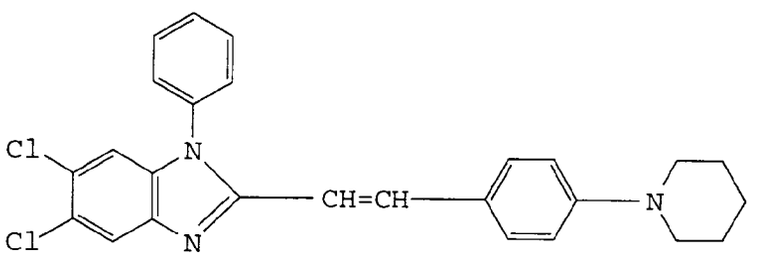

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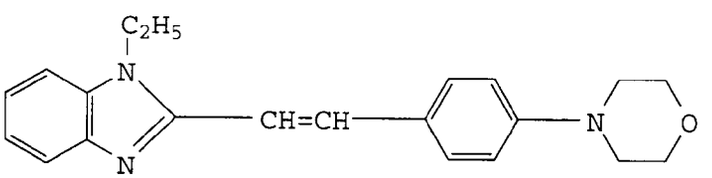

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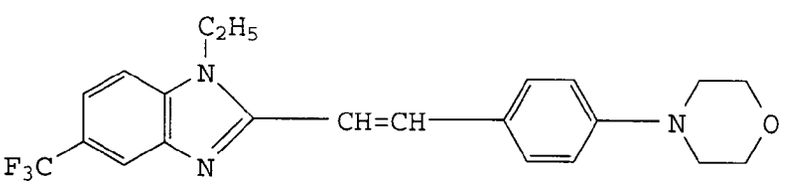

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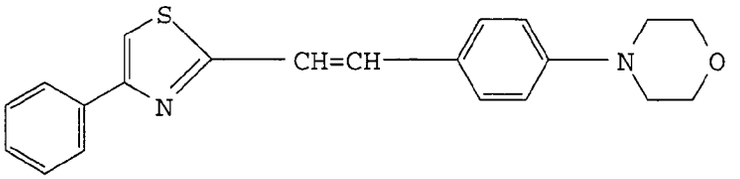

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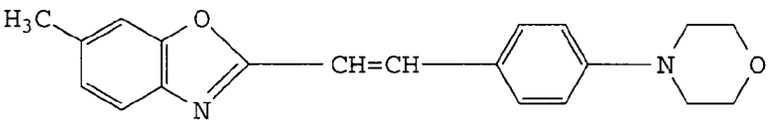

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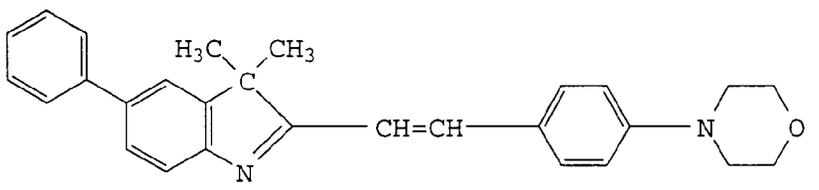

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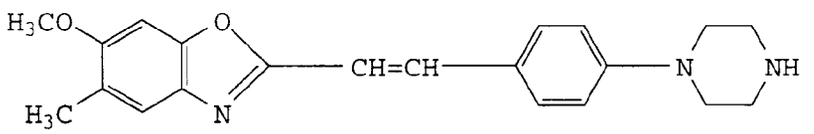

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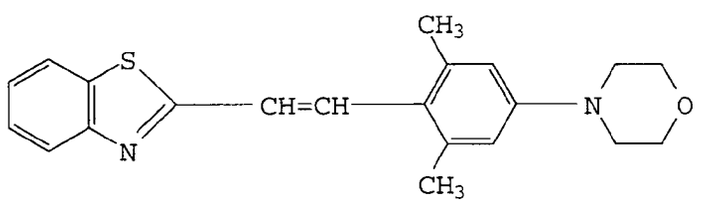

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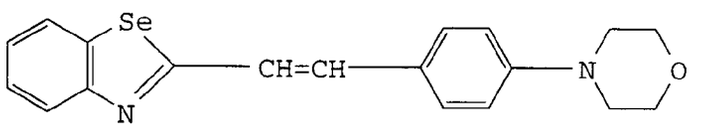

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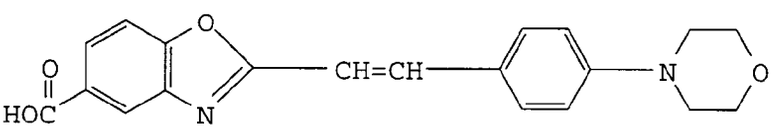

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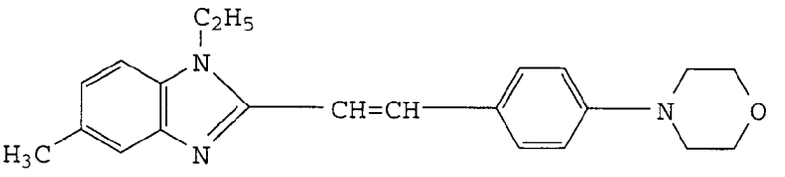

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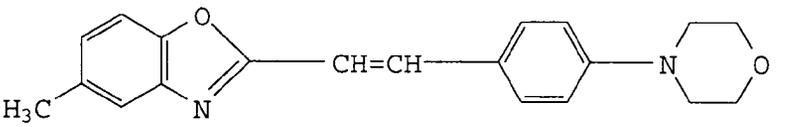

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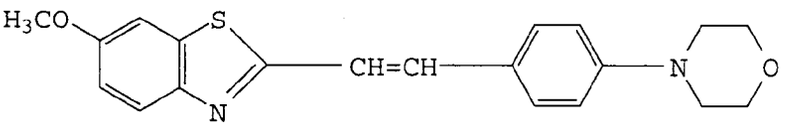

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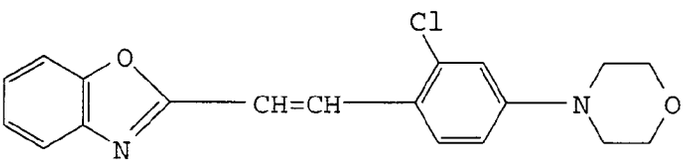

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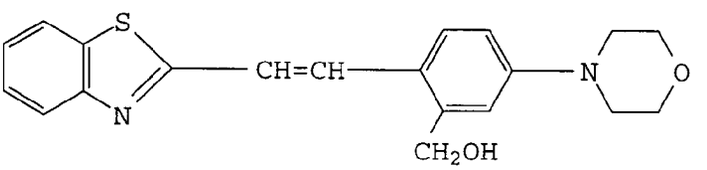

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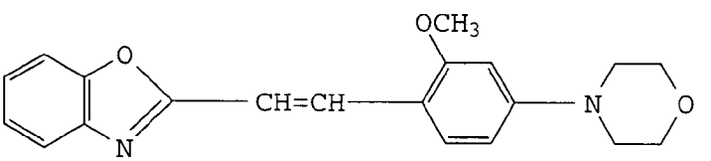

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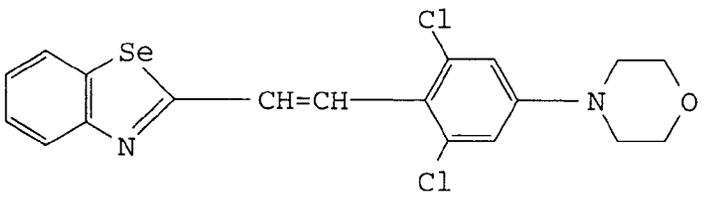

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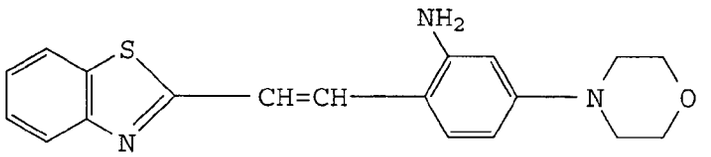

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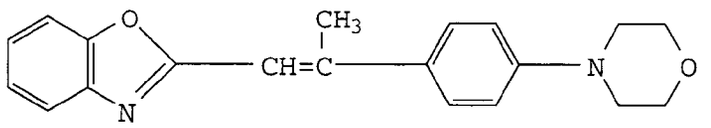

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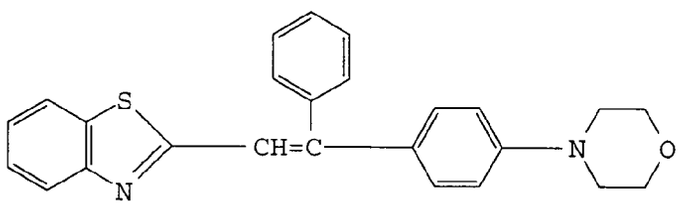

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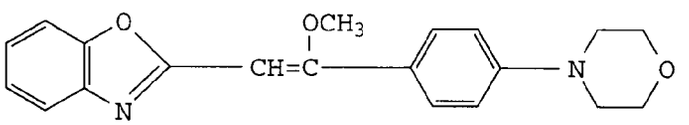


the compound of the present invention is contained in an amount of 2×10^{-8} to 1×10^{-2}, preferably 2×10^{-7} to 1×10^{-4} mol per mol of silver halide.

The examples of synthesizing the compounds of the present invention are given below. Other compounds may also be synthesized easily in the similar manner.

Synthesis Example 1. (synthesis of Exemplified Compound 39)

5g of 2,5-dimethyl benzoxazole, 6.5g of morphorino benzaldehyde and 1.5g of sodium hydride (mineral oil 60%) were dissolved in 15ml of dimethyl formamide and the mixture was stirred for one hour in the room temperature. After the reaction was completed, the solution was added to 200ml of water and deposited solid was filtered. After drying solid ingredient, the object product was obtained by recrystallization using ethyl acetate. The amount obtained was 5.7g and the yield was 52%.

Synthesis Example 2. (synthesis of Eexemplified Compound 40)

6.1g of 6-methoxy- 2-methyl benz thiazole, 6.5g of p-morphorino benzaldehyde, 1.5g of hydrogenated sodium hydride and 20ml of dimethylformamide were mixed under stirring for one hour at the room temperature. After the reaction was completed, the mixed solution was added to 200ml of water and deposited solid ingredient was filtered. After drying the solid ingredient, the objective product was obtained through recrystalliztion from ethyl acetate. The amount obtained was 7.2g and the yield was 60%.

The silver halide used for the photographic emulsion layer of the photographic light-sensitive material of the present invention, any one or more selected from silver bromide, silver iodobromide, silver chloroiodobromide, silver chlorobromide, and silver chloride can be used. A preferable silver halide is a silver iodobromide of which silver iodide content is not more than 30 mol%, silver bromide or silver chlorobromide.

Moreover, the silver halide grain crystals contained in the photographic emulsion may be regular shaped crystals such as cubic, octahedral or tetradecahedral shaped crystals; one with crystal imperfections such as one having twin planes; or irregular shaped crystals such as spherical shaped grains; and combined one thereof.

The silver halide emulsion used for the light-sensitive material of the present invention usually is subjected to, after physical ripening and chemical ripening, spectral sensitization. Additives which can be used in these processes are illustrated in Research Disclosures No.17643, No.18716, and No.308119 (They are hereinafter referred to as RD 17643, RD18716, and RD 308119, respectively.

Page and column in RD 308119, RD 17643 and RD 18716, in which references are made, are given below:

Item	Page and Section in RD 308119	Page in RD 17643	Page in RD 18716
Chemical sensitizer	996 III-A	23	648
Spectral sensitizer	996 IV-A-A, B, C, D, H, I and J	23 - 24	648 - 649
Super sensitizer	996 IV-A-E and J	23 - 24	648 - 649
Antifoggant	998 VI	24 - 25	649
Stabilizer	998 VI	24 - 25	649

Moreover, well-known photographic additives, which can be used in the present invention, are illustrated in above-mentioned Research Disclosure as shown below.

Item	Page and section of RD 308119	Page of RD 17643	Page of RD 18716
Anti-stain agent	1002 VII-I	25	650
Dye image stabilizer	1002 VII-J	25	
Whitening agent	998 V	24	
Ultraviolet ray	1003 VIIIC, XIIIC	25 - 26	

Light absorbent	1003 VIII	25 - 26	
Optical scattered agent	1003 VIII		
Filter dyestuff	1003 VIII	25 - 26	
Binder	1003 IX	26	651
Electrostatics prevention agent	1006 XIII	27	650
Hardener	1004 X	26	651
Plasticizer	1006 XII	27	650
Lubricant	1006 XII	27	650
Active agent and coating aid	1005 XI	26 - 27	650
Matting agent	1007 XVI		
Developing agent	1011 XXB		

Various couplers can be used for the light-sensitive material of the present invention according to the color-forming required in each of color-sensitive layers. The specific example is illustrated in above-mentioned Research Disclosure. The related description place is shown as below.

Item	Page of item RD 308119	Page eyes of item RD 17643
Yellow-dye-forming coupler	1001 VII-D	VII C-G
Magenta coupler	1001 VII-D	VII C-G
Cyan dye forming coupler	1001 VII-D	VII C-G
Colored coupler	1002 VII-G	VII G
DIR coupler	1001 VII-F	VII F
BAR coupler	1002 VII-F	
P.U.G. releasing coupler	1001 VII-F	
Alkali soluble coupler	1001 VII-E	

When various additives are used for the light-sensitive material of the present invention, these may be added by using the dispersion method described in RD 308119 XIV.

In the present invention, the support described on page 28 of above-mentioned RD 17643, page 647-8 of RD 18716, and in XVIII of RD 308119 can be used.

Auxiliary layers such as a filter layer and a inter-layer, etc. described in the above-mentioned RD 308119

VII-K can be provided to the light-sensitive material of the present invention.

The light-sensitive material of the present invention can take various layer arrangements such as a conventional layer order, reverse-layer order, and the unit constitutions described in the above-mentioned RD 308119 VII-K.

The present invention can be applied to various color photographic materials such as the color negative film for general use or cine-use, the color reversal film for the slide or the televisions, the color paper, the color positive films, and the color reversal paper.

The light-sensitive material of the present invention can be subjected to the development processing by the usual method described at pages 28 - 29 of RD 17643, page 615 of RD 18716, and section XIX, RD 308119.

Examples

Next, the present invention is explained more specifically with reference to examples. However, the scope of the present invention is not limited by these.

Example 1

A method of preparing emulsion EmA-1 used in this example is shown below:

Preparation of Emulsion EmA-1:

The manner of preparing emulsion EmA-1 is described.

Following aqueous solutions (a-1) through (a-4) were used.

Solution (a-1)	
Gelatin	51.93 g
28% aqueous ammoniacal solution	1056 ml
56% acetic acid	10590 ml
Water to make	11827 ml

Solution (a-2)	
Silver nitrate	1587 g
28% aqueous ammoniacal solution	1294 ml
Water to make	2669 ml

Aqueous solution (a-3)

Gelatin	34.93 g
Potassium bromide	1454.7 g
Water to make	3493 ml.

Emulsified solution (a-4) containing silver iodide fine grains (an average grain size: 0.06 μm)	
Silver iodide fine grain emulsion, which contains 1 mol of AgI and 45.6 g of gelatin, and is made to a total volume of 1467 ml	1239 ml
4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene	5.22 g
Water to make	2294 ml

To the above-mentioned Solution (a-1), which was violently stirred at 60°C, 0.407 mol equivalent monodispersed silver iodobromide emulsion, of which average grain size is 0.27 μm and the silver iodide content of which is 2 mol%, was added as seed grains and pH and pAg of the solution was controlled by use of aqueous solutions of acetic acid and potassium bromide.

Thereafter, while controlling pH and pAg of the emulsion as shown in Table 1, aqueous solutions of (a-2), (a-3), and (a-4) were added at the flowing rates as shown in Table 2 and Table 3 by the simultaneous double-jet mixing method. Table 1 is a grain rowth condition of EmA-1.

Table 1

Ag (%)	0		29	29*		56		100
pH	7.0	→	7.0	6.0	→	→	→	6.0
pAg	7.5	→	7.5	9.7	↘	10.1	→	10.1

*: Arrows are used to designate a variation of a pH or pAg value;
(→): maintaining
(↘): continuously-lowering
(↓): rapidly-lowering

Table 2 represents addition flowing rates of aqueous solutions (a-2) and (a-3) and Table 3 represents flowing rates of aqueous solution (a-4).

Table 2

Time (min)	Flowing rate (ml/min)	
	(a-2)	(a-3)
0	11.56	10.98
8.61	10.21	9.70
19.4	9.30	8.83
28.8	5.72	5.44
70.3	9.13	8.68
76.5	13.65	12.91
78.2	18.25	12.91
90.6	32.81	54.47
102.7	77.01	86.56
113.4	103.66	111.75
114.4	103.66	111.75

Table 3

Time (min)	Flowing rate (ml/min)
0	0
28.8	0
28.8	83.69
34.5	90.16
35.1	31.80
59.8	42.13
60.3	12.09
76.5	14.42
82.2	22.53
82.4	16.78
96.3	0
112.7	0
112.7	0
114.4	0

Next, by adding aqueous phenylcarbamyl gelatin solution and controlling pH of the solution, the grain emulsion was to be flocculated to perform desalinization washing.

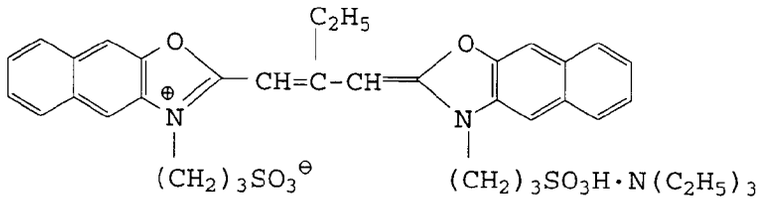
Thus, a monodispersed emulsion EmA-1, of which silver iodide content is 8.0-mol % and the average grain size is 0.8 μm, was prepared.

After adjusting pAg of EmA-1 to 8.0 and adding 2.0×10^{-6} mol/mol AgX of sodium thiosulfate to the emulsion, the emulsion was chemically ripened for a period of 60 minutes at a temperature of 55°C and pH of 5.8. Then, by adding a solution containing 4.4×10^{-7} mol/mol AgX of chloroauric acid and ammonium thiocyanate, the emulsion was ripened furthermore for 60 minutes.

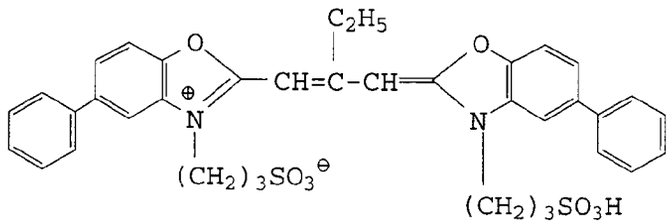
Afterwards, compounds of the present invention and comparison compounds 1-5 as shown in table 4 were added to this emulsion and the amount of 1/10 of all added amount of the sensitizing dye was added individually. Sensitizing dyes SD-A, SD-B and SD-C as shown below was made to adsorb together on the grains and the spectral sensitization was performed. Furthermore, magenta couplers M-A, M-B, and M-C were added thereto.

Then, after adding an appropriate amount of 2-hydroxy-4,6-dichrolotriazine sodium salt as a hardener to respective emulsions, they were respectively coated on a subbed triacetate support so that the coated amount of silver is 2.0 g/m^2 and photographic material samples were obtained.

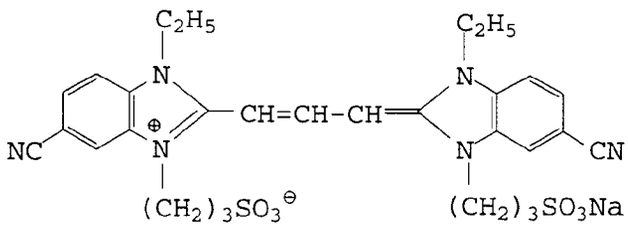
SD-A



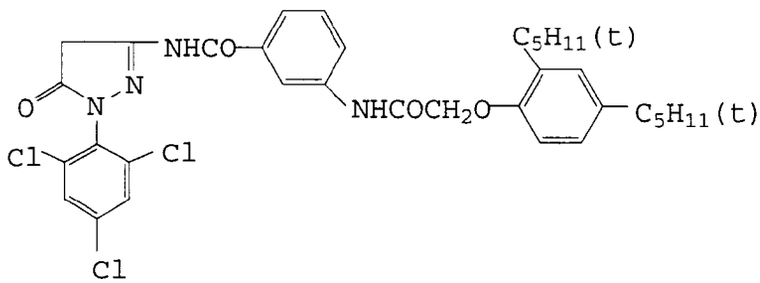
SD-B



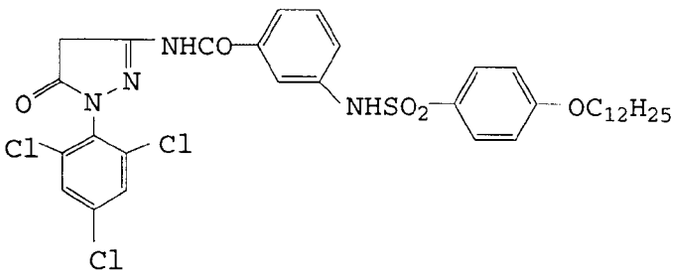
SD-C



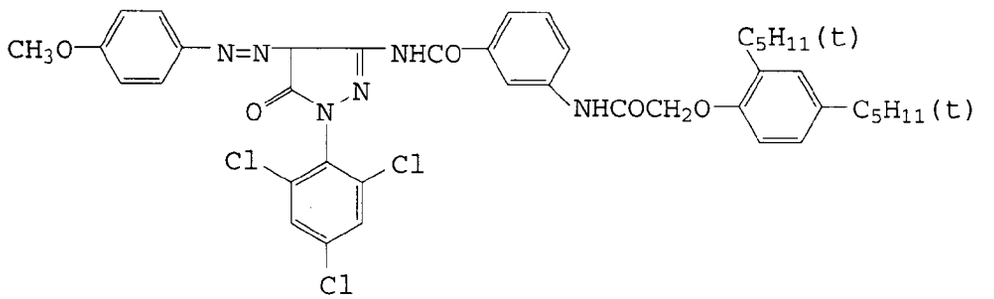
M-A



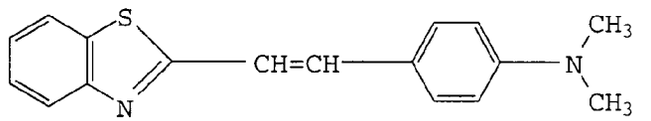
M-B



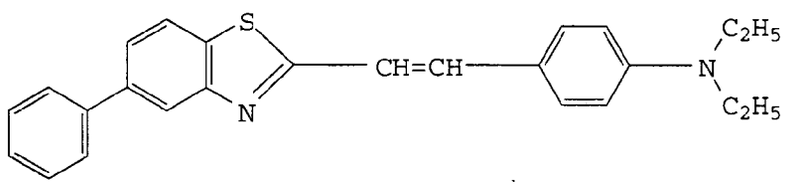
M-C



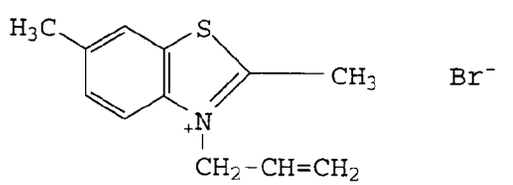
Comparative Compound-1 (Comp. 1)



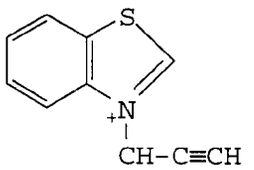
Comparative Compound-2 (Comp. 2)



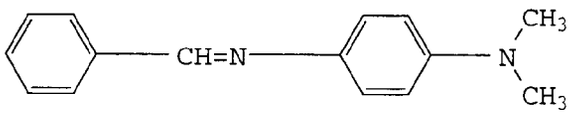
Comparative Compound-3 (Comp. 3)



Comparative Compound-4 (Comp. 4)



Comparative Compound-5 (Comp. 5)



Each of these samples was exposed through an optical wedge to green light and then developed according to the following processing steps. Furtheremore, samples which were aged for one week after exposure were similarly developed. The photographic performance was comparatively evaluated. The results thereof are shown in Table 4. A green photosensitivity in Table 4 was represented by relative sensitivity wherein the sensitivity of the sample 1 (comparison) was represented as 100.

Processing Step (38°C)	Processing Time
Color Development	3'15"
Bleaching	6'30"
Washing	3'15"
Fixing	6'30"
Washing	3'15"
Stabilizing	1'30"
Drying	

The composition of the processing solution used in the respective processing steps are given below:

(Color Developer)	
4-amino-3-methyl-N-ethyl-N-β-hydroxyethyl aniline sulfate	4.75 g
Sodium sulfite anhydride	4.25 g
Hydroxyl amine 1/2 sulfates	2.0 g
Potassium carbonate anhydride	37.5 g
Sodium bromide	1.3 g
Nitrilotriacetic acid trisodium salt	2.5 g
Potassium hydroxide	1.0 g
Add water to make the total volume 1000 ml and adjust the pH of the solution to 10.6 using sodium hydroxide.	

(Bleaching Solution)

Ethylenediaminetetraacetic acid iron (III) ammonium salt	100.0 g
Ethylenediaminetetraacetic acid di ammonium salts	10.0 g
Potassium Ammonium	150.0 g
Glacial acetic acid	10.0 g

Add water to make the total vqlume 1000 ml and adjust the pH of the solution to 6.0 using ammonia water.

(Fixing Solution)	
Ammonium thiosulfate	175.0 g
Sodium sulfite unhydride	8.6 g
Meta sodium sulfite	2.3 g
Add water tomake the total volume 1000 ml and adjust pH of the solution to 6.0 using acetic acid.	

(Stabiling Solution)	
Formalin (37% aqueous solution)	1.5 ml
Konidax (product of Konica Corporation)	7.5 ml
Add water to make the total volume 1000 ml	

Table 4

Sample No.	Compound No.	Emulsion	Fog	Sensitivity (fresh)	Sensitivity (aged for 1 week after exposure)	Remarks
1	Comp. 1	EmA-1	0.30	100	60	Comp.
2	Comp. 2	EmA-1	0.31	100	62	Comp.
3	Comp. 3	EmA-1	0.32	99	65	Comp.
4	Comp. 4	EmA-1	0.32	100	60	Comp.
5	Comp. 5	EmA-1	0.31	100	58	Comp.
6	1	EmA-1	0.24	104	100	Inv.
7	2	EmA-1	0.21	105	100	Inv.
8	3	EmA-1	0.23	104	99	Inv.
9	4	EmA-1	0.20	105	100	Inv.
10	5	EmA-1	0.23	104	100	Inv.
11	6	EmA-1	0.21	104	99	Inv.
12	7	EmA-1	0.20	105	100	Inv.
13	8	EmA-1	0.24	104	100	Inv.
14	9	EmA-1	0.20	105	100	Inv.
15	10	EmA-1	0.23	104	99	Inv.
16	11	EmA-1	0.21	105	100	Inv.
17	12	EmA-1	0.24	105	100	Inv.
18	13	EmA-1	0.21	104	100	Inv.
19	14	EmA-1	0.23	104	100	Inv.
20	15	EmA-1	0.24	104	99	Inv.
21	16	EmA-1	0.21	105	100	Inv.
22	17	EmA-1	0.20	104	100	Inv.
23	18	EmA-1	0.21	104	100	Inv.
24	19	EmA-1	0.24	105	99	Inv.
25	20	EmA-1	0.21	104	100	Inv.
26	21	EmA-1	0.24	105	99	Inv.
27	22	EmA-1	0.25	104	100	Inv.
28	23	EmA-1	0.24	105	100	Inv.
29	24	EmA-1	0.20	104	99	Inv.
30	25	EmA-1	0.21	104	100	Inv.
31	26	EmA-1	0.21	104	100	Inv.
32	27	EmA-1	0.21	105	99	Inv.
33	28	EmA-1	0.23	105	100	Inv.

Table 4 (continued)

Sample No.	Compound No.	Emulsion	Fog	Sensitivity (fresh)	Sensitivity (aged for 1 week after exposure)	Remarks
34	29	EmA-1	0.21	104	100	Inv.
35	30	EmA-1	0.21	104	100	Inv.
36	31	EmA-1	0.20	104	100	Inv.
37	32	EmA-1	0.21	105	99	Inv.
38	33	EmA-1	0.21	104	100	Inv.
39	34	EmA-1	0.21	105	100	Inv.
40	35	EmA-1	0.21	104	100	Inv.
41	36	EmA-1	0.21	104	100	Inv.
42	37	EmA-1	0.20	105	100	Inv.
43	38	EmA-1	0.21	105	100	Inv.
44	39	EmA-1	0.20	105	101	Inv.
45	40	EmA-1	0.21	104	100	Inv.
46	41	EmA-1	0.21	104	99	Inv.
47	42	EmA-1	0.21	105	100	Inv.
48	43	EmA-1	0.20	103	100	Inv.
49	44	EmA-1	0.21	105	99	Inv.
50	45	EmA-1	0.21	104	100	Inv.
51	46	EmA-1	0.20	104	99	Inv.
52	47	EmA-1	0.21	105	100	Inv.
53	48	EmA-1	0.21	104	100	Inv.

Herein, sensitivity is defined by reciprocal of the exposure at which fog density +0.1 is given. Sensitivity of the sample is represented as relative sensitivity when sensitivity of fresh Sample No.1 is assumed to be 100.

It is understood from Table of 4 that the sensitivity of the samples of the present invention have achieved superior results in latent image-fading property comparing to the comparative samples.

Example 2

The following emulsions Em-1 to Em-8 was prepared and a multi-layered light-sensitive material 101 was made.

Em-1: A mono-dispersion type silver halide emulsion containing silver halide grains of which average grain size is 0.8 μm and average silver iodide content is 8.0 mol% and which contain relatively low silver iodide content in the surface portion of the grain.

Em-2: A mono-dispersion type silver halide emulsion containing silver halide grains of which average grain size is 0.38 μm and average silver iodide content is 8.0 mol % and which contain relatively low silver iodide content in the surface portion.

Em-3: A mono-dispersion type silver halide emulsion containing silver halide grains of which average grain size is 0.65 μm and average silver iodide content is 8.0 mol% and which contain relatively low silver iodide content in the surface portion.

Em-4: A mono-dispersion type silver halide emulsion containing silver halide grains of which average grain size is 0.85 μm and average silver iodide content is 8.0 mol% and which contain relatively low silver iodide content in the surface portion.

Em-5: A mono-dispersion type silver halide emulsion containing silver halide grains of which average grain size is 1.20 μm and average silver iodide content is 6.0 mol% and which contain relatively low silver iodide content in the surface portion.
Em-6: A mono-dispersion type silver halide emulsion containing silver halide grains of which average grain size is 0.70 μm and average silver iodide content is 8.0 mol% and which contain relatively low silver iodide content in the surface portion.
Em-7: A mono-dispersion type silver halide emulsion containing silver halide grains of which average grain size is 1.40 μm and average silver iodide content is 8.0 mol% and which contain relatively low silver iodide content in the surface portion.
Em-8: A mono-dispersion type silver halide emulsion containing silver halide grains of which average grain size is 0.08 μm and average silver iodide content is 4.0 mol% and which contain relatively low silver iodide content in the surface portion.

(EmB-1)

The emulsion EmB-1 was prepared in the same manner as emulsion Em-2 disclosed in Japanese Patent O.P.I. Publication No. 3-241336(1991), as follows.

Preparation of silver iodide fine grains

Into a reaction vessel, an aqueous solution containing 5% by weight of ossein gelatin was added. While stirring the solution at 40°C, a 3.5-N aqueous silver nitrate solution and a 3.5-N aqueous potassium iodide solution were added for 30 minutes at a fixed rate.

PAg was kept at 13.5 during the addition by a conventional pAg-controlling method. The formed silver iodide was a mixture of β-AgI and γ-AgI grains having the average size of 0.06 μm. This emulsion is called a silver iodide fine grain emulsion.

Preparation of silver halide seed emulsion containing spherical shaped twin crystal grains

A mono-dispersion type silver halide seed emulsion containing spherical shaped twin crystals was prepared in the method as shown below:

<Solution A3>	
Ossein gelatin	150 g
Potassium bromide	53.1 g
Iodination potassium	24 g
Add water to make the total volume 7.2 liters	

<Solution B3>	
Silver nitrate	1.8 kg
Add Water to make the total volume 6 liters	

<Solution C3>

Potassium bromide 1327 g

1-phenyl-5-mercapto tetrazole (dissolved in methanol)

0.3 g

Add water to make the total volume 3 liters

<Solution D3>	
Aqueous Ammonia solution (28%)	705 ml

While stirring A3 solution, solution B3 and the solution C3 were added to solution A3 by double jet mixing method for 30 seconds and silver halide nucleii were formed. pBr over this period of time was 1.09 - 1.15.

1 minute 30 seconds later, solution C3 was added taking 20 seconds and ripening was carried out for five minutes. The concentration of potassium bromide during the ripening was 0.071 mols/liter and that of ammonia was 0.63 mols/liter.

Then PH of the emulsion was was adjusted to 6.0 and the emulsion was desalted and washed. After observation using an electron microscope, this seed emulsion was found to be a mono-dispersion type emulsion containing grains having average grain size of 0.36 μm and the distribution width of 18%. This emulsion is hereinafter refferred to a seed emulsion.

Next, an emulsion of the present invention having an average grain size of 1.25 μm was prepared by using three kinds of aqueous solution shown as follows, the silver iodide fine grain emulsion and the seed emulsion.

Solution A2:

Gelatin 231.9 g

10% methanol solution of

$HO(CH_2CH_2O)_m[CH(CH_3)CH_2O]_{17}(CH_2CH_2O)_nH$

(average molecular weight: 1300) 30.0 ml

28% aqueous ammonia solution 1056 ml

Add water to make the total volume 11827 ml

Solution B2:	
Silver nitrate	1587 g
28% aquous ammonia solution	1295 ml
Add water to make the total volume 2669 ml	

Solution C2:	
Potassium bromide	1572 g
Add water to make the total volume 3774 ml	

Emulsion D2 containing fine grains of silver iodide:	
Silver iodide fine grain emulsion	1499.3 g
4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene	5.2 g
10% aqueous solution of potassium hydroxide	14.75 ml
Add water to make the total volume 1373 ml	

The seed emulsion of 0.407 equivalent mols is added to aqueous solution A2 as above-mentioned, violently stirred at 60°C temperature and pH and pAg have been adjusted by using acetic acid and potassium bromide aqueous solution.

Thereafter, while controlling pH and pAg as shown in Table 5, solutions B_2 and C_2, and solution D_2 were each added, by the triple jet method, at flowing rates as shown in Tables 6 to 8.

After addition, the mixed solution was flocculated to desalt by adding phenylcarbamyl gelatin aqueous solution to desalt and adjusting pH of the solution. Next, pH and pAg were each adjusted to 5.80 and 8.06 at 40°C.

Thus, there was obtained monodispersed silver bromoiodide emulsion having average grain size of 1.25 μm, an average silver iodide content of 8.0 mol% and the grain size distribution width of 13.2%.

This emulsion hereinafter is referred to as EmB-1.

From the emulsion formula, the grain structure of EmB-1 and the volume ratio of each phase are shown in Table 9.

Table 5 is a grain growth condition of EmB-1.

Table 5

Ag (%)	0		29		29		56		100
pH	7.0	→*	7.0	↓	6.0	→	6.0	→	6.0
pAg	7.8	→	7.8	↓	9.7	↘	10.1	→	10.1

*: Arrows are used to designate a variation of a pH or pAg value;
(→): maintaining
(↘): continuously-lowering
(↓): rapidly-lowering

Table 6 is an addition pattern of B2, and Table 7 is an addition pattern of C2, and Table 8 is an addition pattern of D2.

Table 6

Time of addition (min.)	Addition speed (ml/min.)
0	12.2
25.6	13.0
42.6	12.9
43.9	8.4
67.5	11.0
97.3	14.8
97.7	20.6
105.0	22.3
105.4	25.4
112.3	32.1
112.6	35.1
129.4	90.3
145.7	194.2
145.7	200.5
147.4	203.9

Table 7

Time of addition (min.)	Addition speed (ml/min.)
0	10.9
25.6	11.7
42.6	11.6
43.9	7.6
97.5	13.3
97.7	18.6
105.0	20.0
105.0	36.5
112.0	56.2
112.3	60.6
121.2	106.0
121.4	91.4
132.4	263.3
132.7	141.8
147.4	230.0

Table 8

Time of addition (ml/min.)	Addition speed (ml/min.)
0	0
43.9	0
43.9	73.6
51.7	80.6
52.5	28.5
84.3	40.4
84.9	11.6
97.7	13.0
105.0	14.1
105.4	16.3
112.3	20.6
112.6	6.2
130.4	17.5
132.7	22.1
145.7	34.4

Table 9

	1st phase (seed)	2nd phase	3rd phase			4th phase	5th phase	6th phase
Formula iodide content (mol%)	2	0	35			10	3	0
D_2/B_2 (%)*	0	0	100	35	10	10	3	0
Volume ratio (%)	3.8	9.2	15.8			6.7	58.7	5.8
			1.8	9.2	4.8			

* Molar ratio of addition rate of solution D_2 to solution B_2.

Emulsion EmB-1 has the following characteristics.	
Average grain size	1.25 μm
Monodispersibility (width of distribution)	14.0%
Average silver iodide content	8.0%
Silver iodide content deviation in the outer part of the grain	0.0 mol%
Silver iodide content relative standard deviation	9.0%
Surface silver iodide content	0.0 mol%
Average aspect ratio	3.3

After adjusting PAg, pH and temperature of the emulsion EmB-1 at 8.5, 5.8 and 55°C, respectively, sensitizing dyes S-5, S-6, S-7 and S-8 were added thereto and the the emulsion was allowed to stand for 30 minutes so that dyes were adsorbed on the silver halide grains. Then, 1.0×10^{-6} mol/mol AgX of sodium thiosulfate was added. 10 minutes later, a solution mixture containing 2.2×10^{-7} mol/mol AgX of chloroauric acid and thiocyanic acid ammonium salt was added to the emulsion, and it was further ripened for 60 minutes. Thereafter, inventive or comparative compounds as shown in Table are respectively added thereto.

Basic structure of the multi-layered photographic material(Sample101) is shown below:

In the following descriptions, the amount of the compound incorporated into the sample is given in terms of gram per m^2 unless otherwise noted. Moreover, the amount of silver halide and colloidal silver was expressed in terms of equivalent amount of silver and the added amount of the sensitizing dye is given in terms of mols per mol of AgX contained in the same layer.

Sample-101

First layer: anti-halation layer	
Black colloidal silver	0.18 g
Gelatin	1.57 g
Ultraviolet ray absorbent (UV-1)	0.17 g
High-boiling solvent (Oil-1)	0.14 g

Second layer: first intermediate layer	
Gelatin	1.00 g

Third layer: first red-sensitive emulsion layer

Silver bromoiodide emulsion (Em-2)	0.66 g
Silver bromoiodide emulsion (Em-3)	0.29 g
Gelatin	1.29 g

Sensitizing dye (S-1)	3.21×10^{-4} mols
Sensitizing dye (S-2)	2.71×10^{-4} mols
Sensitizing dye (S-3)	3.45×10^{-5} mols
Coupler (C-1)	0.96 g
Colored coupler (CC-1)	0.07 g
High-boiling solvent (Oil-1)	0.52 g

Fourth layer: second intermediate layer	
Gelatin	0.75 g

Fifth layer: first green-sensitive emulsion layer (Em-2)	
Silver bromoiodide emulsion	0.66 g
Silver bromoiodide emulsion (Em-3)	0.29 g
Gelatin	1.08 g
Sensitizing dye (S-7)	2.67×10^{-4} mols
Sensitizing dye (S-6)	2.23×10^{-4} mols
Sensitizing dye (S-5)	4.48×10^{-5} mols
Sensitizing dye (S-8)	7.04×10^{-6} mols
Coupler (M-4)	0.13 g
Coupler (M-2)	0.29 g
Colored coupler (CM-2)	0.082 g
High-boiling solvent (Oil-3)	0.51 g

Sixth layer: second green-sensitive emulsion layer

Silver bromoiodide emulsion (Em-4)	0.76 g
Gelatin	0.80 g
Sensitizing dye (S-7)	1.45×10^{-4} mols
Sensitizing dye (S-6)	1.21×10^{-4} mols

Sensitizing dye (S-5)	2.43×10^{-5} mols
Sensitizing dye (S-8)	3.82×10^{-6} mols
Coupler (M-4)	0.036 g
Coupler (M-2)	0.077 g
Colored coupler (CM-1)	0.035 g
High-boiling solvent (Oil-3):	0.15 g

Seventh layer: third intermediate layer	
Gelatin	0.55 g
SC-1	0.032 g

Eighth layer: first blue-sensitive emulsion layer	
Silver bromoiodide emulsion (Em-3)	0.76 g
Gelatin	1.16 g
Sensitizing dye (S-11)	2.88×10^{-4} mols
Sensitizing dye (S-9)	7.19×10^{-5} mols
Coupler (Y-1)	0.40 g
High-boiling solvent (Oil-3)	0.16 g

Ninth layer: fourth intermediate layer	
Gelatin	0.75 g
SC-1	0.044 g

10th layer: second red-sensitive emulsion layer

Silver bromoiodide emulsion (Em-1)	0.95 g
Gelatin	0.93 g
Sensitizing dye (S-1)	1.74×10^{-4} mols
Sensitizing dye (S-2)	1.47×10^{-5} mols
Sensitizing dye (S-3)	1.87×10^{-5} mols

Coupler (C-1) 0.33 g

High-boiling solvent (Oil-1) 0.33 g

11th layer: third red-sensitive emulsion layer	
Silver bromoiodide emulsion (Em-5)	2.30 g
Gelatin	1.49 g
Sensitizing dye (S-1)	1.16×10^{-4} mols
Sensitizing dye (S-2)	9.80×10^{-5} mols
Sensitizing dye (S-3)	1.25×10^{-5} mols
Coupler (C-2)	0.19 g
SC-1	0.027 g
High-boiling solvent (Oil-1)	0.43 g

12th layer: fifth intermediate layer	
Gelatin	0.75 g
SC-1	0.044 g

13th layer: third green-sensitive emulsion layer	
Silver bromoiodide emulsion (EmB-1)	1.82 g
Gelatin	0.62 g
Sensitizing dye (S-7)	9.62×10^{-5} mols
Sensitizing dye (S-6)	8.00×10^{-5} mols
Sensitizing dye (S-5)	1.61×10^{-5} mols
Sensitizing dye (S-8)	2.53×10^{-6} mols
Coupler (M-3)	0.06 g
Coupler (M-2)	0.13 g
Colored coupler (CM-2)	0.01 g
High-boiling solvent (Oil-1)	0.35 g

14th layer: sixth intermediate layer

Gelatin 0.75 g

SC-1 0.044 g

15th layer: second blue-sensitive emulsion layer	
Silver bromoiodide emulsion (Em-6)	1.06 g
Gelatin	0.925 g
Sensitizing dye (S-11)	2.17×10^{-4} mols
Sensitizing dye (S-9)	1.12×10^{-5} mols
Coupler (Y-1)	0.31 g
High-boiling solvent (Oil-3)	0.13 g

16th layer: third blue-sensitive emulsion layer	
Silver bromoiodide emulsion (Em-7)	1.84 g
Gelatin	1.10 g
Sensitizing dye (S-11)	1.44×10^{-4} mols
Sensitizing dye (S-9)	5.65×10^{-5} mols
Coupler (Y-1)	0.52 g
High-boiling solvent (Oil-3)	0.21 g

17th layer: first protective layer	
Silver bromoiodide emulsion (Em-8)	0.10 g
Gelatin	1.52 g
Ultraviolet ray absorbent (UV-1)	0.006 g
Ultraviolet ray absorbent (UV-2)	0.099 g
High-boiling solvent (Oil-1)	0.0065 g
High-boiling solvent (Oil-4)	0.0065 g

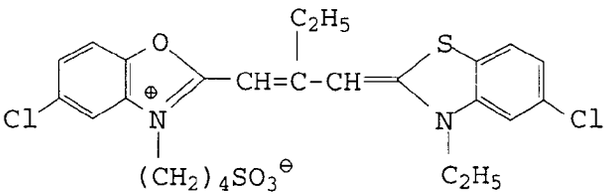
18th layer: second protective layer

Gelatin	0.55 g
Alkali soluble matting agent (average grain size 2 μm silica)	0.12 g
Poly methyl methacrylate (average grain size 3 μm)	0.02 g
Lubricant (WAX-1)	0.04 g

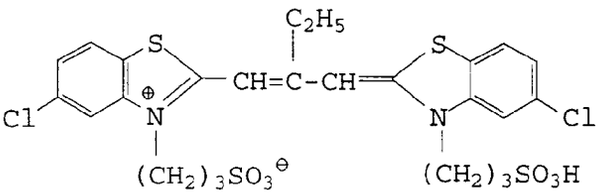
Besides the above-mentioned composition, coating aid (Su-1) dispersion aid (Su-2, Su-3), gelatin hard-

ener (H-I, H-2), stabilizing agent (Stab-1), anti-foggant (AF-1, AF-2), and antiseptic (DI-1) were added to each layer.

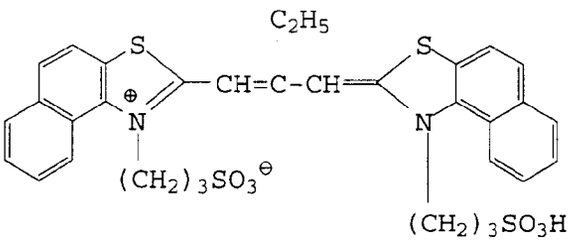
S-1



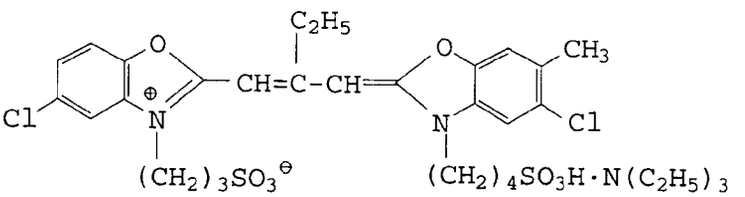
S-2



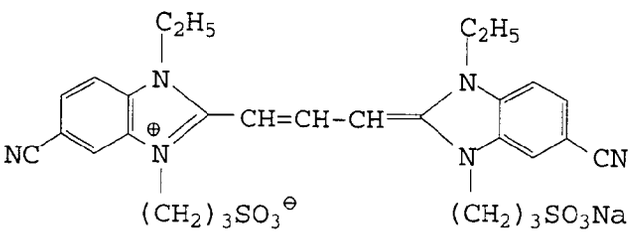
S-3



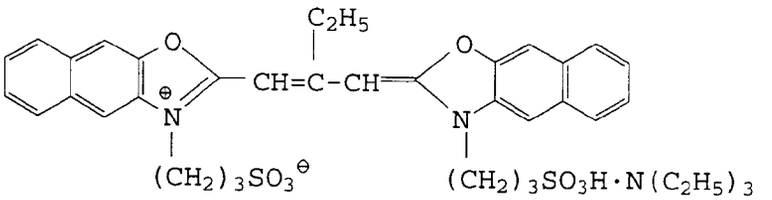
S-4



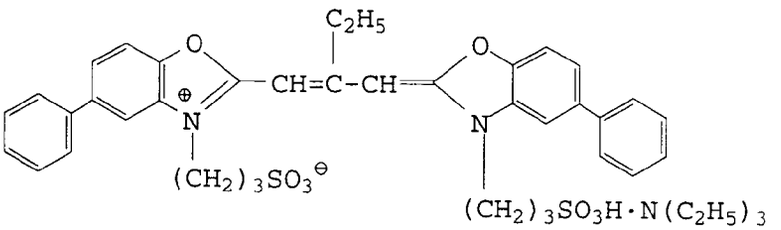
S-5



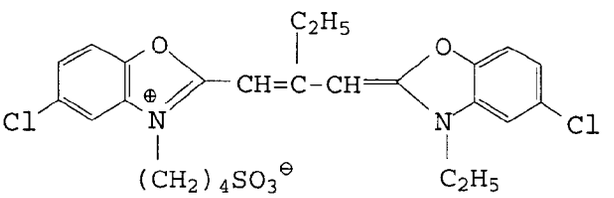
S-6



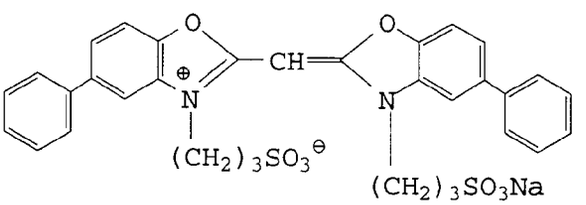
S-7



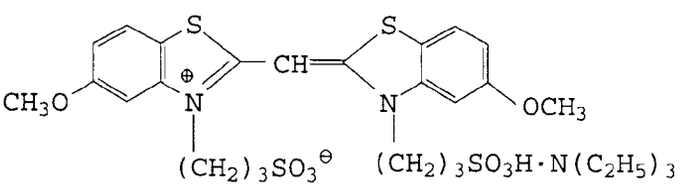
S-8



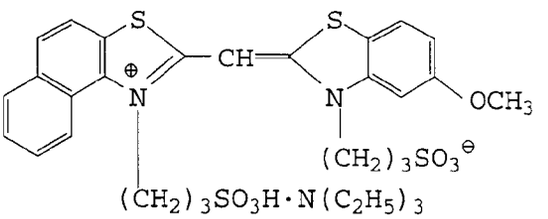
S-9



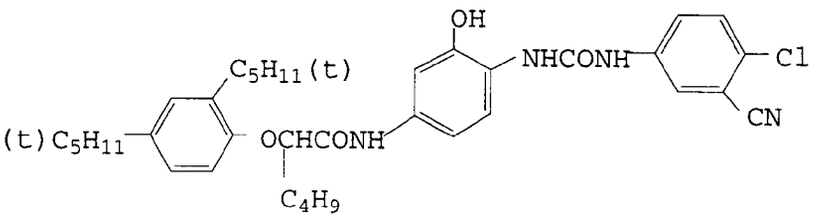
S-10



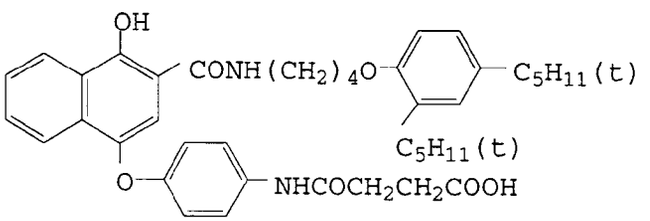
S-11



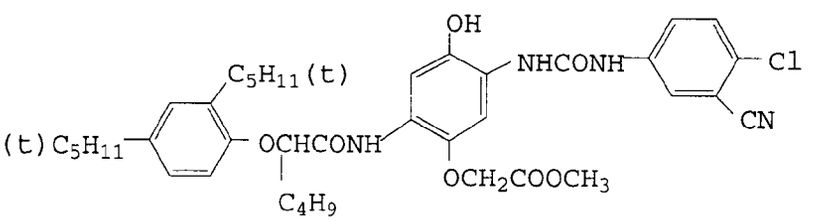
C-1



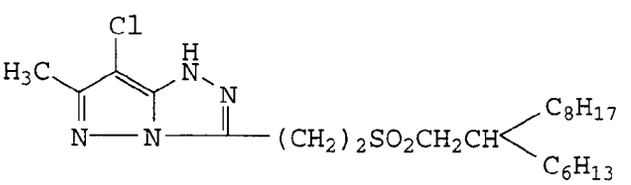
C-2



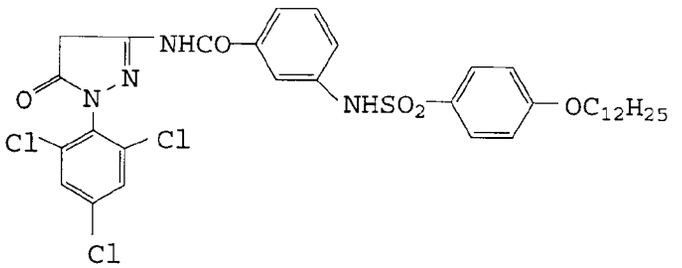
C-3



M-1



M-2



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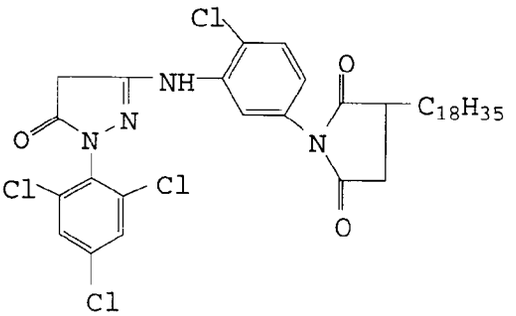

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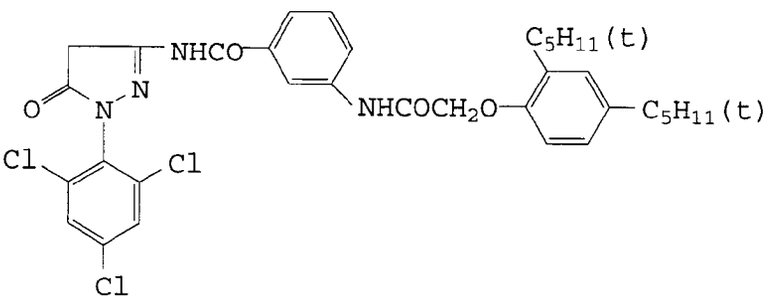
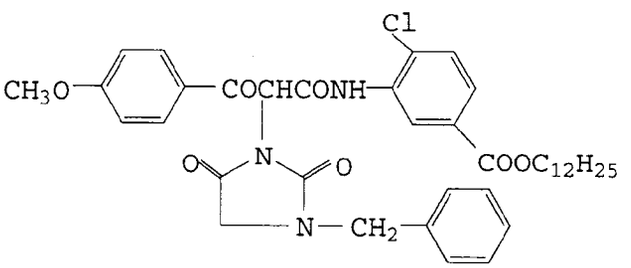
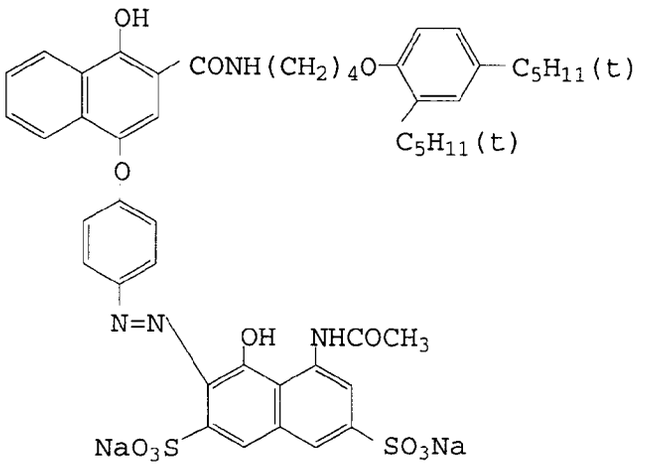


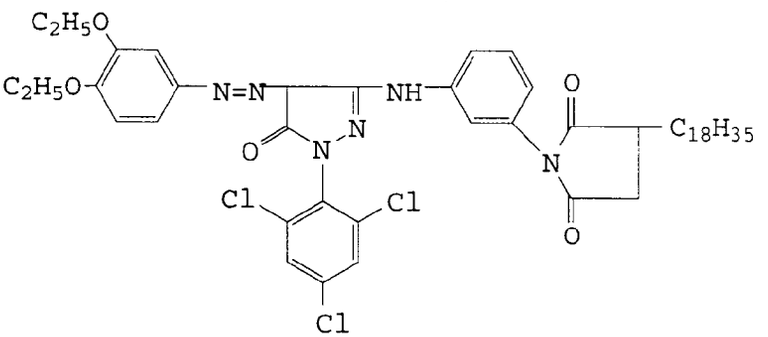
Y-1



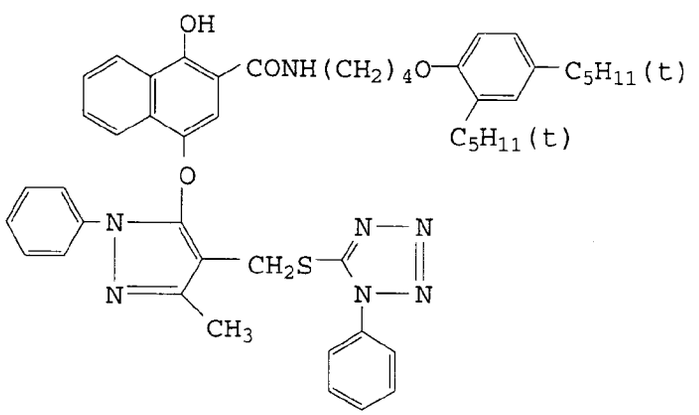
CC-1



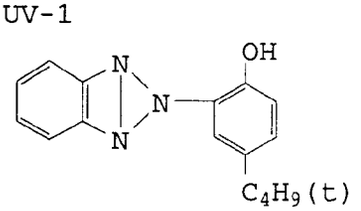
CM-1



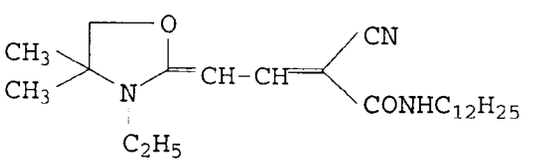
D-1



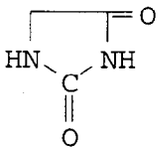
UV-1



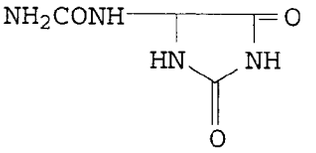
UV-2



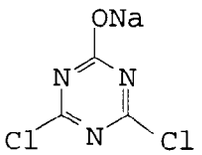
HS-1



HS-2



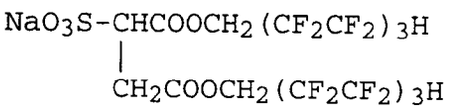
H-1



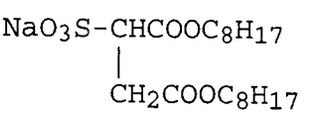
H-2

$(CH_2=CHSO_2CH_2)_2O$

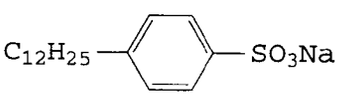
Su-1



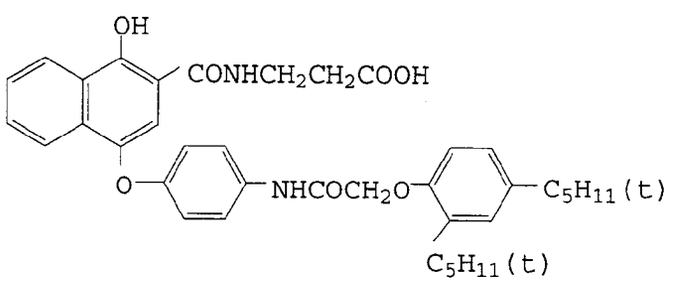
Su-2



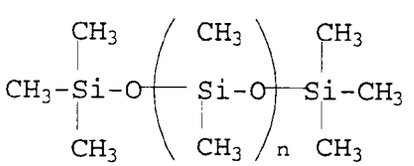
Su-3



Sc-1

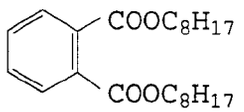


WAX-1

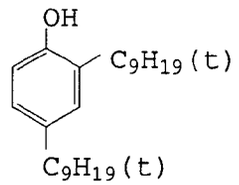


$\overline{MW}$ = 30,000

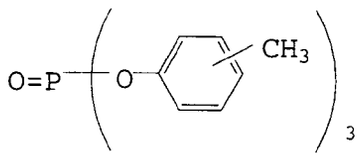
Oil-1



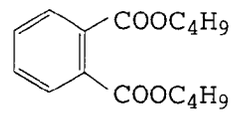
Oil-2



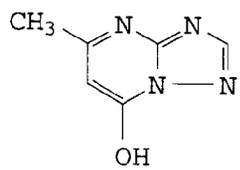
Oil-3



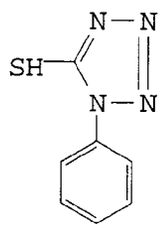
Oil-4



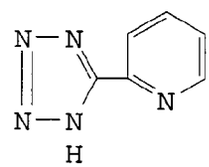
Stab-1



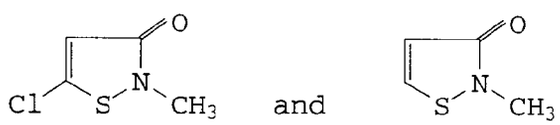
AF-1



AF-2



DI-1



The samples were exposed to yellow light through an optical wedge, and thereafter subjected to the following photographic processing.

Processing Step (38°C)	Time
Color Development (Standard)	2'45"
Bleaching	6'30"

Washing	3'15"
Fixing	6'30"
Washing	3'15"
Stabilization	1'30"
Dryingness	

Compositions of the processing solutions used in each processing steps are the same as those used in Example 1.

Relative sensitivity of the respective samples were measured by using green light. Resaults thereof are given in Table 9.

In the table, sensitivity is defined in the same manner as in Eexample 1 and is represented as relative sensitivity by which sensitivity of Sample 101 is to be 100.

Table 9

Sample No.	Compound No.	Emulsion	Fog	Sensitivity (fresh)	Sensitivity (aged for 1 week after exposure)	Remarks
1	Comp. 1	EmB-1	0.50	100	50	Comp.
2	Comp. 2	EmB-1	0.51	101	45	Comp.
3	Comp. 3	EmB-1	0.50	99	52	Comp.
4	Comp. 4	EmB-1	0.49	100	48	Comp.
5	Comp. 5	EmB-1	0.50	100	51	Comp.
6	1	EmB-1	0.39	120	110	Inv.
7	2	EmB-1	0.31	125	116	Inv.
8	3	EmB-1	0.38	119	109	Inv.
9	4	EmB-1	0.32	126	117	Inv.
10	5	EmB-1	0.37	120	110	Inv.
11	6	EmB-1	0.32	127	118	Inv.
12	7	EmB-1	0.31	128	117	Inv.
13	8	EmB-1	0.38	120	110	Inv.
14	9	EmB-1	0.32	129	118	Inv.
15	10	EmB-1	0.38	118	111	Inv.
16	11	EmB-1	0.31	127	118	Inv.
17	12	EmB-1	0.36	119	110	Inv.
18	13	EmB-1	0.32	127	117	Inv.
19	14	EmB-1	0.37	120	109	Inv.
20	15	EmB-1	0.38	120	110	Inv.
21	16	EmB-1	0.31	128	119	Inv.
22	17	EmB-1	0.32	126	118	Inv.
23	18	EmB-1	0.32	128	117	Inv.
24	19	EmB-1	0.37	127	109	Inv.
25	20	EmB-1	0.32	128	117	Inv.
26	21	EmB-1	0.38	119	109	Inv.
27	22	EmB-1	0.37	118	110	Inv.
28	23	EmB-1	0.38	119	110	Inv.
29	24	EmB-1	0.32	127	118	Inv.
30	25	EmB-1	0.31	127	117	Inv.
31	26	EmB-1	0.31	128	118	Inv.
32	27	EmB-1	0.32	128	118	Inv.
33	28	EmB-1	0.38	118	109	Inv.

Table 9 (continued)

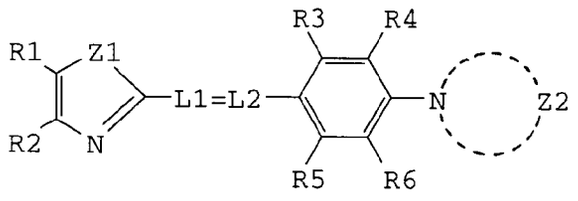
Sample No.	Compound No.	Emulsion	Fog	Sensitivity (fresh)	Sensitivity (aged for 1 week after exposure)	Remarks
34	29	EmB-1	0.32	127	118	Inv.
35	30	EmB-1	0.31	128	118	Inv.
36	31	EmB-1	0.31	128	118	Inv.
37	32	EmB-1	0.32	126	118	Inv.
38	33	EmB-1	0.31	127	117	Inv.
39	34	EmB-1	0.38	119	108	Inv.
40	35	EmB-1	0.32	128	119	Inv.
41	36	EmB-1	0.32	127	118	Inv.
42	37	EmB-1	0.31	128	118	Inv.
43	38	EmB-1	0.32	128	118	Inv.
44	39	EmB-1	0.32	128	117	Inv.
45	40	EmB-1	0.31	129	117	Inv.
46	41	EmB-1	0.32	127	118	Inv.
47	42	EmB-1	0.31	128	118	Inv.
48	43	EmB-1	0.32	127	117	Inv.
49	44	EmB-1	0.31	126	118	Inv.
50	45	EmB-1	0.32	127	117	Inv.
51	46	EmB-1	0.31	128	117	Inv.
52	47	EmB-1	0.32	128	118	Inv.
53	48	EmB-1	0.31	129	118	Inv.

Herein sensitivity is defined by the reciprocal of the exposure by which the density of fog +0.1 is given and was represented with a relative value, wherein a blue sensitivity of each fresh sample was assumed to be 100. As for the compound of the present invention of samples 6 - 53, it is understood that the latent-image regression after exposure is small as compared with samples 1 - 5 in which the comparison compounds were added.

Claims

1. A silver halide photographic light-sensitive material comprising a support having thereon a silver halide emulsion layer, wherein said silver halide emulsion layer contains a compound represented by the following formula [I]

Formula [I]



wherein R1 and R2 each represent a hydrogen atom, an alkyl group, an alkenyl group, an alkynyl group, an aryl group or a heterocyclic group, provided that R1 and R2 may combine with each other to form a ring; R3, R4, R5 and R6 each represent a hydrogen atom or a substituent; Z1 represents a oxygen atom, a selenium atom, a sulfur atom, a tellurium atom, -N(R7)- or -C(R8)(R9)-, where R7, R8 and R9 each represent a hydrogen atom, an alkyl group, an alkenyl group, an alkynyl group, an aryl group or a heterocyclic group; Z2 represents a group of non-metal atoms necessary to form a 5- or 6-membered heterocyclic ring; L1 and L2 each represent a methine group.

2. The photographic material of claim 1, wherein said silver halide emulsion layer comprises silver iodobromide, silver bromide or silver chlorobromide grains.

3. The photographic material of claim 1, wherein said compound is contained in an amount of 2×10^{-8} to 1×10^{-2} moles per mole of silver halide.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number EP 94300819.3

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)
A	DE - A - 2 147 586 (FUJI PHOTO FILM CO. LTD.) * Totality * --	1-3	G 03 C 1/24
A	JP - A - 3-219 233 (KONICA CO.) * Totality * ----	1-3	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

G 03 C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
VIENNA	18-04-1994	BECK

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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