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(71) Applicant: **KONICA CORPORATION**
26-2, Nishi-shinjuku 1-chome Shinjuku-ku
Tokyo(JP)

(72) Inventor: **Ohtani, Hirofumi, Konica Corporation**
1 Sakura-machi
Hino-shi, Tokyo(JP)

(74) Representative: **Türk, Gille, Hrabal, Leifert**
Brucknerstrasse 20
W-4000 Düsseldorf 13 (DE)

(54) Silver halide photographic light-sensitive material.

(57) A silver halide photographic light-sensitive material comprises a support and provided thereon, a silver halide photographic emulsion layer containing silver halide grains, wherein said silver halide grains are subjected to reduction sensitization, and contain a polyvalent metal in an amount of not less than 10^{-6} mol per mol of silver halide.

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FIELD OF THE INVENTION

The present invention relates to a silver halide light-sensitive material (hereinafter also referred to as a light-sensitive material), particularly to a light-sensitive material using an emulsion comprising silver halide grains doped with a polyvalent metal and subjected to reduction sensitization.

BACKGROUND OF THE INVENTION

There is an eager demand for higher sensitivities and lower fogging in present light-sensitive materials. Further, improvement in preservability is also increasingly demanded to maintain these photographic properties over a much longer period.

There have so far been studied in the art various sensitizing techniques such as use of an internally high iodide containing core/shell emulsion for preventing recombination of electrons and positive holes, selective growth of chemically sensitized specks for raising latent image forming efficiency, and use of supersensitizers for raising efficiency of electron transfer from sensitizing dyes to silver halide crystal grains. But, a more systematic and overall combination of plural techniques is required to meet the growing demand for higher sensitivities.

The most typical technique for higher sensitivities is the use of an internally high iodide containing core/shell silver halide emulsion, in which the core is shelled with silver iodobromide having a silver iodide content lower than that in the core, or with silver bromide. But this emulsion type involves a contradiction between the prevention of electron-positive hole recombination, which is attributable to the presence of high iodide containing cores, and the deterioration in developability, which is becomes worse by the increase in total iodide content that depends primarily upon the iodide content of such cores; therefore, solution of this contradiction has been demanded.

Among the many techniques disclosed so far to attain the intended high sensitivity, reduction sensitization is the most typical.

For example, B.H. Carroll used tin compounds in U.S. Pat. No.2,487,850, S.C. Rowe used polyamine compounds in U.S. Pat. No.2,512,925, P.A. Faelens employed dioxythiourea in British Pat. No.789,823, and S.S. Collier tried various approaches to reduction sensitization by use of dimethylamine borane, stannous chloride and hydrazine as materials as well as high pH ripening and low pAg ripening as sensitizing conditions, as seen in Photographic Science and Engineering, Vol.23, p.113 (1979).

Further, use of ascorbic acid as a reducing agent is disclosed in Japanese Pat. O.P.I. Pub. Nos.136852/1990 and 196232/1990.

These reduction sensitization methods, though capable of performing sensitization, have a serious problem that their effects are lowered with aging, and solution to this has been desired. In addition, each of these methods involves a large rise in fog and is not satisfactorily sufficient judging from the recent requirements of lower fogging and higher sensitivity.

SUMMARY OF THE INVENTION

The first object of the present invention is to provide a silver halide photographic light-sensitive material containing a silver halide emulsion high in sensitivity and less in fog. The second object of the present invention is to provide a silver halide photographic light-sensitive material containing a silver halide emulsion free from change in fog and sensitivity caused by aging.

The above objects of the invention are attained by a silver halide photographic light-sensitive material having, on a support, at least one silver halide emulsion layer, wherein the silver halide emulsion is subjected to reduction sensitization, and silver halide grains in the emulsion contain a polyvalent metal in an amount not less than 10^{-6} mol per mol of silver halide.

DETAILED DESCRIPTION OF THE INVENTION

The constituents of the invention are hereunder described in detail.

The reduction sensization of the invention may be carried out in the course of silver halide grain formation, after the formation of grains, or after chemical ripening. However, it is preferable to carry out the reduction sensitization during grain formation in view of higher sensitivities.

Preferred reducing agents are thiourea dioxide and ascorbic acid and derivatives thereof. Other preferred reducing agents include polyamines such as hydrazine and diethylenetriamine; dimethylamine boranes; and sulfites.

Examples of the ascorbic acid derivative include L-ascorbic acid, sodium L-ascorbate, potassium L-ascorbate, DL-ascorbic acid, sodium D-ascorbate, L-ascorbic acid-6-acetate and L-ascorbic acid-6-palmitate.

Preferably, the addition amount of the reducing agent is varied according to types of reducing agents; sizes, compositions and crystal habits of silver halide grains; and environmental conditions such as temperature, pH and pAg of a reaction system. However, in the case of thiourea dioxide, favorable results can be added in an amount of about 0.01 to 2 mg per mol of silver halide. In the case of ascorbic acid, the addition amount is preferably within the range of 50 mg to 2 g per mol of silver halide.

Preferred conditions for the reduction sensitization are a temperature range of 40 to 70 °C, a time range of 19 to 200 minutes, a pH range of 5 to 11, and a pAg range of 1 to 10 (here, the pAg value is given by (logarithm of Ag^+ ion concentration) × -1).

Silver nitrate is preferably used as a water soluble silver salt. By the addition of a water soluble silver salt, the so-called silver ripening, one of the reduction sensitizing techniques, is carried out. The pAg during silver ripening is 1 to 6, preferably 2 to 4. Other conditions such as temperature, pH and time are preferably the same as those in the above reduction sensitization.

As stabilizers for a silver halide emulsion containing silver halide grains subjeted to the reduction sensitization of the invention, conventional stabilizers described later can be used. Favorable results can often be produced by simultaneous use of the antioxidants disclosed in Japanese Pat. O.P.I. Pub. No.82831/1982 and/or the thiosulfonic acids disclosed in V.S. Gahler's article, Zeitshrift für Wissenschaftliche Photographie Bd.63, 133 (1969) and Japanese Pat. O.P.I. Pub. No.1019/1979. Addition of these compounds may be made in any of the emulsion preparation processes from the growth of crystals to the preparation of coating emulsion before coating.

The objects of the invention cannot be attained only by these reduction sensitizing techniques, and it is necessary that a polyvalent metal be contained in silver halide grains in conjunction as described hereinafter.

The polyvalent metal used in the invention is a metal capable of forming a polyvalention, and usable polyvalent metals are Mg, Ca, Sr, Ba, Al, Sc, Y, La, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Mo, Ru, Rh, Pd, Os, Ir, Pt, Cd, Hg, Re, Tl, In, Sn, Pb and Bi. These metals may be added in the form of salts, such as ammonium salts, acetates, nitrates, sulfates, phosphates and hydroxylates, which can be dissolved at the time of grain formation.

Such salts include, for example, $CdBr_2$, $CdCl_2$, $Cd(NO_3)_2$, $Pb(NO_3)_2$, $Pb(CH_3COO)_2$, $K_3[Fe(CN)_6]$, $(NH_4)_4[Fe(CN)_6]$, K_3IrCl_6, $(NH_4)_3RhCl_6$.

Among them, Fe, Ir, Cd, Pb, In, Os and Re are particularly preferred as polyvalent metals; preferred ligands are CN, CO and O_2.

Typical examples thereof include $[Re(CN)_6]^{-4}$, $[Ru(CN)_6]^{-4}$, $[Os(CN)_6]^{-4}$, $[ReF(CN)_5]^{-4}$, $[RuF(CN)_5]^{-4}$, $[OsF(CN)_5]^{-4}$,$[ReCl(CN)_5]^{-4}$, $[RuCl(CN)_5]^{-4}$, $[OsCl(CN)_5]^{-4}$, $[ReBr(CN)_5]^{-4}$, $[RuBr(CN)_5]^{-4}$, $[Fe(O)_2Cl_4]^{-3}$, $[Fe(O)_2Br_4]^{-3}$, $[Fe(O)_2I_4]^{-3}$, $[Re(O)_2(N_3)_4]^{-3}$, $[Re(O)_2(OCN)_4]^{-3}$, $[Re(O)_2(SCN)_4]^{-3}$, $[Re(O)_2(SeCN)_4]^{-3}$, $[Re(O)_2(TeCN)_4]^{-3}$, $[Re(O)_2(CN)_4]^{-3}$, $[Os(O)_2Cl_4]^{-2}$, $[Os(O)_2Br_4]^{-2}$, $[Os(O)_2I_4]^{-2}$, $[Os(O)_2(N_3)_4]^{-2}$, $[Os(O)_2(OCN)_4]^{-2}$, $[Os(O)_2(SCN)_4]^{-2}$, $[Os(O)_2(SeCN)_4]^{-2}$, $[Ru(CO)Cl_4(N_3)]^{-3}$, $[Ru(CO)Br_4(N_3)]^{-3}$, $[Ru(CO)I_4(N_3)]^{-3}$, $[Fe(CO)(CN)_5]^{-3}$, $[Fe(CO)Cl(CN)_4]^{-3}$, $[Fe(CO)Br(CN)_4]^{-3}$, $[Fe(CO)I(CN)_4]^{-3}$, $[Fe(CO)Cl_4(CN)]^{-3}$, $[Fe(CO)Br_4(CN)]^{-3}$, $[Fe(CO)I_4(CN)]^{-3}$, $[Co(CO)(CN)_5]^{-2}$, $[Co(CO)(SCN)_5]^{-2}$, $[Co(CO)(N_3)_5]^{-2}$, $[Co(CO)(CN)_4Cl]^{-2}$, $[Co(CO)(CN)_4Br]^{-2}$, $[Co(CO)(CN)_4I]^{-2}$, $[V(NO)(CN)_5]^{-3}$, $[Cr(NO)(CN)_5]^{-3}$, $[Mn(NO)(CN)_5]^{-3}$, $[Fe(NO)(CN)_5]^{-2}$, $[Ru(NO)Cl_5]^{-2}$, $[Ru(NO)Br_5]^{-2}$, $[Ru(NO)I_5]^{-2}$, $[Ru(NO)F_5]^{-2}$, $[Ru(NO)Cl_3(H_2O)_2]^{0}$, $[Ru(NO)Cl_3(H_2O)]^{-1}$ and $[Ru(NO)Cl_4(OCN)]^{-2}$.

The addition amount of the polyvalent metal is not less than 10^{-6} mol, preferably 10^{-6} to 10^{-4} per mol of silver halide. An addition amount less than 10^{-6} mol does not bring out the favorable effect of the invention.

The objects of the invention can be attained more effectively as the addition amount increases.

Preferably, the polyvalent metal compound is added in the form of solution of a suitable solvent, such as water, methanol or acetone.

In order to stabilize the solution, an aqueous solution of hydrogen halide (e.g., HCl, HBr) or an alkali halide (e.g., KCl, KBr, NaBr) may be added thereto. If necessary, there may be incorporated an acid or an alkali. The polyvalent metal compound may be added in a reaction vessel before grain formation or in the course of grain formation.

The polyvalent metal compound may also be dissolved in an aqueous solution of a water soluble silver salt (e.g., $AgNO_3$), or in that of an alkali halide (e.g., NaCl, KBr, KI), and then added continuously during the formation of silver halide grains. Further, there may also be prepared a solution of the polyvalent metal compound independently of the water soluble silver salt or alkali halide, to add continuously at a suitable time during the formation of grains. Combination of various addition methods is also carried out.

The amount of polyvalent cations doped in silver halide grains can be quantitatively determined by atomic absorption spectroscopy or inductively coupled plasma (ICP) emission spectroscopy. For cations having a high atomization temperature such as Ir, ICP emission spectral analysis is used, and to analyze Pb, Cd or Fe, atomic absorption spectroscopy can be employed.

A sample for the analysis is usually prepared as follows: Firstly, an emulsion is diluted with water and centrifuged to separate silver halide grains from gelatin. In this procedure, if polyvalent cations are considered to be present in the emulsion as a sparingly soluble salt, a solvent which can dissolve it, such as an acid, is added in conjunction with water to remove them. The silver halide grains so separated from the emulsion are then converted into a sample for the analysis by dissolving them in an ammonium thiosulfate solution.

The wording "silver halide grains contain a polyvalent metal" means a case where the polyvalent metal being present in the inner portion of grains, a case where it being present in the vicinity of the outermost layer of grains, a case where it being present in the outermost layer, and combinations thereof.

The preferable location where the polyvalent metal is doped depends upon preparation methods, compositions and crystal forms of emulsion grains. Thus, though not limititive, doping at the inner portion of grains is preferred to that near the outermost layer.

It has not yet been made clear as to why the effect of the invention is exhibited as super-additivity when reduction sensitization and doping with the polyvalent metal are combined. But it is conceivable that the reason lies in prevention of electron-positive hole recombination attributable to reduction sensitization (which is positive hole trapping) and polyvalent metal doping (which is electron trapping); or prevention of electron-positive hole recombination attributable to reduction sensitization (which is positive hole trapping) and polyvalent metal doping (which is different in state of positive hole trapping caused by reduction sensitization). Anyway, there isn't much doubt that combination of the techniques different in functions brings out the effects with super-additivity.

The term "super-additivity" used here means the phenomenon that the effect of the invention is revealed beyond the sum of the effect of reduction sensitization and the effect of polyvalent metal doping.

Photographic emulsion layers in the light-sensitive material of the invention may use any type of silver halide grains among silver bromide, silve iodobromide, silver iodochlorobromide, silver chlorobromide and silver chloride. Silver bromide or silver chlorobromide is preferable, and silver iodobromide containing not more than 30 mol% silver iodide is more preferable.

The effect of the invention by polyvalent metal doping is equally revealed in core/shell grains of internally high AgI containing type, grains having the same AgI content along their diameters, and AgBr grains. When core/shell grains of internally high AgI containing type or multilayered grains of internally high AgI containing type are used, it is preferable that the polyvalent metal be doped in the core or intermediate layer.

Silver halide grains in the photographic emulsion may be the so-called regular grains having a symmetrical crystal form such as cubic, octahedral or tetradecahedral form; or they may have an irregular crystal form such as a spherical crystal form, have a crystal defect such as twin planes or have the above crystal forms in combination.

These silver halide grains may be small-sized grains not larger than 0.1 micron in diameter or large-sized grains having a projected area diameter up to 10 microns. These may also be monodispersed ones having a narrow grain size distribution or polydispersed ones having a wide grain size distribution.

In making the light-sensitive material of the invention, the emulsion of the invention and other silver halide emulsions independent of the invention used when necessary are preferably subjected to physical ripening, chemical ripening and spectral sensitization appropriate for respective spectrally sensitive layers. Additives usable in such processes are illustrated in Research Disclosure Nos. 17643, 18716, 308119 (hereinafter abbreviated as RD17643, RD18716 and RD308119, respectively).

Locations of the relevant descriptions are as follows:

Item	Page, Section of RD308119		Page of RD17643	Page of RD18716
Chemical sensitizer	996	III-A	23	648
Spectral sensitizer	996	IV-A-A,B C,D,H,I,J	23-24	648-9
Supersensitizer	996	IV-A-E,J	23-24	648-9
Antifoggant	998	VI	24-25	649
Stabilizer	998	VI	24-25	649

Conventional photographic additives usable in the invention are also illustrated in the above Research Disclosures. Locations of the relevant descriptions are as follows:

Item	Page, Section of RD308119		Page of RD17643	Page of RD18716
Anticolor-mixing agent	1002	VII-I	25	650
Dye image stabilizer	1002	VII-J	25	
Whitening agent	998	V	24	
UV absorbent	1003	VIII-C XIII-C	25-26	
Light absorbent	1003	VIII	25-26	
Light scattering agent	1003	VIII		
Filter dye	1003	VIII	25-26	
Binder	1003	IX	26	651
Antistatic agent	1006	XIII	27	650
Hardener	1004	X	26	651
Plasticizer	1006	XII	27	650
Lubricant	1006	XII	27	650
Surfactant & coating aid	1005	XI	26-27	650
Matting agent	1007	XVI		
Developing agent (contained in light-sensitive material)	1011	XX-B		

The light-sensitive material of the invention may use various couplers according to colors to be formed in respective layers. Typical examples thereof are illustrated in the above Research Disclosures as shown below.

Item	Page, Section of RD308119		Section of RD17643
Yellow coupler	1001	VII-D	VII C-G
Magenta coupler	1001	VII-D	VII C-G
Cyan coupler	1001	VII-D	VII C-G
Colored coupler	1002	VII-G	VII G
BAR coupler	1001	VII-F	
DIR coupler	1002	VII-F	VII F
Other useful-residue releasing coupler	1001	VII-F	
Alkali soluble coupler	1001	VII-E	

When these additives are used in the light-sensitive material of the invention, these can be incorporated by the dispersion method described in Section IV of RD308119.

In the invention, there may be used the supports described on page 28 of RD17643, on pages 647-8 of RD 18716 and in Section XVII of RD308119.

In the light-sensitive material of the invention, there may be provided auxiliary layers such as the filter layer and intermediate layer described in Section VII-K of RD308119.

The light-sensitive material of the invention may have various layer configurations such as conventional layer order, inverted layer order and unit layer structure.

The invention can be applied to a variety of color light-sensitive materials represented by color negative films for general purpose or for cinema, color reversal films for slide or for TV, color paper, color positive films and color reversal paper.

The light-sensitive material of the invention can be processed by the usual methods described on pages 28-29 of RD17643, on 615 page of RD18716 and in Section XIX of RD308119.

EXAMPLES

The present invention is described in detail with the following examples, but the embodiment of the invention is not limited to them.

Example 1

First, the method for preparing an emulsion used in this example, EmA-1, is described.

Preparation of Emulsion EmA-1

In the preparation, the following aqueous solutions (a-1) to (a-4) were used.

Aqueous solution (a-1)	
Gelatin	51.93 g
28% Aqueous ammonia	1056 ml
56% Acetic acid	10590 ml
Water was added to	11827 ml

Aqueous solution (a-2)	
Silver nitrate	1587 g
28% Aqueous ammonia	1294 ml
Water was added to	2669 ml

Aqueous solution (a-3)	
Gelatin	34.93 g
Potassium bromide	1454.7 g
Water was added to	3493 ml

Emulsion solution (a-4) containing fine silver iodide grains (average grain size: 0.06 μm)	
Fine silver iodide grain stock solution (containing 45.6 g/mol AgI of gelatin, made up to 1467 ml)	1239 ml
4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene	5.22 g
Water was added to	2294 ml

While vigorously stirring aqueous solution (a-1) at 60 °C, 0.407 mole equivalent of a monodispersed silver iodide emulsion, comprising grains containing 2 mol% silver iodide and having an average size of 0.27 μm, was added as seed emulsion. Then, the pH and pAg were adjusted with acetic acid and an aqueous solution of potassium bromide.

Subsequently, while controlling the pH and pAg as shown in Table 1, aqueous solutions (a-2), (a-3) and (a-4) were added by the double-jet method at flow rates shown in Tables 2 and 3. Table 1 shows the grain growth conditions 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

* The environments of pH and pAg were quickly changed when the Ag content reached 29%.

Table 2 shows the addition rates of aqueous solutions (a-2) and (a-3); Table 3 gives the addition rate of aqueous solution (a-4).

Table 2

Time (min)	Addition 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)	Addition 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

To the resulting solution was added a solution of phenylcarbamyl gelatin, and then the pH was adjusted in order to deposit grains, followed by desalting and washing. The resulting emulsion EmA-1 comprised monodispersed grains having an average particle size of 0.8 μm and an average silver iodide content of 8.0 mol%.

Subsequently, emulsions EmA-2 to EmA-4 of the invention were prepared.

Preparation of Emulsion EmA-2

Emulsion EmA-2 was prepared in exactly the same manner as in EmA-1, except that an aqueous solution containing 1×10^{-5} mol/mol AgX of $K_4[Fe(CN)_6]$ was continuously added from 28.8 to 34.5 minutes after starting addition of the above aqueous solutions (a-2), (a-3) and (a-4), with grains kept growing. This EmA-2 was an emulsion in which only high silver iodide containing cores were doped with iron ions.

Preparation of Emulsion EmA-3

Emulsion EmA-3 was prepared in exactly the same manner as in EmA-1, except that an aqueous solution containing 1×10^{-5} mol/mol AgX of $K_4[Fe(CN)_6]$ was continuously added from 35.1 to 96.3 minutes after starting the addition of the above aqueous solutions, while grains were growing. This EmA-3 was an emulsion in which only intermediate layers were doped with iron ions.

Preparation of Emulsion EmA-4

Emulsion EmA-4 was prepared in exactly the same manner as in EmA-3, except that when the growth of intermediate layers doped with iron ions was complete, unnecessary iron ions were removed by washing and then the outermost shell was formed. This EmA-4 was an emulsion in which doping with iron ions was strictly limited to intermediate layers.

Preparation of Emulsion EmA-5

Emulsion EmA-5 was prepared in exactly the same manner as in EmA-1, except that addition of the above aqueous solutions was discontinued 34.5 minutes after the start of the addition and then silver ripening was carried out for 30 minutes at pAg = 3 and pH = 6 by adding 3.5 N silver nitrate solution. This EmA-5 was an emulsion subjected to reduction sensitization by silver ripening at the interface between the high silver iodide containing core and the intermediate layer.

Preparation of Emulsion EmA-6

Emulsion EmA-6 was prepared in exactly the same manner as in EmA-1, except that 1×10^{-6} mol/mol AgX of thiourea dioxide was added 34.5 minutes after starting addition of the above aqueous solutions. This EmA-6 was an emulsion subjected to reduction sensitization with thiourea dioxide at the interface between the high silver iodide containing core and the intermediate layer.

Preparation of Emulsion EmA-7

Emulsion EmA-7 was prepared in exactly the same manner as in EmA-1, except that 1×10^{-3} mol/mol AgX of ascorbic acid was added 35.5 minutes after starting addition of the above aqueous solutions. This EmA-7 was an emulsion subjected to reduction sensitization with ascorbic acid at the interface between the high silver iodide containing core and the intermediate layer.

Preparation of Emulsion EmA-8

Emulsion EmA-8 was prepared in exactly the same manner as in EmA-7, except that 5×10^{-5} mol/mol AgX of $C_2H_5SO_2SNa$ was added 33.5 minutes after starting addition of the above aqueous solutions. This EmA-8 was an emulsion subjected to addition of $C_2H_5SO_2SNa$ and reduction sensitization with ascorbic acid near the interface between the high silver iodide containing core and the intermediate layer.

Preparation of Emulsion EmA-9

Emulsion EmA-9 was prepared in exactly the same manner as in EmA-1, except that only high silver iodide containing cores were doped with iron ions and reduction sensitization was carried out at the interface between the high silver iodide containing core and the intermediate layer, by referring to the procedures of EmA-2 and EmA-8.

Preparation of Emulsion EmA-10

Emulsion EmA-10 was prepared in exactly the same manner as in EmA-1, except that only intermediate layers were doped with iron ions and reduction sensitization by silver ripening was carried out at the interface between the high silver iodide containing core and the intermediate layer, by referring to the procedures of EmA-3 and EmA-5.

Preparation of Emulsion EmA-11

Emulsion EmA-11 was prepared in exactly the same manner as in EmA-1, except that only intermediate layers were doped with iron ions and reduction sensitization was carried out using thiourea dioxide at the interface between the high silver iodide containing core and the intermediate layer, by referring to the procedures of EmA-3 and EmA-6.

Preparation of Emulsion EmA-12

Emulsion EmA-12 was prepared in exactly the same manner as in EmA-1, except that only intermediate layers were doped with iron ions and reduction sensitization was carried out using ascorbic acid at the interface between the high silver iodide containing core and the intermediate layer, by referring to the procedures of EmA-3 and EmA-7.

Preparation of Emulsion EmA-13

Emulsion EmA-13 was prepared in exactly the same manner as in EmA-1, except that only intermediate layers were doped with iron ions and reduction sensitization was carried out using ascorbic acid and $C_2H_5SO_2SNa$ at the interface between the high silver iodide containing core and the intermediate layer, by referring to the procedures of EmA-3 and EmA-8.

Preparation of Emulsion EmA-14

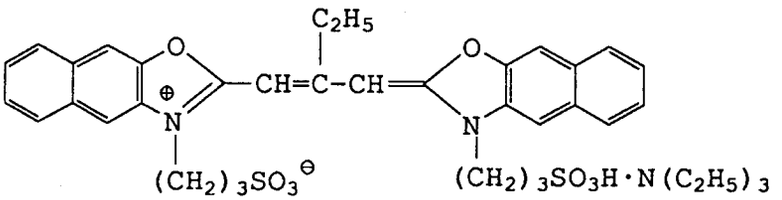
Emulsion EmA-14 was prepared in exactly the same manner as in EmA-1, except that doping with iron ions was perfectly limited to intermediate layers alone and reduction sensitization was carried out using ascorbic acid and $C_2H_5SO_2SNa$ at the interface between the high silver iodide containing core and the intermediate layer, by referring to the procedures of EmA-4 and EmA-8.

Each of the resulting emulsions EmA-1 to EmA-14 was adjusted to pAg 8.0 and ripened for 60 minutes under conditions of 55 °C and pH 5.8 by adding 2.0×10^{-6} mol/mol AgX of sodium thiosulfate. After adding a mixed solution of 4.4×10^{-7} mol/mol AgX of chloroauric acid and ammonium thiocyanate, each emulsion was further ripened for 60 minutes.

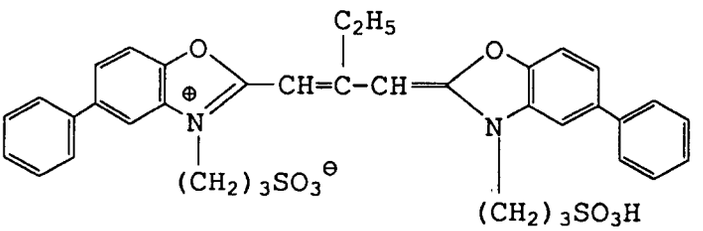
Then, each emulsion was spectrally sensitized by allowing it to adsorb the combination of the following sensitizing dyes SD-A, SD-B and SD-C. Further, magenta couplers M-A, M-B and M-C were added thereto.

After adding a proper amount of sodium 2-hydroxy-4,6-dichlorotriazine evenly, each emulsion was applied to a subbed cellulose triacetate support so as to give a silver coating weight of 2.0 g/m^2, followed by coating to give light-sensitive material samples 1 to 14.

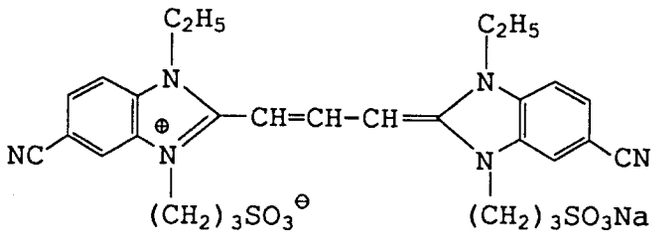
SD-A



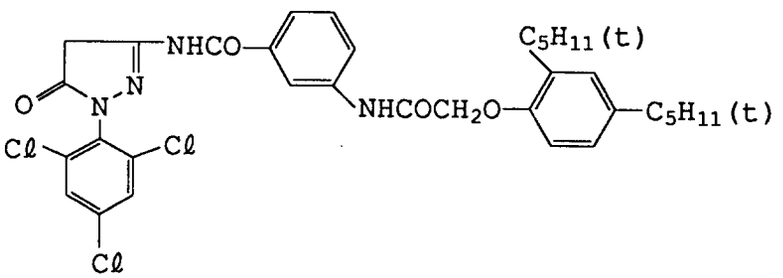
SD-B



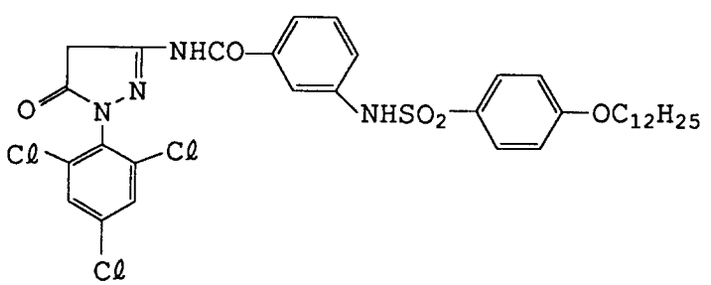
SD-C



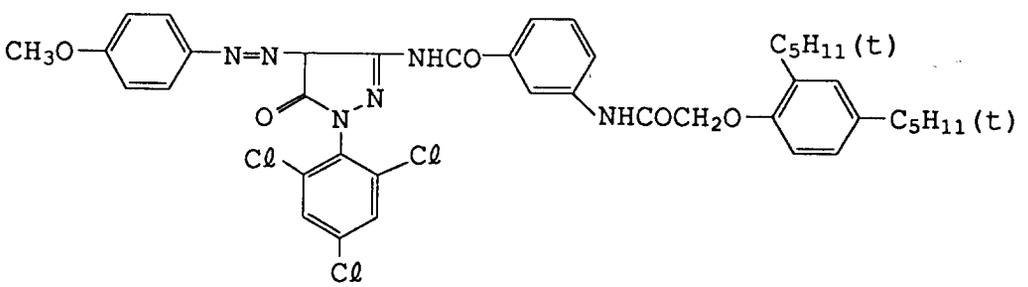
M-A



M-B



M-C



Each sample was wedgewise exposed to green light by the usual method, color-developed in the following color developing processes and then evaluated for photographic properties. The evaluation results are shown in Table 14, where the sensitivity is given by a value relative to the sensitivity of sample 1 (comparison) which is set at 100.

Process (at 38 °C)	Processing Time
Color developing	3 min 15 sec
Bleaching	6 min 30 sec
Washing	3 min 15 sec
Fixing	6 min 30 sec
Washing	3 min 15 sec
Stabilizing	1 min 30 sec
Drying	

Compositions of processing solutions used in the respective processes were as follows:

Color Developer	
4-Amino-3-methyl-N-ethyl-N-β-hydroxyethylaniline sulfate	4.75 g
Anhydrous sodium sulfite	4.25 g
Hydroxylamine 1/2sulfate	2.0 g
Anhydrous potassium carbonate	37.5 g
Sodium bromide	1.3 g
Trisodium nitrilotriacetate (monohydrate)	2.5 g
Potassium hydroxide	1.0 g
	Water was added to 1000 ml, and the pH was adjusted to10.6 with sodium hydroxide.

Bleach	
Ammonium ferric ethylenediaminetetraacetate	100.0 g
Diammonium ethylenediaminetetraacetate	10.0 g
Ammonium bromide	150.0 g
Glacial acetic acid	10.0 g
Water was added to 1000 ml, and the pH was adjusted to 6.0 with aqueous ammonia.	

Fixer	
Ammonium thiosulfate	175.0 g
Anhydrous sodium sulfite	8.6 g
Sodium metasulfite	2.3 g
Water was added to make 1000 ml, and the pH was adjusted to 6.0 with acetic acid.	

Stabilizer	
Formalin (37% aqueous solution)	1.5 ml
Koniducks (made by Konica Corp.)	7.5 ml
Water was added to 1000 ml.	

Table 4

Sample No.	Emulsion	Fogging	Green Sensitivity	Sensitivity after 1-week Standing
1	A-1	0.20	100	80
2	A-2	0.22	120	100
3	A-3	0.18	180	150
4	A-4	0.15	220	180
5	A-5	0.22	170	140
6	A-6	0.25	175	150
7	A-7	0.25	180	150
8	A-8	0.15	200	170
9 (Invention)	A-9	0.22	250	200
10 (Invention)	A-10	0.25	270	270
11 (Invention)	A-11	0.22	280	280
12 (Invention)	A-12	0.20	275	270
13 (Invention)	A-13	0.15	300	290
14 (Invention)	A-14	0.15	310	310

It can be seen from Table 4 that samples 9 to 14 using chemically sensitized emulsions of the invention have original sensitivities higher than those of comparative samples and virtually retain their high sensitivi-

ties even after standing for one week.

Example 2

The following emulsions were prepared and used to prepare a multilayer light-sensitive material, sample 101.

Em-1: surface low silver iodide containing, monodispersed emulsion; average grain size: 0.8 μm; average silver iodide content: 8.0 mol%

Em-2: surface low silver iodide containing, monodispersed emulsion; average grain size: 0.38 μm; average silver iodide content: 8 mol%

Em-3: surface low silver iodide containing, monodispersed emulsion; average grain size: 0.65 μm; average silver iodide content: 8 mol%

Em-4: surface low silver iodide containing, monodispersed emulsion; average grain size: 0.85 μm; average silver iodide content: 8 mol%

Em-5: surface low silver iodide containing, monodispersed emulsion; average grain size: 1.20 μm; average silver iodide content: 6 mol%

Em-6: surface low silver iodide containing, monodispersed emulsion; average grain size: 0.70 μm; average silver iodide content: 8 mol%

Em-7: surface low silver iodide containing, monodispersed emulsion; average grain size: 1.40 μm; average silver iodide content: 8 mol%

Em-8: surface low silver iodide containing, monodispersed emulsion; average grain size: 0.08 μm; average silver iodide content: 4 mol%

Preparation of EmB-1

Emulsion EmB-1 was the same emulsion as Em-2 described in Japanese Pat. O.P.I. Pub. No.241336/1991 and prepared as follows:

[Preparation of Fine Silver Iodide Grains]

While stirring at 40 °C 5-wt% aqueous ossein gelatin solution was placed in a reaction vessel and 1 mol each of 3.5 N aqueous silver nitrate solution and 3.5 N potassium iodide aqueous solution were added thereto at a constant addition rate over a period of 30 minutes.

During the addition, the pAg was kept at 13.5 by a usual controlling means. The resulting silver iodide was a mixture of β-AgI and γ-AgI each having an average grain size of 0.06 μm. This emulsion is hereinafter referred to as the fine silver iodide grain emulsion.

[Preparation of Spherical Twin Seed Emulsion]

A monodispersed, spherical seed emulsion was prepared in the following manner:

Solution A_3	
Ossein gelatin	150 g
Potassium bromide	53.1 g
Potassium iodide	24 g
Water was added to	7200 ml

Solution B_3	
Silver nitrate	1800 g
Water was added to	6000 ml

Solution C_3	
Potassium bromide	1327 g
1-Phenyl-5-mercaptotetrazole (dissolved in methanol)	0.3 g
Water is added to make	3000 ml

Solution D_3	
Aqueous ammonia (28%)	705 ml

Solutions B_3 and C_3 were added by the double jet method in 30 seconds to solution C_3 being vigorously stirred at 49 °C to form nuclei, with the pBr controlled between 1.09 and 1.15.

After 1 minute and 30 seconds, solution D_3 was added thereto in 20 seconds, followed by a 5-minute ripening at a KBr concentration of 0.071 mol/l and an ammonia concentration of 0.63 mol/l.

The pH was then adjusted to 6.0, and desalted and washed. An electron microscopic observation of the resulting emulsion proved that it comprised monodispersed spherical grains having an average size of 0.36 μm and a grain size distribution extent of 18%. This emulsion is hereinafter referred to as the seed emulsion.

Using the following three aqueous solutions and emulsion solution containg the silver iodide fine grain emulsion, and the seed emulsion, there was prepared an emulsion of the invention comprising grains having an average size of 1.25 μm.

Aqueous solution A_2	
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: about 1300)	30.0 ml
28% Aqueous ammonia	1056 ml
Water was added to	11827 ml

Aqueous solution B_2	
Silver nitrate	1587 g
28% Aqueous ammonia	1295 ml
Water was added to	2669 ml

Aqueous solution C_2	
Potassium bromide	1572 g
Water was added to	3774 ml

Emulsion solution D_2 containing the fine silver iodide grain emulsion	
The silver iodide fine grain emulsion	1499.3 g
4-Hydroxy-6-methyl-1,3,3a,7-tetrazaindene	5.2 g
10% Aqueous potassium hydroxide solution	14.75 ml
Water was added to	1373 ml

While stirring aqueous solution A_2 vigorously at 60 °C, 0.407 mole equivalent of the seed emulsion was added, and the pH and pAg were adjusted with acetic acid and an aqueous potassium bromide solution.

Then, aqueous solutions B_2 and C_2 as well as emulsion solution D_2 containing fine silver iodide grains were added thereto by the triple-jet method at addition rates shown in Tables 6, 7 and 8, with the pH and pAg controlled as shown in Table 5.

After completion of the addition, an aqueous phenylcarbamyl gelatin solution was added to deposit grains by adjusting the pH of the mixed solution. Grains deposited were subjected to desalting and washing, followed by adjustment of the resulting emulsion at 40 °C to pH 5.80 and pAg 8.06. Obtained was a monodispersed silver iodobromide emulsion comprising grains having an average size of 1.25 μm, an average silver iodide content of 8.0 mol% and a grain size distribution extent of 13.2%. This emulsion is hereunder referred to as Em-2. In Table 9, Em-2's recipe-based grain structure and the volume ratio of respective phases are summarized. Table 5 shows the grain growth conditions of Em-2.

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
In the table 5, → indicates to keep pH or pAg constant, ↘ continuous drop, and ↓ sharp drop.									

Table 6 shows the addition pattern of aqueous solution B_2, Table 7 that of aqueous solution C_2, and Table 8 that of aqueous solution D_2.

Table 6

Time (min)	Addition Rate (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 (min)	Addition Rate (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 (min)	Addition Rate (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	2nd Phase	3rd Phase			4th Phase	5th Phase	6th Phase
Recipe-based Silver Iodide Content (mol%)	2	0	35			10	3	0
Ratio of D_2/B_2 Molar Addition Rate (%)	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			

This Em-2 had the following properties:

Average grain size:	1.25 μm
Monodispersity (extent of distribution):	14.0%
Average silver iodide content:	8.0 mol%
Deviation in silver iodide content at grain periphery:	0.0 mol%
Relative standard deviation of silver iodide content:	9.0%
Surface silver iodide content:	0.0 mol%
Average aspect ratio:	3.3

Preparation of EmB-2

EmB-2 was prepared as an emulsion of the invention in exactly the same manner as in EmB-1, except that when formation of the 2nd phase was complete, silver sensitization was carried out for 30 minutes at pAg 3 and pH 6 by adding a silver nitrate solution. EmB-2 was an emulsion subjected only to reduction sensitization.

0103

Preparation of EmB-3

EmB-3 was prepared in the same manner as in EmB-1, except that Pb was used for doping by adding 1×10^{-4} mol/mol AgX of aqueous $Pb(NO_3)_2$ solution to the 3rd phase of EmB-1. This emulsion was one doped using Pb alone as polyvalent metal.

Preparation of EmB-4

EmB-4 was prepared in the same manner as in EmB-3, except that Os was used for doping by adding 1×10^{-4} mol/mol AgX of aqueous $K_4Os(CN)_6$ solution instead of $Pb(NO_3)_2$. This was an emulsion doped using Os alone as polyvalent metal.

Preparation of EmB-5

EmB-5 was prepared in the same manner as in EmB-2, except that Pb was used for doping by adding 1×10^{-4} mol/mol AgX of $Pb(NO_3)_2$ to the 3rd phase of EmB-2. This was an emulsion subjected to reduction sensitization and further doped using Pb alone as polyvalent metal.

Preparation of EmB-6

EmB-6 was prepared in the same manner as in EmB-2, except that 1×10^{-4} mol/mol AgX of $K_4O_5(CN)_6$ was doped to the 3rd phase of EmB-2.

The difference among EmB-1 to EmB-6 was only whether or not these were subjected to reduction sensitization and doping with a polyvalent metal; their grain size and core/shell structure were the same.

The component of the multilayer sample 101 is described below.

In the following descriptions of the composition, addition amounts of compounds are in grams per square meter unless otherwise indicated. Amounts of silver halides and colloidal silvers are shown in amounts of silver present, and addition amounts of sensitizing dyes are given in moles per mol of AgX.

Sample 101

1st layer: antihalation layer	
Black colloidal silver	0.18 g
Gelatin	1.57 g
UV absorbent (UV-1)	0.17 g
High boiling solvent (Oil-1)	0.14 g

2nd layer: 1st intermediate layer	
Gelatin	1.00 g

3rd layer: 1st red-sensitive emulsion layer	
Silver iodobromide emulsion (EmB-2)	0.66 g
Silver iodobromide emulsion (EmB-3)	0.29 g
Gelatin	1.29 g
Sensitizing dye (S-1)	3.21×10^{-4} mol
Sensitizing dye (S-2)	2.71×10^{-4} mol
Sensitizing dye (S-3)	3.45×10^{-5} mol
Coupler (C-1)	0.96 g
Colored coupler (CC-1)	0.07 g
High boiling solvent (Oil-1)	0.52 g

4th layer: 2nd intermediate layer	
Gelatin	0.75 g

5th layer: 1st green-sensitive emulsion layer	
Silver iodobromide emulsion (EmB-2)	0.66 g
Silver iodobromide emulsion (EmB-3)	0.29 g
Gelatin	1.08 g
Sensitizing dye (S-7)	2.67×10^{-4} mol
Sensitizing dye (S-6)	2.23×10^{-4} mol
Sensitizing dye (S-5)	4.48×10^{-5} mol
Sensitizing dye (S-8)	7.04×10^{-6} mol
Coupler (M-4)	0.13 g
Coupler (M-2)	0.29 g
Colored coupler (CM-1)	0.082 g
High boiling solvent (Oil-3)	0.51 g

6th layer: 2nd green-sensitive emulsion layer	
Silver iodobromide emulsion (EmB-4)	0.76 g
Gelatin	0.80 g
Sensitizing dye (S-7)	1.45×10^{-4} mol
Sensitizing dye (S-6)	1.21×10^{-4} mol
Sensitizing dye (S-5)	2.43×10^{-5} mol
Sensitizing dye (S-8)	3.82×10^{-6} mol
Coupler (M-4)	0.036 g
Coupler (M-2)	0.077 g
Colored coupler (CM-2)	0.035 g
High boiling solvent (Oil-3)	0.15 g

7th layer: 3rd intermediate layer	
Gelatin	0.55 g
SC-1	0.032 g

8th layer: 1st blue-sensitive emulsion layer	
Silver iodobromide emulsion (EmB-3)	0.76 g
Gelatin	1.16 g
Sensitizing dye (S-11)	2.88×10^{-4} mol
Sensitizing dye (S-9)	7.19×10^{-5} mol
Coupler (Y-1)	0.40 g
High boiling solvent (Oil-3)	0.16 g

9th layer: 4th intermediate layer	
Gelatin	0.75 g
SC-1	0.044 g

10th layer: 2nd red-sensitive emulsion layer	
Silver iodobromide emulsion (EmB-1)	0.95 g
Gelatin	0.93 g
Sensitizing dye (S-1)	1.74×10^{-4} mol
Sensitizing dye (S-2)	1.47×10^{-5} mol
Sensitizing dye (S-3)	1.87×10^{-5} mol
Coupler (C-1)	0.33 g
High boiling solvent (Oil-1)	0.33 g

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

12th layer :5th intermediate layer	
Gelatin	0.75 g
SC-1	0.044 g

13th layer: 3rd green-sensitive emulsion layer	
Silver iodobromide emulsion (EmB-1)	1.82 g
Gelatin	0.62 g
Sensitizing dye (S-7)	9.62×10^{-5} mol
Sensitizing dye (S-6)	8.00×10^{-5} mol
Sensitizing dye (S-5)	1.61×10^{-5} mol
Sensitizing dye (S-8)	2.53×10^{-6} mol
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: 6th intermediate layer	
Gelatin	0.75 g
SC-1	0.044 g

15th layer: 2nd blue-sensitive emulsion layer	
Silver iodobromide emulsion (EmB-6)	1.06 g
Gelatin	0.925 g
Sensitizing dye (S-11)	2.17×10^{-4} mol
Sensitizing dye (S-9)	1.12×10^{-5} mol
Coupler (Y-1)	0.31 g
High boiling solvent (Oil-3)	0.13 g

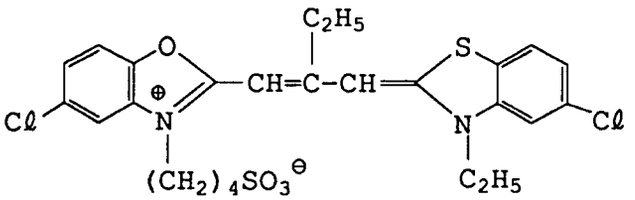
16th layer: 3rd blue-sensitive emulsion layer	
Silver iodobromide emulsion (EmB-7)	1.84 g
Gelatin	1.10 g
Sensitizing dye (S-11)	1.44×10^{-4} mol
Sensitizing dye (S-9)	5.65×10^{-5} mol
Coupler (Y-1)	0.52 g
High boiling solvent (Oil-3)	0.21 g

17th layer: 1st protective layer	
Silver iodobromide emulsion (EmB-8)	0.10 g
Gelatin	1.52 g
UV absorbent (UV-1)	0.006 g
UV absorbent (UV-2)	0.099 g
High boiling solvent (Oil-1)	0.0065 g
High boiling solvent (Oil-4)	0.0065 g

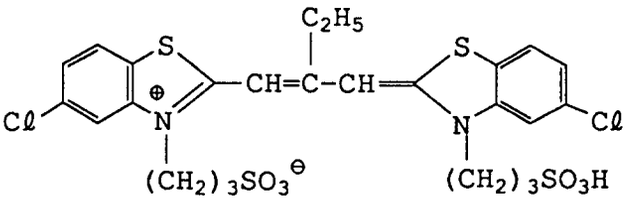
18th layer: 2nd protective layer	
Gelatin	0.55 g
Alkali soluble matting agent (silica; average particle size: 2 μm)	0.12 g
Polymethylmethacrylate (average particle size: 2 μm)	0.02 g
Lubricant (WAX-1)	0.04 g

Besides the above compositions, there were added in each layer coating aid (Su-1), dispersants (Su-2, Su-3), gelatin hardeners (H-1, H-2), stabilizer (Stab-1) antifoggants (AF-1, AF-2) and antiseptic agent (DI-1).

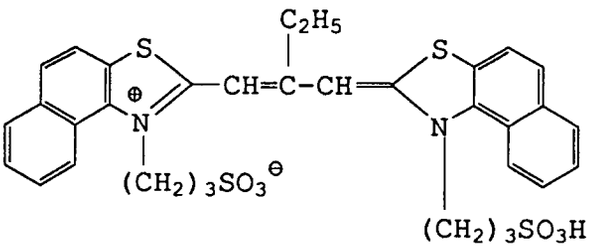
S-1



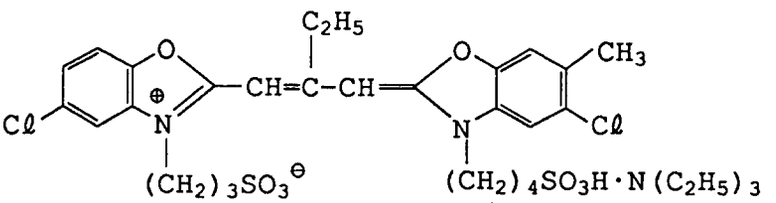
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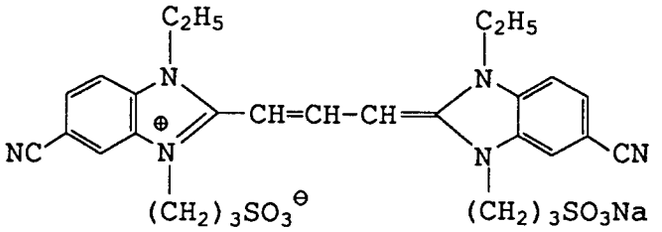
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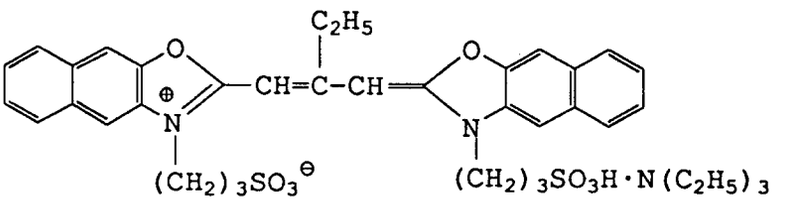
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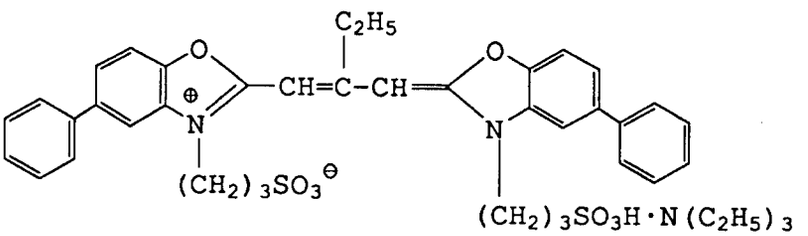
S-5



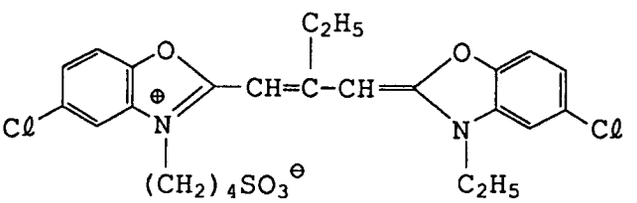
S-6



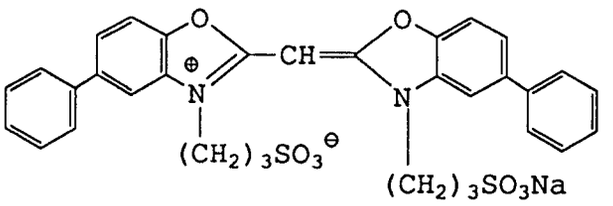
S-7



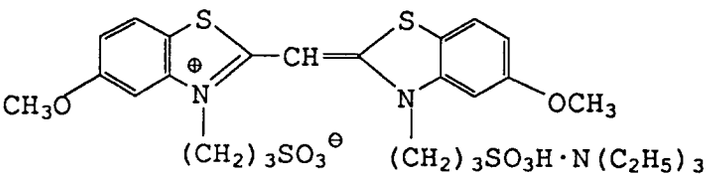
S-8



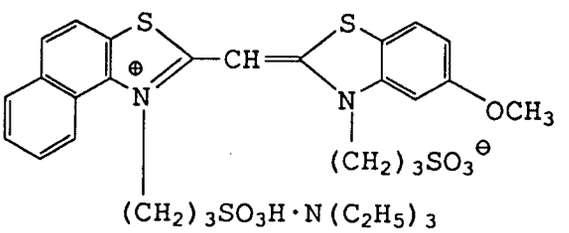
S-9


O
CH
O
N
N
$(CH_2)_3SO_3^{\ominus}$
$(CH_2)_3SO_3Na$

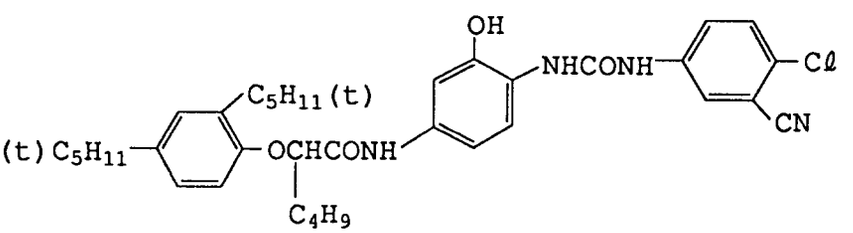
S-10


S
CH
S
CH_3O
N
N
OCH_3
$(CH_2)_3SO_3^{\ominus}$
$(CH_2)_3SO_3H \cdot N(C_2H_5)_3$

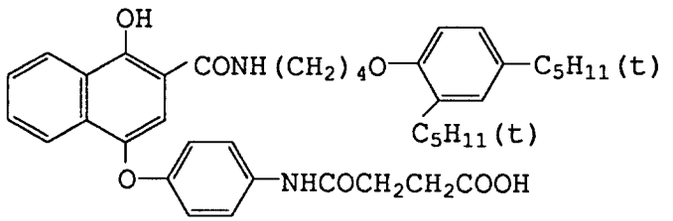
S-11


S
CH
S
N
N
OCH_3
$(CH_2)_3SO_3^{\ominus}$
$(CH_2)_3SO_3H \cdot N(C_2H_5)_3$

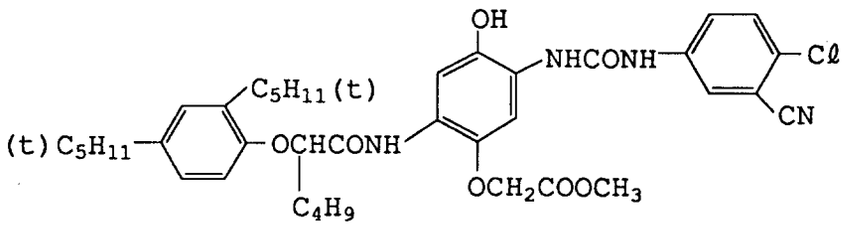
C-1


OH
NHCONH
Cl
CN
$C_5H_{11}(t)$
$(t)C_5H_{11}$
OCHCONH
C_4H_9

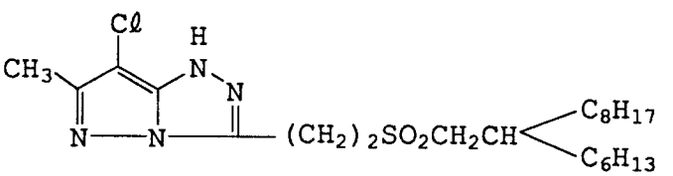
C-2



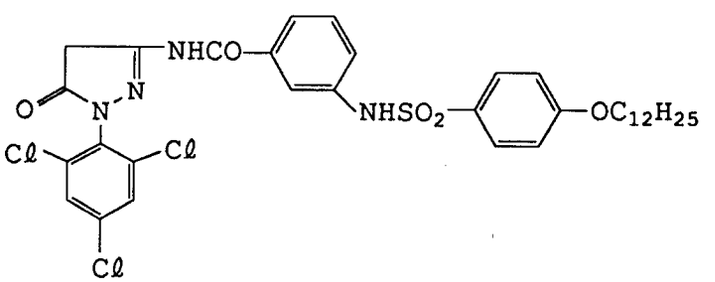
C-3



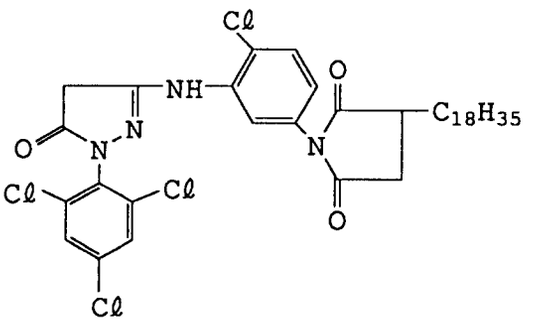
M-1



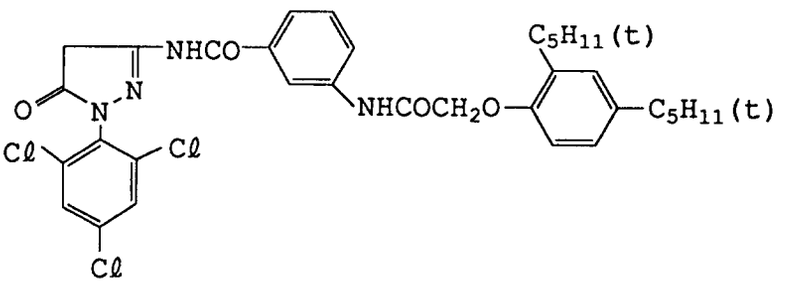
M-2



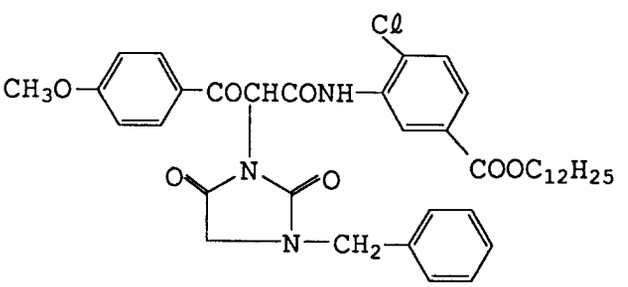
M-3



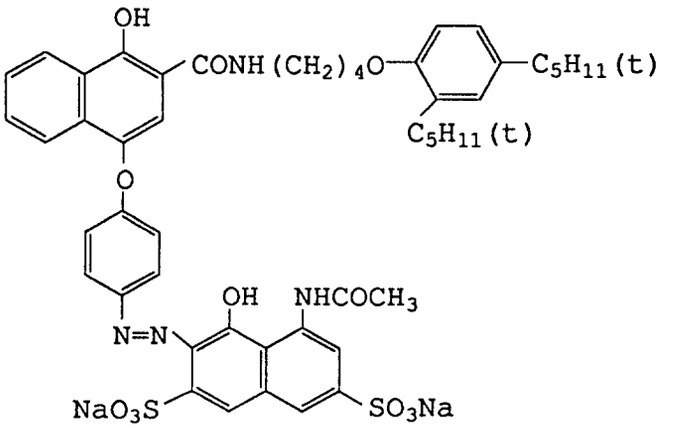
M-4



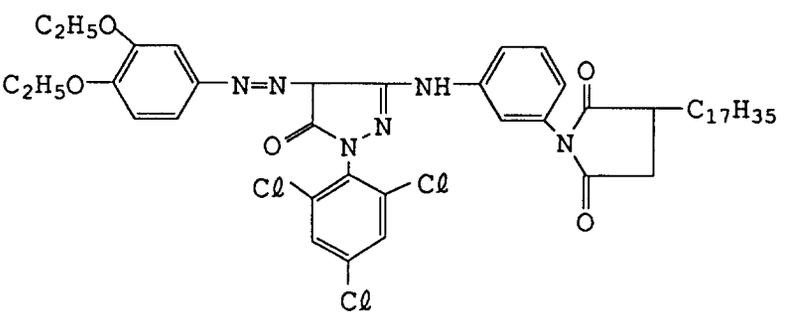
Y-1



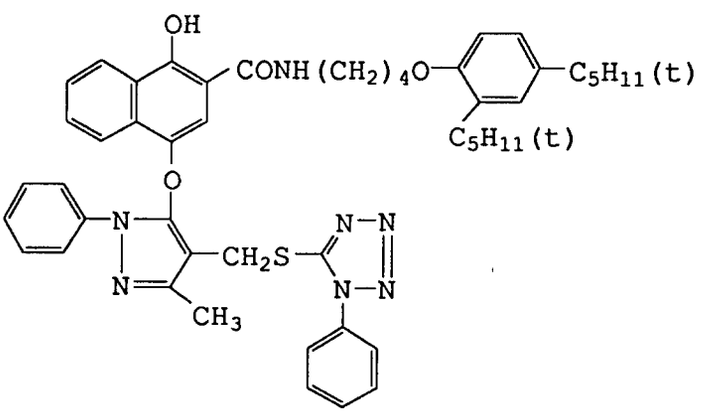
CC-1



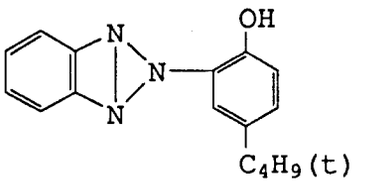
CM-1



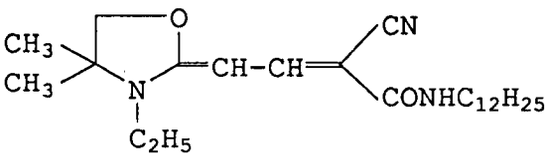
D-1



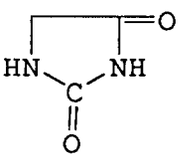
UV-1



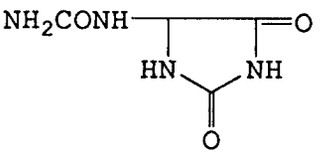
UV-2



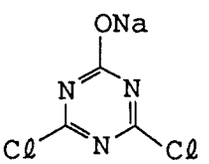
HS-1



HS-2



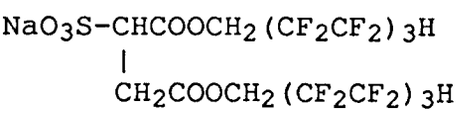
H-1



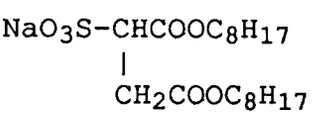
H-2

$(CH_2=CHSO_2CH_2)_2O$

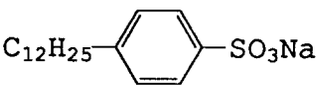
Su-1



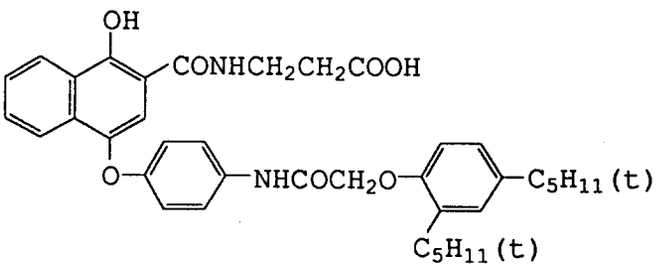
Su-2



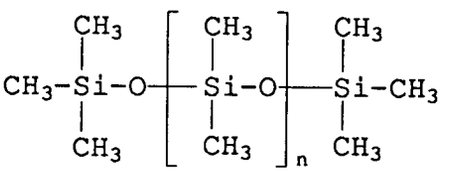
Su-3



Sc-1

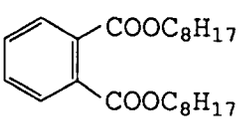


WAX-1

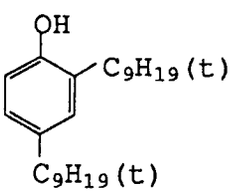


$\overline{MW}$ = 30,000

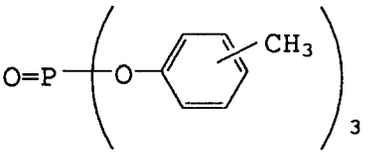
Oil-1



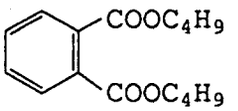
Oil-2



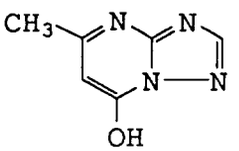
Oil-3



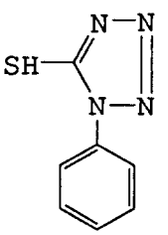
Oil-4



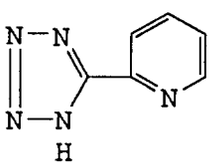
Stab-1



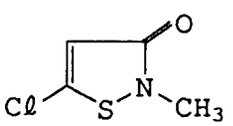
AF-1



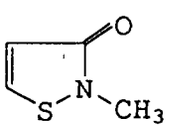
AF-2



DI-1



or



Multilayer samples 102 to 106 were prepared in exactly the same way as in sample 101, except that EmB-2 to EmB-6 were used in place of EmB-1 used in the 3rd green-sensitive emulsion layer, the 13th layer, of sample 101.

Samples 101 to 106 were subjected to wedgewise exposure through a yellow filter and processed in the following procedure.

Process (38 ° C)	Processing Time
Color developing standard	2 min 45 sec
Bleaching	6 min 30 sec
Washing	3 min 15 sec
Fixing	6 min 30 sec
Washing	3 min 15 sec
Stabilizing	1 min 30 sec
Drying	

Composition of the precessing solutions used in the respective processes were the same as that used in Example 1.

The relative sensitivity was determined for each sample using green light. The results are shown in Table 10, where the sensitivity has the same meaning as that in Example 1 and is expressed by values relative to the sensitivity of sample 101 after one-day standing which is set at 100.

Table 10

Sample No.	Emulsion	Fogging	Green Sensitivity
101	EmB-1	0.30	100
102	EmB-2	0.35	120
103	EmB-3	0.32	130
104	EmB-4	0.32	130
105 (Invention)	EmB-5	0.28	180
106 (Invention)	EmB-6	0.29	175

It can be understood that samples 105 and 106, using emulsions subjected to both reduction sensitization and polyvalent metal doping, are low in fog and high in sensitivity as compared with the other samples.

Example 3

A multilayer, color light-sensitive material, sample 201, was prepared by forming layers of the following compositions on a subbed triacetylcellulose film support. In the following descriptions of the composition, figures for respective components show coating amounts in g/m^2, those for silver halides indicate coating amounts in silver equivalent, and those for sensitizing dyes show coating amounts in moles per mole of silver halide contained in the same layer.

Sample 201

1st layer: antihalation layer	
Black colloidal silver	(silver) 0.18
Gelatin	0.40

2nd layer: intermediate layer	
2,5-di-t-pentadecylhydroquinone	0.18
EX-1	0.07
EX-3	0.02
EX-11	0.002
U-1	0.06
U-2	0.08
U-3	0.10
HBS-1	0.10
HBS-2	0.02
Gelatin	1.04

3rd layer: 1st red-sensitive emulsion layer	
EmC-1	(silver) 0.50
Sensitizing dye I	6.9×10^{-5}
Sensitizing dye II	1.8×10^{-5}
Sensitizing dye III	3.1×10^{-4}
EX-2	0.335
EX-10	0.020
Gelatin	0.87

4th layer : 2nd red-sensitive emulsion layer	
EmC-2	(silver) 1.0
Sensitizing dye I	5.1×10^{-5}
Sensitizing dye II	1.4×10^{-5}
Sensitizing dye III	2.3×10^{-4}
EX-2	0.400
EX-3	0.050
EX-10	0.015
Gelatin	1.30

5th layer: 3rd red-sensitive emulsion layer	
EmC-3	(silver) 1.60
EX-3	0.010
EX-4	0.080
EX-2	0.097
HBS-1	0.22
HBS-2	0.10
Gelatin	1.63

6th layer: intermediate layer	
EX-5	0.040
HBS-1	0.20
Gelatin	0.80

7th layer: 1st green-sensitive emulsion layer	
EmC-1	(silver) 0.30
Sensitizing dye V	3.0×10^{-5}
Sensitizing dye VI	1.0×10^{-5}
Sensitizing dye VII	3.8×10^{-4}
EX-6	0.260
EX-1	0.021
EX-7	0.030
EX-8	0.025
HBS-1	0.100
HBS-3	0.010
Gelatin	0.63

8th layer: 2nd green-sensitive emulsion layer	
EmC-2	(silver) 0.45
Sensitizing dye V	2.1×10^{-5}
Sensitizing dye VI	7.0×10^{-5}
Sensitizing dye VII	2.6×10^{-4}
EX-6	0.094
EX-8	0.018
EX-7	0.026
HBS-1	0.160
HBS-3	0.008
Gelatin	0.50

9th layer: 3rd green-sensitive emulsion layer	
EmC-3	(silver) 1.2
EX-12	0.040
EX-1	0.025
HBS-1	0.25
HBS-2	0.10
Gelatin	1.54

10th layer: yellow filter layer	
Yellow colloidal silver	(silver) 0.05
EX-5	0.08
HBS-1	0.03
Gelatin	0.95

11th layer: 1st blue-sensitive emulsion layer	
EmC-1	(silver) 0.22
Sensitizing dye VIII	3.5×10^{-4}
EX-9	0.721
EX-8	0.042
HBS-1	0.28
Gelatin	1.10

12th layer: 2nd blue-sensitive emulsion layer	
EmC-2	(silver) 0.45
Sensitizing dye VIII	2.1×10^{-4}
EX-9	0.154
EX-10	0.007
HBS-1	0.05
Gelatin	0.78

13th layer: 3rd blue-sensitive emulsion layer	
EmC-3	(silver) 0.77
Sensitizing dye VIII	2.2×10^{-4}
EX-9	0.20
HBS-1	0.07
Gelatin	1.69

14th layer: 1st protective layer	
Emulsion 1	(silver) 0.5
U-4	0.11
U-5	0.17
HBS-1	0.05
Gelatin	1.00

15th layer: 2nd protective layer	
Polymethylmethacrylate particles (diameter; about 1.5 μm)	0.54
S-1	0.20
Gelatin	1.20

In addition to the above components, gelatin hardener (H-1), surfactants, and thickener (B-1) were added to each layer; the coating amount of thickener (B-1) was 0.165 g/m^2.

Emulsions used were as follows:

EmC-1: a monodispersed, internally high silver iodide containing, dual structure core/shell emulsion; average grain size: 0.46 μm; average silver iodide content; 8.0 mol%.

EmC-2: a monodispersed, internally high silver iodide containing, dual structure core/shell emulsion; average grain size: 0.78 μm; average silver iodide content; 8.0 mol%.

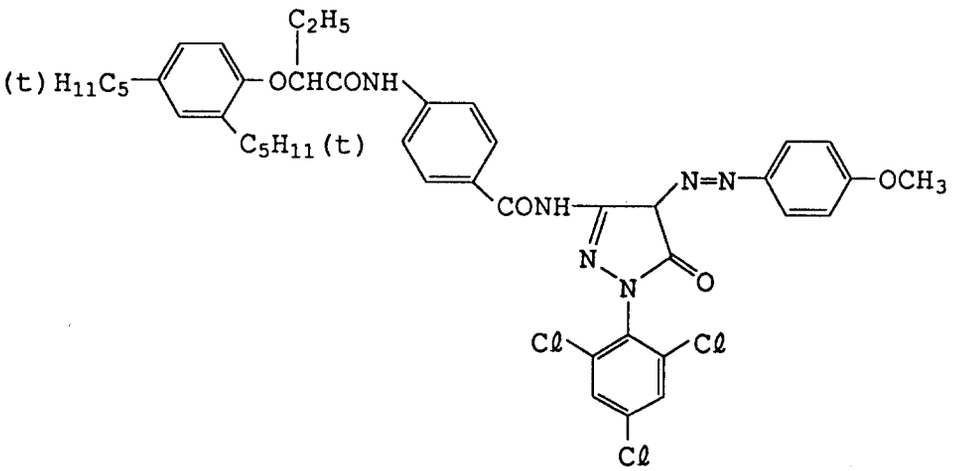
EmC-3: an emulsion same as Em-B-2 described in Japanese Pat. O.P.I. Pub. No.241336/1991.

EmC-4: an emulsion prepared as an emulsion of the invention in the same manner as EmC-3, except that 5×10^{-5} mol/mol AgX of $C_2H_5SO_2SNa$ was added 1 minute before the completion of core formation of EmC-3, and that 1×10^{-3} mol/mol AgX of ascorbic acid was added 1 minute after the start of shell formation.

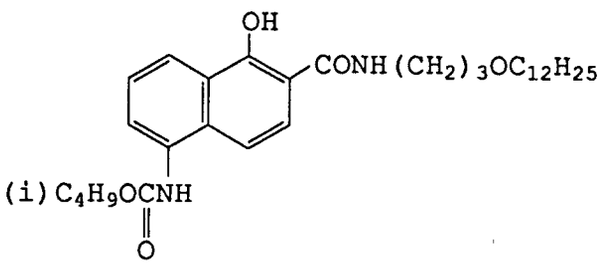
EmC-5: an emulsion prepared in the same manner as in EmC-3, except that 1×10^{-5} mol/mol AgX of aqueous $K_4[Fe(CN)_6]$ solution was added to solution C_{4-2} of EmC-3.

EmC-6: an emulsion prepared in the same manner as in EmC-4, except that 1×10^{-5} mol/mol AgX of aqueous $K_4[Fe(CN)_6]$ solution was added to solution C_{4-2} of EmC-4.

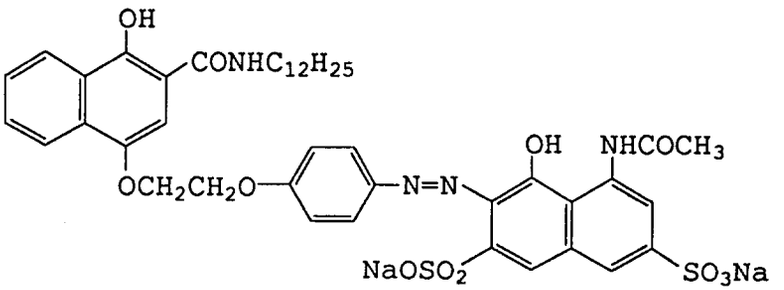
EX-1



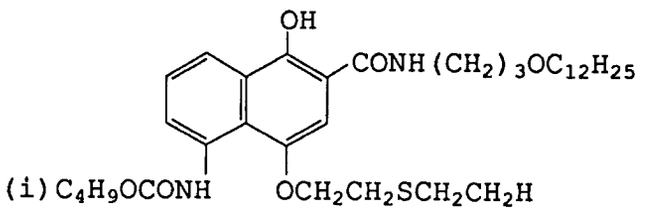
EX-2



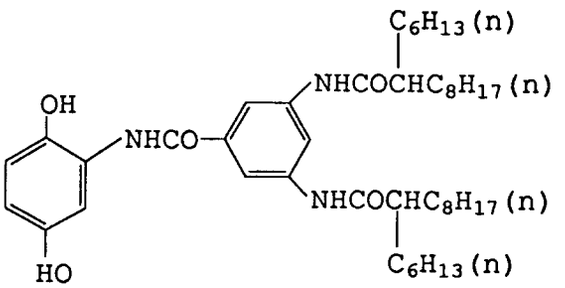
EX-3


OH
CONHC12H25
OCH2CH2O
N=N
OH
NHCOCH3
NaOSO2
SO3Na

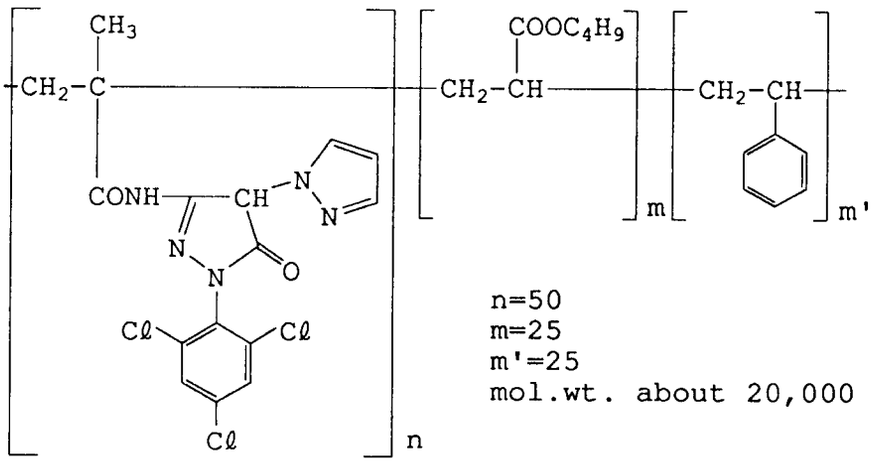
EX-4


OH
CONH(CH2)3OC12H25
(i)C4H9OCONH
OCH2CH2SCH2CH2H

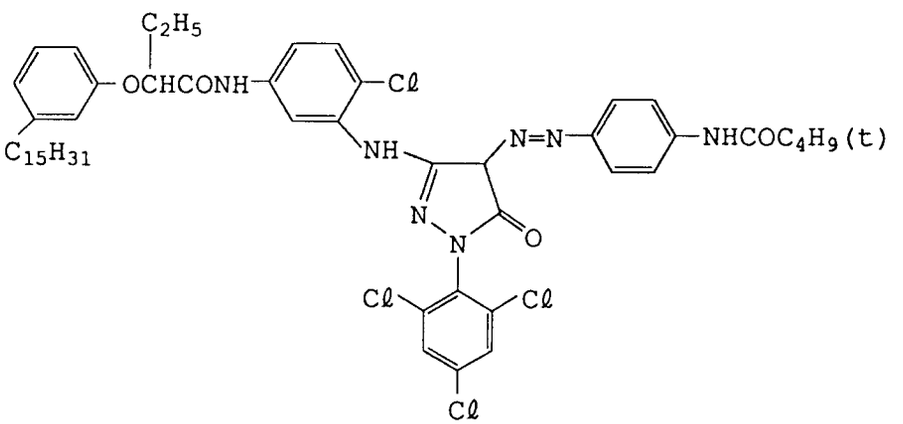
EX-5


C6H13(n)
NHCOCHC8H17(n)
OH
NHCO
NHCOCHC8H17(n)
C6H13(n)
HO

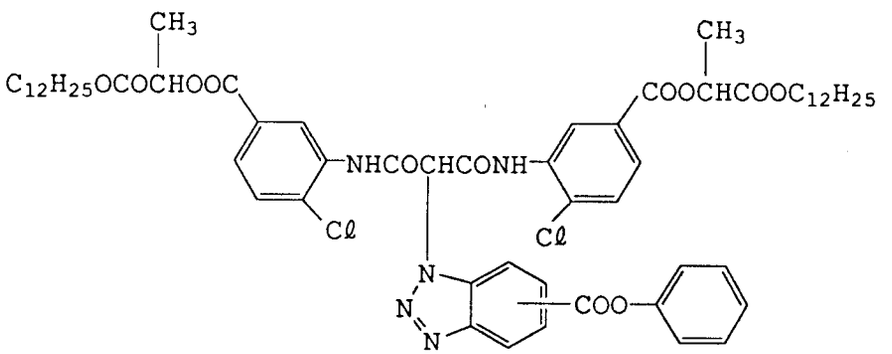
EX-6



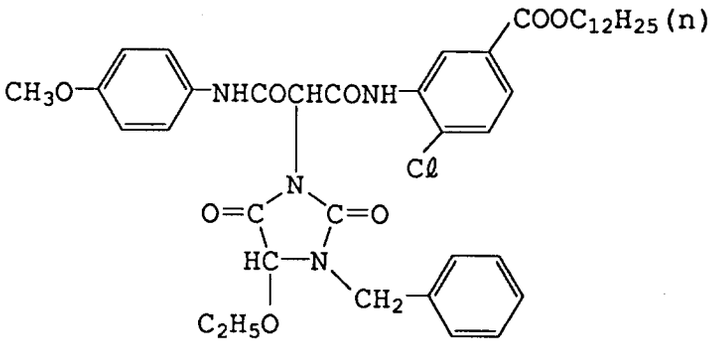
EX-7



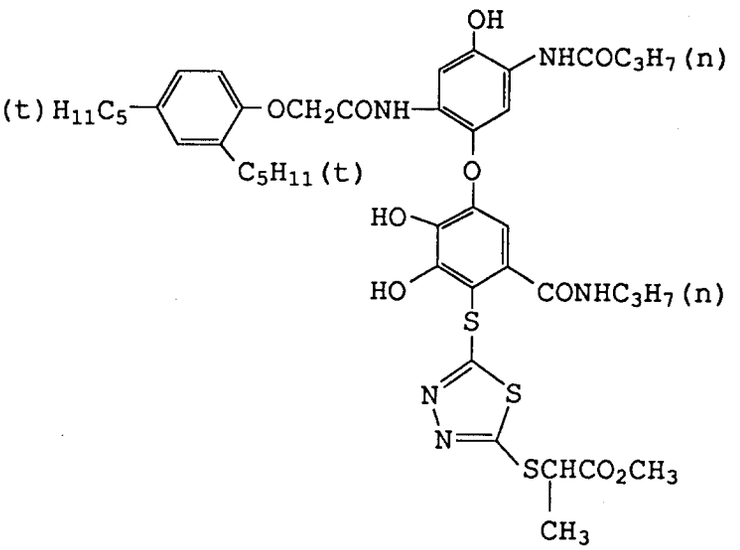
EX-8



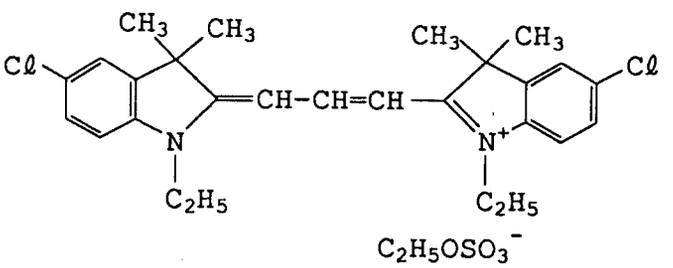
EX-9



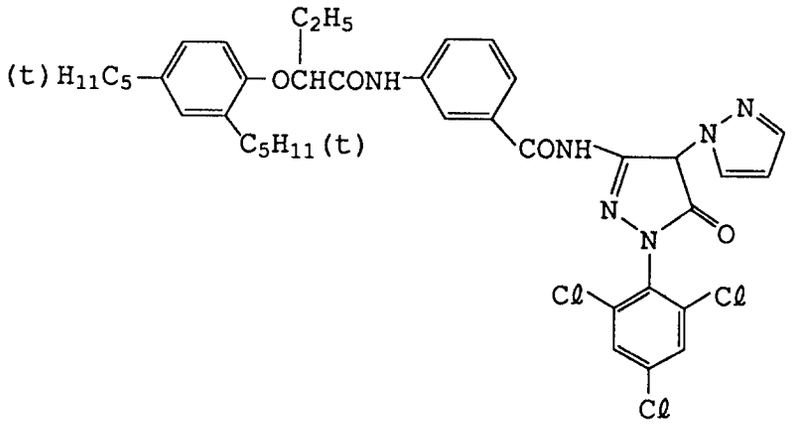
EX-10



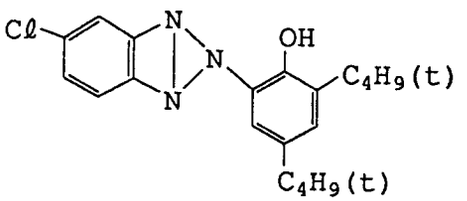
EX-11



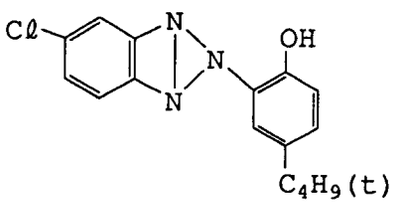
EX-12



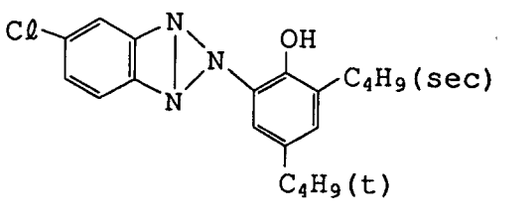
U-1



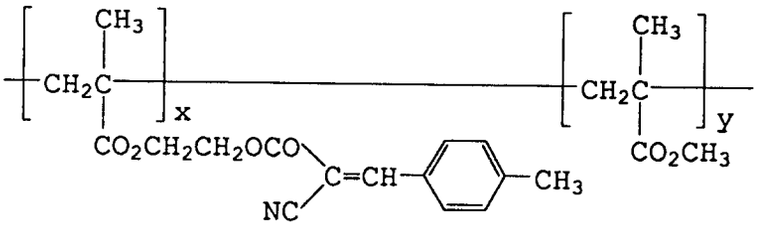
U-2



U-3

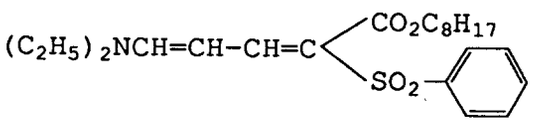


U-4



x:y = 70:30 (wt%)

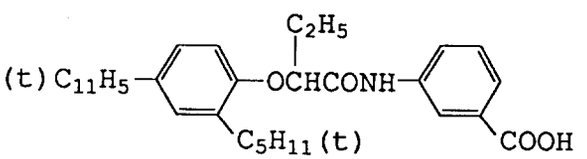
U-5



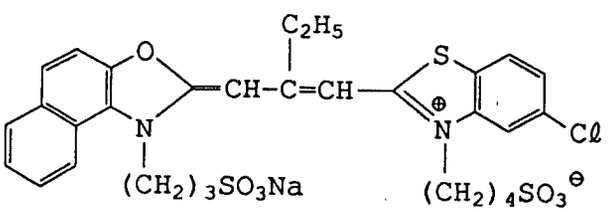
HBS-1 tricresyl phosphate

HBS-2 di-n-butyl phthalate

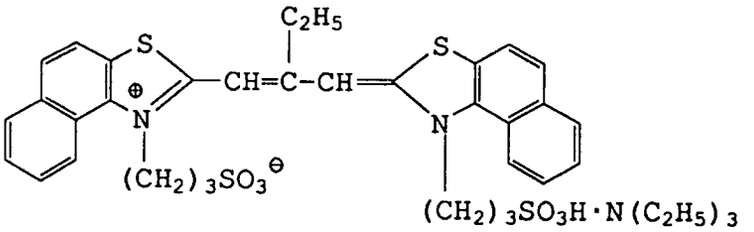
HBS-3



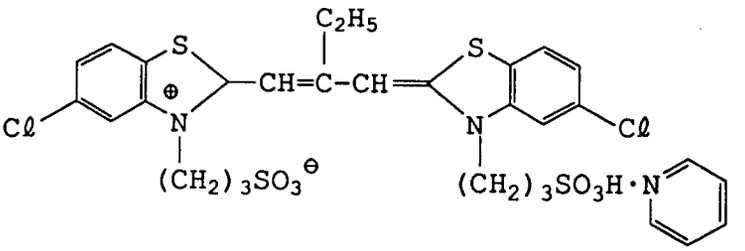
Sensitizing dye I



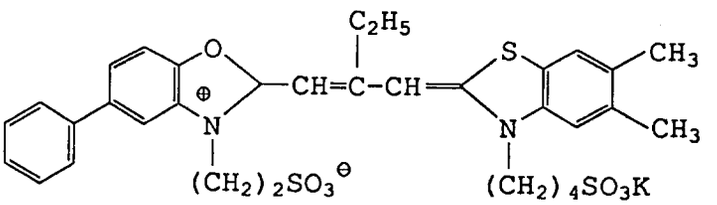
Sensitizing dye II



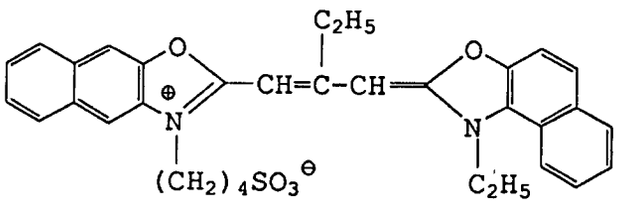
Sensitizing dye III



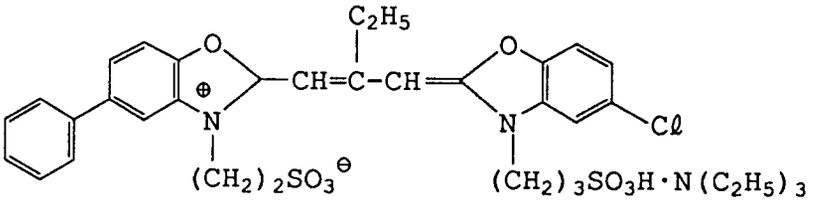
Sensitizing dye V



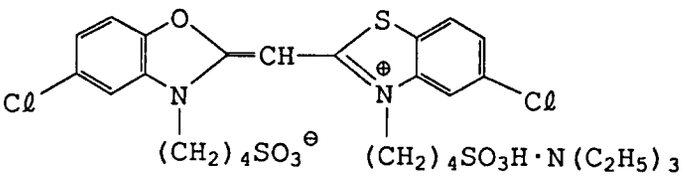
Sensitizing dye VI



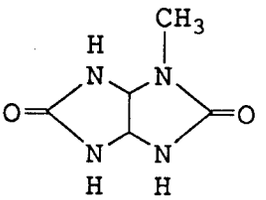
Sensitizing dye VII



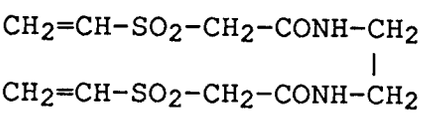
Sensitizing dye VIII



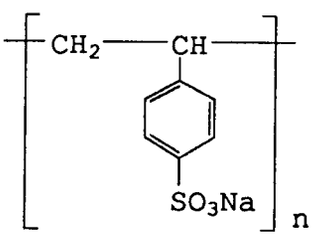
S-1



II-1



B-1



Multilayer samples 202 to 204 were prepared in the same manner as in multilayer sample 201, except that EmC-4 to EmC-6 were used in place of EmC-3. Each sample was exposed and processed as in Example 2 to obtain the results shown in Table 11.

Table 11

Sample No.	Emulsion	Fogging	Green Sensitivity
201	EmC-3	0.32	100
202	EmC-4	0.35	120
203	EmC-5	0.25	115
204 (Invention)	EmC-6	0.25	175

As is seen in Table 11, sample 204, which was subjected to both reduction sensitization and polyvalent metal doping, was remarkably low in fogging and high in sensitivity.

Claims

1. A silver halide photographic light-sensitive material comprising a support and provided thereon, a silver halide photographic emulsion layer containing silver halide grains, wherein said silver halide grains are subjected to reduction sensitization, and contain a polyvalent metal in an amount of not less than 10^{-6} mol per mol of silver halide.

2. The material of claim 1, wherein said silver halide grains contain silver iodobromide containing not more than 30 mol% silver iodide.

3. The material of claim 1 or 2, wherein said reduction sensitization is conducted with thiourea dioxide, ascorbic acid, polyamines, dimethylamine boranes or sulfites.

4. The material of claim 1, 2 or 3, wherein said polyvalent metal comprises a metal capable of forming a polyvalent ion.

5. The material of claim 4, wherein said polyvalent metal comprises Fe, Ir, Cd, Pb, In, Os or Re.

6. The material of claims 1, or 2 to 5, wherein said silver halide grains contain said polyvalent metal in an amount of 10^{-6} to 10^{-4} mol per mol of silver halide.

7. The material of claims 1, or 2 to 6, wherein said silver halide grains contain silver iodobromide containing not more than 30 mol% silver iodide.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 93 10 0369

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)
X	EP-A-0 423 399 (AGFA-GEVAERT NAAMLOZE VENNOOTSCHAP) * page 4, line 51 - page 5, line 3; claim 1 *	1-7	G03C1/08 G03C1/09 G03C1/10
X	EP-A-0 368 304 (FUJI PHOTO FILM CO., LTD.) * page 3, line 21 - line 45 * * page 6, line 20 - line 23; claims 1-4 *	1-4,6,7	
X	EP-A-0 397 125 (EASTMAN KODAK COMPANY) * page 4, line 33 - line 35; claims 1-13; table 1 *	1-7	
X	US-A-4 269 927 (ROBERT E. ATWELL) * column 11, line 50 - line 61; claims 1,2 *	1-7	
A	EP-A-0 318 987 (FUJI PHOTO FILM CO., LTD.) * page 6, line 5 - line 48; claims 1-3 *	1-7	

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 MARCH 1993	HINDIAS E.

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
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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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