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 [33] **Japan**
 [31] **42/10285**

[54] **SPECTRALLY SENSITIZED PHOTOGRAPHIC
 SILVER HALIDE EMULSION**
6 Claims, No Drawings

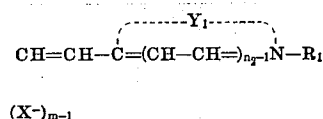
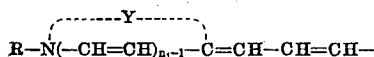
[52] U.S. Cl. **96/126,**
96/107
 [51] Int. Cl. **G03c 1/28**
 [50] Field of Search **96/104, 107**

[56] **References Cited**
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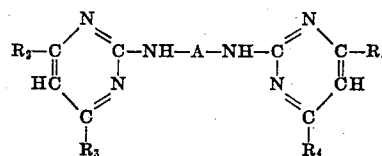
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Attorney—Sughrue, Rothwell, Mion, Zinn & Macpeak

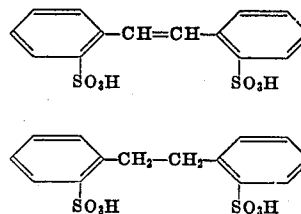
ABSTRACT: A photographic silver halide emulsion containing a sensitizing dye represented by the general formula (I)



wherein Y and Y₁ each represents a member selected from the group consisting of a benzothiazole, benzoselenazole, and a quinoline; R and R₁ represents a member selected from the group consisting of an alkyl group, a substituted alkyl group, an aryl group, an allyl group, an aralkyl group, and a substituted aralkyl group; X⁻ represents an anion; n₁ and n₂ each represents 1 or 2; and m represents 1 or 2, and a compound represented by the general formula (II)



wherein R₂, R₃, R₄ and R₅ each represents a member selected from the group consisting of a halogen atom, a hydroxyl group, an aryloxy group, an arylthio group, and arylamino group and A represents a member selected from the group consisting of



and

SPECTRALLY SENSITIZED PHOTOGRAPHIC SILVER HALIDE EMULSION

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates generally to a spectrally sensitized photographic silver halide emulsion and more particularly a spectrally sensitized photographic silver halide emulsion having an improved antifogging property.

2. Description of the Prior Art

It is well known that by incorporating a sensitizing dye in a silver halide emulsion during the production of photographic light-sensitive elements, the light-sensitive wavelength region of the silver halide emulsion is enlarged and the emulsion is spectrally sensitized.

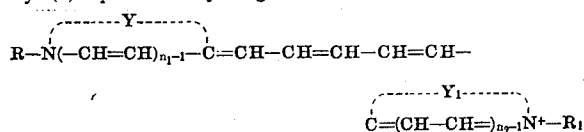
However, when a certain kind of sensitizing dye is incorporated in a silver halide emulsion, the formation of fog tends to increase with an increase in the amount of the sensitizing dye added therein. For example, a photographic silver halide emulsion containing a kind of dicarbocyanine as a sensitizing dye has a high spectral sensitivity and excellent properties as a red-sensitive emulsion for color photographic light-sensitive elements, but when the amount of the sensitizing dye is increased, the formation of fog is suddenly increased. Hereinafter, the fog caused by the addition of dye is called "dye fog."

On the other hand, as an antifogging and a stabilizer for photographic silver halide emulsion there are shown various compounds such as tetraazaindenes, mercaptotetrazoles, and the like, but there are such disadvantages that when a tetraazaindene is incorporated in a silver halide emulsion as an antifogging together with a kind of dicarbocyanine dye, the formation of dye fog is scarcely reduced and also when a mercaptotetrazole is incorporated in a silver halide emulsion as an antifogging together with a kind of a dicarbocyanine dye, the color sensitivity of the emulsion is markedly reduced although the formation of dye fog is reduced.

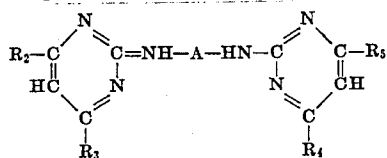
An object of this invention is to provide a photographic silver halide emulsion endowed with improved antifogging properties and stability without reducing the spectral sensitivity.

SUMMARY OF THE INVENTION

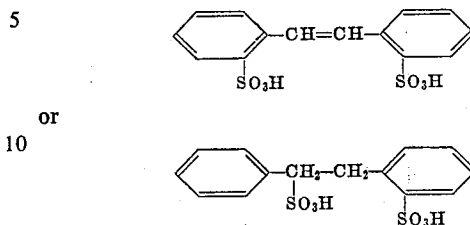
According to the present invention, there is provided a photographic silver halide emulsion containing a sensitizing dye (I) represented by the general formula



wherein Y and Y₁ each represents a nonmetallic atomic group necessary for forming a herocyclic ring selected from benzothiazoles, benzoselenazoles, and quinolines; R and R₁ each represents an alkyl group such as a methyl group, an ethyl group, and a propyl group; a substituted alkyl group such as a 2-hydroxyethyl group, a 2-methoxyethyl group, a carboxymethyl group, a 2-carboxyethyl group, a 3-carboxypropyl group, a 4-carboxybutyl group, a 2-sulfoethyl group, a 3-sulfopropyl group, a 4-sulfobutyl group, a carboethoxymethyl group, a carbomethoxyethyl group, and a carboethoxyethyl group; an aryl group; an allyl group, an aralkyl group and a substituted aralkyl group such as a p-sulfobenzyl group, a p-carboxybenzyl group, or p-sulfophenethyl; X⁻ represents an anion; n₁ and n₂ each represents 1 or 2; and m is 1 (forming an intramolecular salt) or 2, and the compound (II) represented by the general formula



wherein R₂, R₃, R₄ and R₅ each represents a halogen atom, a hydroxyl group, an aryloxy group, or an arylamine group; and A represents



15 the sulfonic acid group of the above group may be in a form of salt, such as an alkali metal salt, an ammonium salt, an amine salt and the like.

It is well known that the sensitizing dye (I) used in this invention gives red sensitivity to photographic silver halide emulsions. A photographic silver halide emulsion having incorporated therein sensitizing dye (I) has a high spectral sensitivity and is excellent in the broadness and the position of the spectral sensitizing wavelength region as a red-sensitive emulsion for photographic light-sensitive color elements, however, there are such difficulties that the sensitizing dye gives markedly dye fogs, which makes the practical use thereof difficult, and the formation of fog of the photographic light-sensitive element using the photographic emulsion containing it increases remarkably.

However, by incorporating the sensitizing dye (I) together with compound (II) of this invention in a photographic silver halide emulsion, the formation of dye fog can be suppressed without substantially lowering the spectral sensitivity and also the formation of fog in the light-sensitive elements employing the photographic silver halide emulsion containing the sensitizing dye can be remarkably reduced.

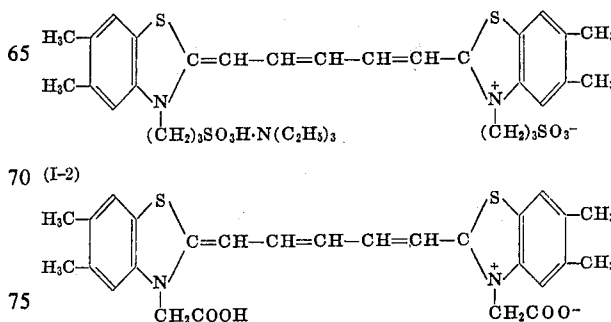
That is, compound (II) prevents the formation of dye fog of a photographic silver halide emulsion containing sensitizing dye (I) and at the same time reduces staining of the image-bearing layer of a photographic light-sensitive element using the photographic silver halide emulsion containing sensitizing dye (I) based on the sensitizing dye after developing and fixing.

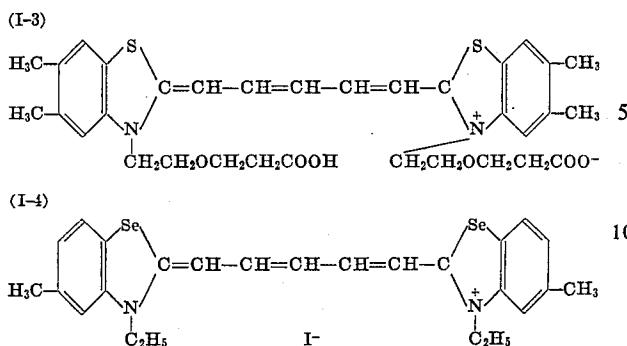
The compound (II) used in this invention has the merits that the color sensitivity thereof in the presence of sensitizing dye (I) is not reduced or in some cases the spectral sensitivity is extremely increased. That is, a kind of compound (II) provides supersensitizing action to a kind of sensitizing dye (I).

Further, a photographic light-sensitive element prepared by using the photographic silver halide emulsion containing sensitizing dye (I) but without containing compound (II) has fault that it tends to cause the reduction in the sensitivity during the preservation thereof, but a photographic light-sensitive element prepared by using the photographic silver halide emulsion containing sensitizing dye (I) and compound (II) shows a low reduction in the sensitivity during the preservation.

DETAILED DESCRIPTION OF THE INVENTION

The typical examples of sensitizing dye (I) used in this invention are illustrated below although the dye is not limited to them only.



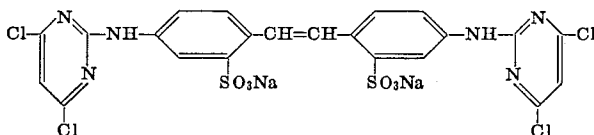


Some of compound (II) used in this invention may be prepared by the following methods, but it can be understood that other compounds of the general type of compound (II) which are not shown in the examples may also be prepared by similar methods.

Synthesis 1

12.4 g. of sodium 4,4'-diaminostilbene-2,2'-disulfonate, 11.0 g. of 2,4,6-trichloropyrimidine, 100 ml. of acetone and 100 ml. of water were mixed and heated with stirring at 55°-65° C.

By neutralizing hydrochloric acid formed during the reaction maintained at a neutral to weak acidic condition. After the reaction was complete, the reaction mixture was cooled by ice and the precipitated product was filtered to provide compound (II-0) having the following structure:



Synthesis 2

Preparation of Compound (II-7):

A solution of 17.8 g. of compound (II-0) prepared above and 5.7 g. of β -naphthylamine in 100 ml. of dimethylformamide was heated under refluxing for 3-4 hours in a nitrogen stream. After allowing to cool, the product was filtered to remove salt and then neutralized with an aqueous 10 percent sodium carbonate solution. After removing the unreacted amine by the extraction with benzene, the system was subjected to distillation under a reduced pressure to remove a solvent of dimethylformamide and water. Thereafter, 20 g. of the residue was heated under refluxing in 100 ml. of aniline for about 3 hours, the resulting reaction mixture was poured into about 250 ml. of methanol and the crystal thus precipitated was filtered and dried.

Synthesis 3

Preparation of Compound (II-3)

A mixture of 14.1 g. of compound (II-0), 13.3 g. of sodium-naphtholate, and 1.0 g. of 1,4-diaza-2,2,2-bicyclooctane was heated under refluxing for about 2.5 hours in 70 ml. of dimethylformamide. After allowing to cool, the precipitates were removed by filtration, and the filtrate was subjected to distillation under a reduced pressure to remove dimethylformamide.

The residue was dissolved in a solvent mixture of water and acetone, the solution was mixed with 5 ml. of concentrated hydrochloric acid, and the precipitate thus formed was recovered by filtration. The product was washed with water and dried.

Synthesis 4

Preparation of Compound (II-4)

A mixture of 14.1 g. of compound (II-0), 4.4 g. of thiophenol, and 1.6 g. of sodium hydroxide was heated under refluxing in a mixed solvent of 70 ml. of water and 20 ml. of dioxane. After the reaction, the product was mixed with 5 ml. of concentrated hydrochloric acid and the product precipitated was collected by filtering under suction and washed with water and then methanol followed by drying.

A suitable concentration of sensitizing dye (I) used in this invention is 0.002-0.2 g. per 1 g. molecule of the silver halide in a silver halide emulsion and a suitable concentration of compound (II) is 0.02-10 g. per 1 g.-molecule of the silver halide in a silver halide emulsion, and a preferable concentration ratio of sensitizing dye (I) to compound (II) is from 1:2 to 1:200.

Sensitizing dye (I) may be added to a silver halide emulsion by a manner well known in the field of this art. Compound (II) may be added to a silver halide emulsion as a solution thereof in an organic solvent such as ethanol or methanol and also the solubility thereof may be increased by adding to the organic solvent a desirable amount of water, acetone or an aqueous alkali solution.

It is preferable to add sensitizing dye (I) and compound (II) to a silver halide emulsion prior to coating. Sensitizing dye (I) may be incorporated in a silver halide emulsion before or after the addition of compound (II) or simultaneously with compound (II).

The photographic silver halide emulsion used in this invention may be silver chloride, silver bromide, silver iodide, silver chlorobromide, silver iodobromide and silver chloriodobromide emulsions and also may contain the usual additives such as a chemical sensitizer, a hardening agent, an antifoggant, a wetting agent, a stabilizer, a plasticizer, a developing promoter, an antibronzing agent, and the like. Moreover, the silver halide emulsion may contain a coupler for forming a cyan image by color development.

The photographic silver halide emulsion of this invention may be applied to a suitable support such as a glass plate, a cellulose-derivative film, a synthetic resin film or a baryta-coated paper.

Examples of the present invention are shown below:

Example 1

A silver chlorobromide emulsion containing sensitizing dye (I) shown above was applied to a cellulose acetate film to provide a control sample and a silver chlorobromide emulsion having the same composition as above, containing sensitizing dye (I) and compound (II) mentioned above was applied to a cellulose acetate film. After drying, each of the light-sensitive films thus prepared was red-exposed to a light source of 2,666° K. in color temperature through Fuji #7 Filter (transmitting light having longer wavelengths than 590 m.; made by Fuji Photo Film Co.) and then developed for 6 minutes at 20° C. in the developer having the following composition:

N-Methyl-p-Aminophenol Sulfate 2.0 g.	
Hydroquinone	4.0 g.
Sodium Carbonate (mono-hydrate)	28.0 g.
Sodium Sulfite	40.0 g.
Potassium Bromide	1.0 g.
Water To Make	1.0 l.

About the light-sensitive films, the red sensitivity directly after coating, fogs directly after coating, and fogs formed by developing after storing them for 2 days under the conditions of 80 percent in relative humidity and 50° C. were measured, the results of which are shown in the following table 1.

Table 1

Sensitizing Dye I	Compound II
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(Amount*)	(Amount*)	(A)	(B)	(C)
(a) I-1 (29)		100	0.06	0.10
(b) I-1 (29)	II-1 (1,000)	186	0.04	0.06
(c) I-1 (29)	II-2 (1,000)	200	0.04	0.06
(d) I-1 (29)	II-3 (1,000)	347	0.04	0.06
(e) I-1 (29)	II-4 (1,000)	63	0.04	0.06
(f) I-1 (29)	II-5 (1,000)	174	0.04	0.07
(g) I-1 (29)	II-6 (1,000)	204	0.04	0.06
(h) I-2 (20)		100	0.06	0.09
(i) I-2 (20)	II-1 (1,000)	166	0.04	0.06
(j) I-2 (20)	II-2 (1,000)	118	0.04	0.06
(k) I-2 (20)	II-3 (1,000)	245	0.04	0.06
(l) I-2 (20)	II-4 (1,000)	135	0.04	0.07
(m) I-2 (20)	II-5 (1,000)	159	0.04	0.06
(n) I-2 (20)	II-6 (1,000)	200	0.04	0.06
(o) I-3 (28)		100	0.06	0.10
(p) I-3 (28)	II-1 (1,000)	288	0.04	0.06
(q) I-3 (28)	II-2 (1,000)	182	0.04	0.06
(r) I-3 (28)	II-3 (1,000)	288	0.04	0.06
(s) I-3 (28)	II-4 (1,000)	347	0.04	0.06
(t) I-3 (28)	II-5 (1,000)	191	0.04	0.06
(u) I-3 (28)	II-6 (1,000)	275	0.04	0.06
(v) I-4 (25)		100	0.08	0.10
(w) I-4 (25)	II-2 (1,000)	166	0.04	0.06
(x) I-4 (25)	II-3 (1,000)	245	0.04	0.06
(y) I-5 (20)		100	0.14	0.23
(z) I-5 (20)	II-2 (1,000)	174	0.04	0.08
(aa) I-5 (20)	II-3 (1,000)	240	0.04	0.08

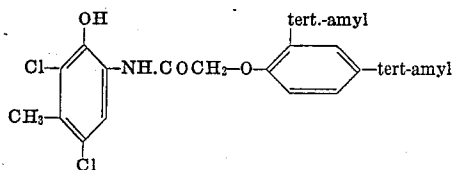
(*) : mg./l gram molecule of silver halide.

In table 1, (A) = red sensitivity directly after coating, (B) = fog directly after coating, and (C) = fog after 2 days in 80 percent of a relative humidity at 50° C.

From the results, it will be understood that the fogs of the light-sensitive films containing sensitive dye I and compound II directly after coating and the fogs thereof formed when preserved in the condition of 80 percent in relative humidity of 50° C. after coating are reduced as compared with those of control samples (sample (a), sample (h), sample (o), sample (v) and sample (y)) and also the red sensitivity of the light-sensitive films of this invention is higher than that of the control films.

Example 2

A silver chlorobromide emulsion containing sensitizing dye I and a dispersion of the coupler having the following formula:



was mixed with a hardening agent and a wetting agent and then applied to a baryta-coated paper to provide a control sample.

On the other hand, a silver chlorobromide emulsion containing sensitizing dye I and the dispersion of the coupler together with compound II was also mixed with a hardening agent and a wetting agent and then applied to a baryta-coated paper to provide the light-sensitive paper of this invention. After drying, each of the light-sensitive papers was developed, color-developed in a color developer having the following composition, and then subjected to fixing, water-washing, bleaching, water-washing, hardening, water-washing, and stabilizing procedures.

Benzyl Alcohol	30 ml.
Sodium Chloride	0.7 g.
Sodium Bromide	0.5 g.
Sodium Sulfide	2.0 g.
Sodium Carbonate (mono-hydrate)	30.0 g.
Sodium Sulfate	3.0 g.
Hydroxylamine Sulfate	2.4 g.
N, N-Diethyl-2-Methyl-p-Phenylene diamine Hydrochloride	5.2 g.
Water To Make	1 l.

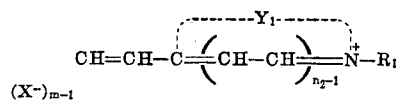
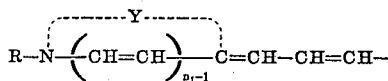
The results are shown in the following:

Table 2

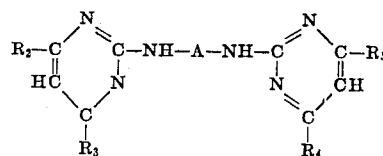
Sensitizing Dye I	Compound II	Red Sensitivity	Fog
(1) I-1 (16)		100	0.32
(2) I-1 (16)	II-7 (110)	120	0.20
(3) I-1 (16)	II-7 (220)	120	0.16
(4) I-1 (16)	II-7 (440)	120	0.12
(5) I-6 (11)		100	0.13
(6) I-6 (11)	II-1 (55)	90	0.08
(7) I-6 (11)	II-1 (110)	85	0.08

What is claimed is:

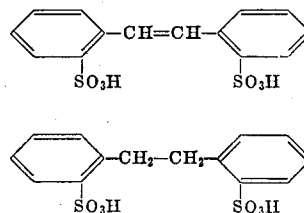
1. A photographic silver halide emulsion containing a sensitizing dye represented by the general formula (I)



wherein Y and Y₁ each represents a member selected from the group consisting of a benzothiazole, a benzoselenazole, and a quinoline; R and R₁ represents a member selected from the group consisting of an alkyl group, a hydroxyalkyl group, a carboxyalkyl group, an alkoxyalkyl group, a sulfoalkyl group, a carboalkoxyalkyl group, an aryl group, an allyl group, an aralkyl group, a sulfoaralkyl group and a carboalkoxyalkyl group; X⁻ represents an anion; n₁ and n₂ each represents 1 and 2; and m represents 1 or 2, and a compound represented by the general formula which reduces fog formation without substantially lowering sensitivity,



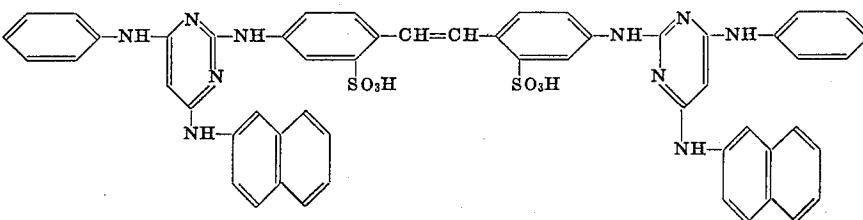
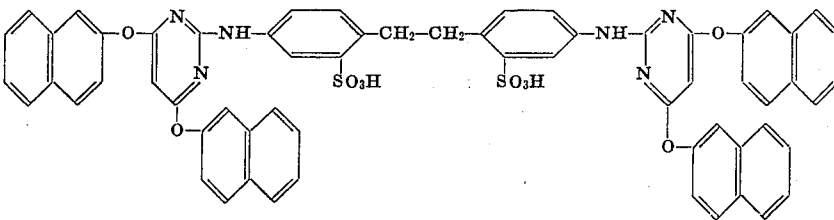
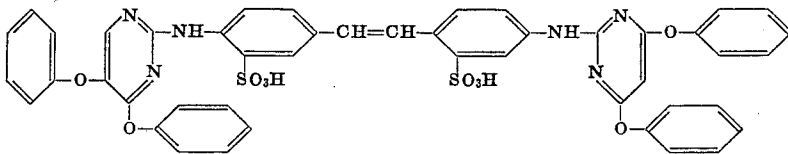
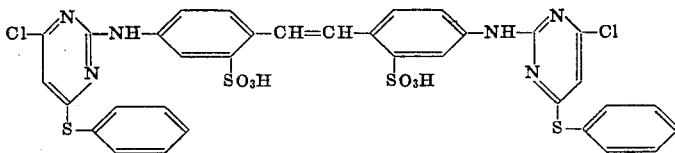
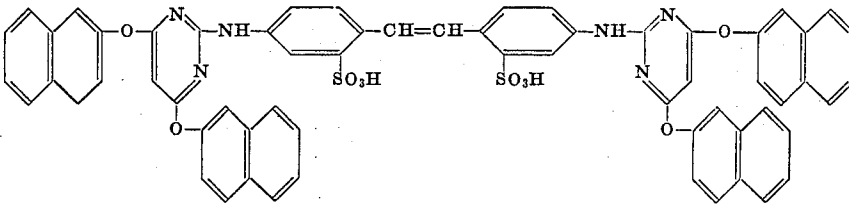
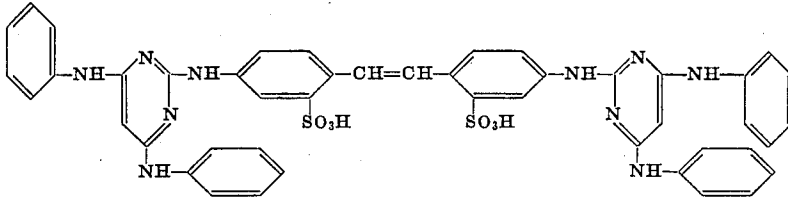
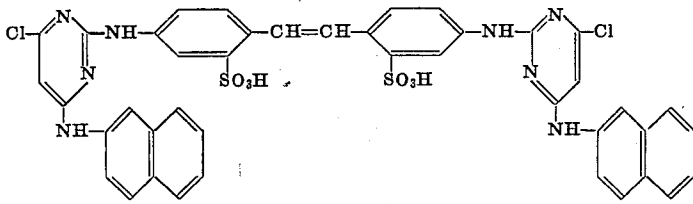
wherein R₂, R₃, R₄, and R₅ each represents a member selected from the group consisting of a halogen atom, a hydroxyl group, an aryloxy group, an arylthio group, and arylamino group and A represents a member selected from the group consisting of



and

2. The photographic silver halide emulsion as claimed in claim 1, wherein said compound represented by the general formula II is one selected from the group consisting of

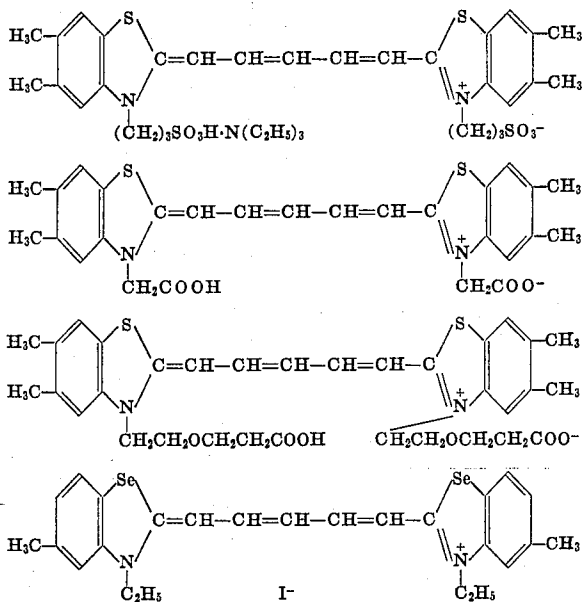
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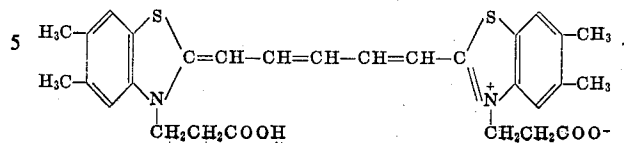
and mixtures thereof.

3. The photographic silver halide emulsion as claimed in

claim 1, wherein said sensitizing dye is one selected from the group consisting of:



and



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and mixtures thereof.

4. A photographic silver halide emulsion as claimed in claim 15 1, wherein the concentration of said sensitizing dye is 0.002-0.2 g. per 1 gram molecule of the silver halide.

5. A photographic silver halide emulsion as claimed in claim 1, wherein the concentration of said compound represented by the general formula (II) is 0.02-10 g. per 1 gram molecule 20 of the silver halide.

6. A photographic silver halide emulsion as claimed in claim 1, wherein the concentration ratio of said sensitizing dye to said compound represented by the general formula (II) is from 1:2 to 1:200. 25

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