United States Patent [19]

Sakazume et al.

[11] **3,769,024**

[45] **Oct. 30, 1973**

[54] **LIGHT-SENSITIVE SILVER HALIDE PHOTOGRAPHIC MATERIAL WITH SENSITIZING DYE COMBINATION**

[75] Inventors: **Kaiichiro Sakazume**, Tokyo; **Eiichi Sakamoto**, Hanno; **Shizuo Saito**, Tokyo, all of Japan

[73] Assignee: **Konishiroku Photo Industry Co., Ltd.**, Tokyo, Japan

[22] Filed: **July 15, 1971**

[21] Appl. No.: **163,100**

[30] **Foreign Application Priority Data**

July 16, 1970 Japan 45/61738

[52] **U.S. Cl.** **96/124**

[51] **Int. Cl.** **G03c 1/28**

[58] **Field of Search** 96/124

[56] **References Cited**

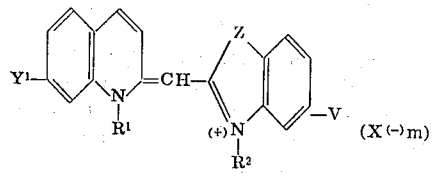
UNITED STATES PATENTS

3,667,960	6/1972	Keisuke Shiba et al.	96/124
3,580,724	5/1971	Sato et al.	96/124
3,615,634	10/1971	Gotze et al.	96/124
3,617,294	11/1971	Shiba et al.	96/124
2,132,866	10/1938	Carroll	96/124

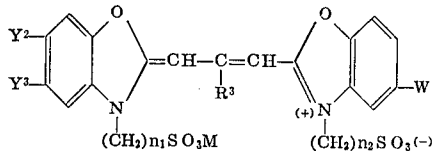
Primary Examiner—Norman G. Torchin
Assistant Examiner—Richard L. Schilling
Attorney—Eric H. Waters et al.

[57] **ABSTRACT**

Photographic materials of improved green sensitivity are described containing a light-sensitive silver halide emulsion and including, in combination, at least one monomethinecyanine dye of the general formula,



wherein Y^1 is a hydrogen atom, a lower alkyl group or a lower alkoxy group; Z is S or Se; V is a hydrogen atom or a lower alkyl group; R^1 is a lower alkyl group or a substituted alkyl group; R^2 is a sulfoalkyl group or a carboxyalkyl group; X is an anion; and *m* is zero or 1, and at least one oxacarbocyanine dye of the general formula,



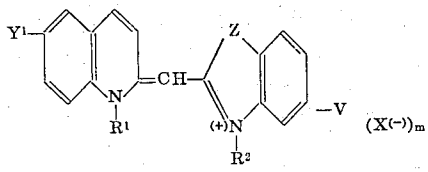
Wherein Y^2 is a hydrogen atom or a lower alkyl group; Y^3 is a hydrogen atom, a lower alkyl group, a lower alkoxyl group, a halogen atom or a phenyl group; W is a halogen atom or a phenyl group; R^3 is a lower alkyl group; M is a hydrogen atom, an alkali metal atom or H.Q (where Q is an organic base); and n_1 and n_2 are individually 2, 3 or 4. Lower fog levels are also noted. Emulsions are detailed as well as materials utilizing such emulsions.

10 Claims, No Drawings

LIGHT-SENSITIVE SILVER HALIDE PHOTOGRAPHIC MATERIAL WITH SENSITIZING DYE COMBINATION

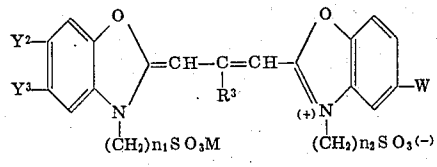
This invention relates to a light-sensitive silver halide photographic material containing a specific combination of sensitizing dyes. More particularly, the invention pertains to a light-sensitive silver halide photographic material characterized by containing in the light-sensitive silver halide photographic emulsion a combination comprising at least one compound of the below-mentioned general formula (I) and at least one compound of the below-mentioned general formula (II).

General formula (I)



wherein Z is S or Se; Y^1 is a hydrogen atom, a lower alkyl group or a lower alkoxy group; R^1 is a lower alkyl group or a substituted alkyl group; V is a hydrogen atom or a lower alkyl group; R^2 is a sulfoalkyl group or a carboxy-alkyl group; X is an anion; and *m* is zero or 1.

General formula (II)



wherein Y^2 is a hydrogen atom or a lower alkyl group; Y^3 is a hydrogen atom, a lower alkyl group, a lower alkoxy group, a halogen atom or a phenyl group; W is a halogen atom or a phenyl group; R^3 is a lower alkyl group; M is a hydrogen atom, an alkali metal atom or H.Q (where Q is an organic base); and n_1 and n_2 are individually 2, 3 or 4.

It is well known that the use of a certain cyanine dye is effective as a means for spectral sensitization of silver halide photographic emulsion. It is also well known that when said sensitizing dye is used in combination with a certain other sensitizing dye or an organic compound, it is possible to impart to the emulsion a light sensitivity which is higher than the sum of sensitivities attained in the case where said compounds are used singly. Such effect is called supersensitization, and many number of such combinations have already been reported. In case such supersensitization is to be applied to a silver halide emulsion, it is necessary that the combination should not only increase the color sensitization effect but also satisfy such conditions as mentioned below.

1. The combination should be proper in spectral sensitization region.

2. The combination should have no detrimental interaction with other photographic additives, and should provide stabilized photographic properties when the emulsion is allowed to stand or the resulting light-sensitive photographic material is stored.

3. The combination should not leave a color stain or fog after development.

The above-mentioned matters become important particularly when the supersensitization is applied to the green-sensitive emulsion of a color photographic material.

That is, the combination is desired to provide a high green-sensitivity and a spectral sensitization zone necessary for the attainment of the best color producibility as a light-sensitive color photographic material. Further, the combination is required to be such that even when used together with a magenta coupler, i.e., a magenta color-forming agent which couples with the oxidation product of a color developer of the p-phenylenediamine type to form a color image, the combination should not bring about any degradation of green sensitivity or desensitization due to interaction with the magenta coupler. However, all the combinations used in the prior art super-sensitization have some of the above-mentioned drawbacks, and have not been satisfactory.

As the result of extensive studies, we have found that not only a marked increase in color sensitization can be attained but also all the above-mentioned conditions can be satisfied by incorporating into a silver halide photographic emulsion a combination of at least one compound of the aforesaid general formula (I) and at least one compound of the aforesaid general formula (II).

Further, according to the present invention, the spectral maximum values of individual sensitizing dyes can be unified to a collective spectral maximum value to make it possible to attain the best green sensitivity. Moreover, even when the emulsion is treated under a safety light, it is possible to obtain a light-sensitive silver halide photographic material having a high green light sensitivity without any significant fogging.

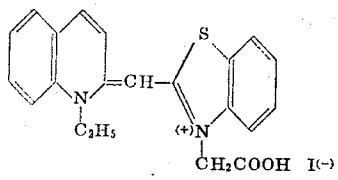
All the sensitizing dyes of the general formulas (I) and (II) are ortho-type sensitizing dyes. Among these, the compound of the formula (I), when used singly, is a green-sensitive sensitizing dye showing the maximum wavelength of color sensitization in a short wavelength region (540 mμ– 550 mμ), whereas the compound of the formula (II) is a green-sensitive sensitizing dye showing the maximum wavelength of color sensitization in a long wavelength region (550 mμ – 560 mμ). When these compounds are used independently, therefore, it is impossible to obtain a green-sensitive silver halide emulsion which sufficiently sensitizes in the required wavelength region. However, we have found that when a specific combination of the compounds of the aforesaid formulas (I) and (II) is used, there is attained a marked green sensitization derived from the synergistic effect of said sensitizing dyes. That is, when the long wavelength portion in the green-sensitive region is reinforced with a short wavelength portion, there are attained not only a high green sensitivity but also a green sensitization having a fresh color-sensitization maximum which cannot be exhibited if the compounds are used singly. Further, when the specific combination of sensitizing dyes according to the present invention is used, the sensitizing dyes necessary in the multi-layer type color photography can be prevented from diffusion into other layers. Such effect is valuable in accomplishing a faithful color reproduction in color photography.

Typical examples of the compounds of the general formulas (I) and (II) are enumerated below, but com-

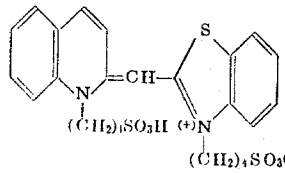
pounds usable in the present invention are not limited only to these compounds.

Examples of the compounds of the general formula (I):

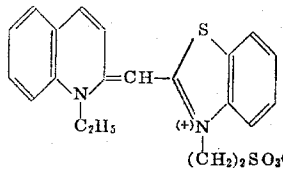
(1)



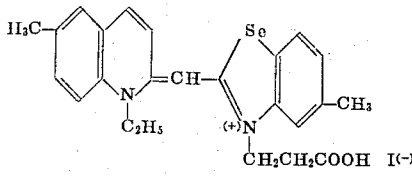
(2)



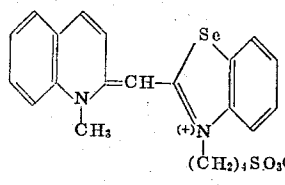
(3)



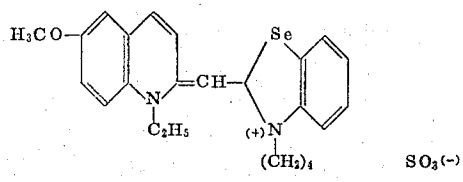
(4)



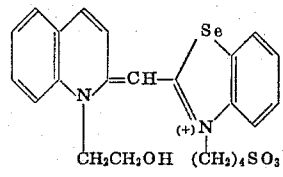
(5)



(6)

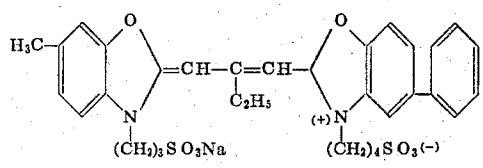


(7)

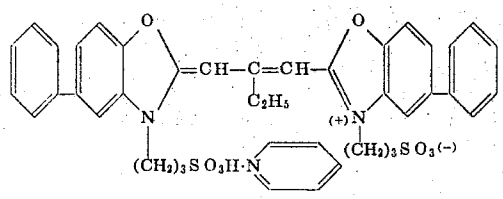


Examples of the compounds of the general formula (II):

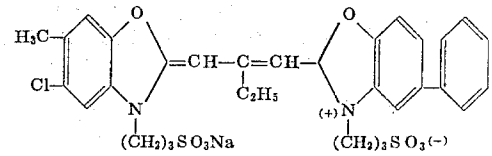
(8)



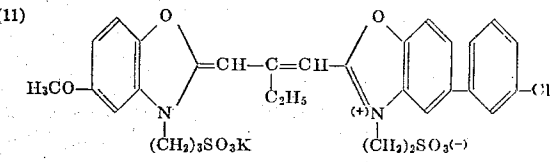
(9)



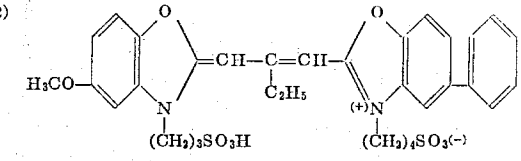
(10)



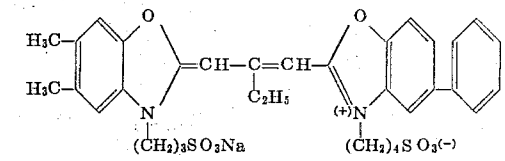
(11)



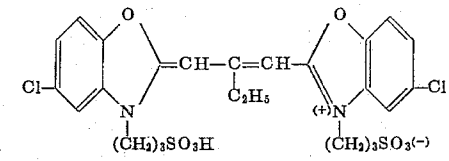
(12)



(13)



(14)



A light-sensitive photographic material according to the present invention, which has been supersensitized by incorporation of a specific combination of the above mentioned compounds, has such excellent properties as mentioned previously, and the combination of the compounds in accordance with the present invention can impart an ideal green sensitivity to silver halide emulsions. Thus, the combination of said compounds is effective as a markedly excellent spectral sensitizer for high sensitivity green-sensitive photographic materials, particularly for green-sensitive emulsions of color photographic materials, according to application purposes. In addition thereto, the combination is applicable to, for example, ordinary black-and-white photographic materials, various light-sensitive materials of the image transfer type, and color photographic materials of the type containing coloring dyes to be treated according to silver-bleaching method.

The distribution of spectral sensitization maxima of the silver halide emulsion according to the present invention is variable depending on the kinds and proportions of the sensitizing dyes of the general formulas (I) and (II). These compounds may be added to a silver halide emulsion after dissolving them either singly or in combination in an optionally water-miscible organic solvent such as methanol or ethanol. The time of addition of these sensitizing dyes to a silver halide photographic emulsion may be at any stage during the preparation of the emulsion, but is preferably immediately after completion of the second ripening, in general. The amounts of the compounds to be added vary depending on the kinds of the compounds and of the silver halide emulsion. Ordinarily, however, the total amount of the compounds of the general formulas (I) and (II) is variable within a wide range from 1 to 200 mg. per kg. of the silver halide emulsion. In this case,

the ratio of the compound (I) to the compound (II) is preferably in the range from 1 : 10 to 5 : 1 by weight.

The emulsion used in the present invention may have been incorporated with a noble metal sensitizer, a sulfur sensitizer or a polyalkylene oxide type compound. Further, the emulsion may have, if necessary, been spectrally sensitized by using the said compounds together with another sensitizing dye such as, for example, a cyanine or merocyanine dye. In addition, the emulsion may have been incorporated according to an ordinary procedure with such photographic additives as stabilizer, surfactant, hardener, etc.

The green-sensitive emulsion for color photographic material used in the present invention may have further been incorporated with magenta couplers which develop colors by reaction of a p-phenylenediamine type color developer, and which have nuclei as, for example pyrazolone and imidazolone nuclei. These couplers may be any of oleophilic or hydrophilic couplers having in the active methylene or methine portions substituents capable of being released by color development reaction, or diffusion-preventing groups or water-solubilizing groups.

Ordinarily, the support used to prepare the light-sensitive material of the present invention may be any of paper, and cellulose triacetate or polyester and the like natural and synthetic high molecular weight films.

The present invention is illustrated in further detail below with reference to examples, but it is needless to say that the invention is not limited to these examples, and various modifications are possible within the scope of the invention set forth in the claim. Example 1

A high speed silver iodobromide emulsion containing 5 mole percent of silver iodide which has been treated with a gelatin coagulant (Japanese Patent Publication No. 16,086/60) was subjected to second ripening according to gold sensitization and sulfur sensitization methods, and then divided into several portions. Each divided emulsion was incorporated with a methanol solution of each of or a mixture of the sensitizing dyes set forth in Table 1. Subsequently, the emulsion was allowed to stand at about 40° C. for 20 minutes to stabilize the color stabilizing action thereof, incorporated with given amounts of a stabilizer, a hardener and a coating aid, coated on a film base and then dried to obtain a green-sensitive photographic material.

The thus obtained samples were individually exposed to a sensitometer Model KS.I (manufactured and sold by Konishiroku Photo Industry Co., Ltd.) using a daylight source of 160 luxes (5,400° K) with a green filter having a transmission maximum at 525 mμ, and then developed at 20° C. for 5 minutes with a developer of the following composition:

Metol (N-methyl-p-aminophenol sulfate)	3 g.
Anhydrous sodium sulfite	50 g.
Hydroquinone	6 g.
Sodium carbonate (monohydrate)	29.5 g.
Potassium bromide	1 g.
Water to make	2 liters

The results obtained were as set forth in Table 1, in which the relative speed is a speed to green light, calculated by assuming as 100 that of Sample No.1 in which the exemplified dye (2) had been incorporated singly.

TABLE 1

Sample No.	Amount of exemplified compound incorporated (per kg. of emulsion)		Relative speed	Fog	Sensitivity maximum (mμ)
1	(2)	50 mg.	100	0.04	545
2	(10)	50 mg.	120	0.05	555
3	(2)	25 mg. +	150	0.03	550
	(10)	25 mg.			
4	(5)	50 mg.	110	0.05	545
5	(12)	50 mg.	130	0.06	560
6	(5)	25 mg. +	160	0.03	555
	(12)	25 mg.			
7	(6)	50 mg.	120	0.05	550
8	(9)	50 mg.	150	0.07	555
9	(6)	25 mg. +	160	0.04	550
	(9)	25 mg.			

Table 1 shows that the combination of the sensitizing dyes according to the present invention improves the green light sensitivity of the photographic material.

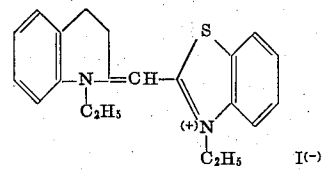
Example 2

A high speed silver iodobromide emulsion for negatives, which had been adjusted to the optimum sensitivity according to gold sensitization and sulfur sensitization, was divided into several portions each 1 kg. in weight. Each divided emulsion was incorporated with a combination of 0.1 percent methanol solutions of the individual compounds set forth in Table 2.

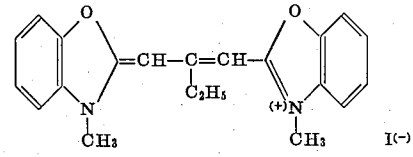
For comparison, one of the divided emulsions was incorporated with a combination of the sensitizing dyes disclosed in U.S. Pat. No. 2,132,866 which had the following formulas:

Control dyes:

(Control I):



(Control II):



Each of the thus treated emulsions was allowed to stand at about 40° C. for 20 minutes to stabilize the color sensitizing action thereof, and then incorporated with a suitable amount of 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene as a stabilizer. Thereafter, 1-(2,4,6-trichlorophenyl)-3-(3-(2,4-di-tert-amyl-phenoxyacetamido)-benzamido)-5-pyrazolone as a magenta coupler was dissolved at an elevated temperature in a mixed solvent comprising di-n-butyl phthalate and ethyl acetate, and then dispersed in a gelatin solution by use of sodium alkylbenzenesulfonate, and a given amount of the resulting dispersion was added to the emulsion. Subsequently, the emulsion was incorporated with a hardener and a coating aid and then adjusted to pH 6.8 to prepare a green-sensitive color photographic emulsion.

This emulsion was uniformly coated on a cellulose triacetate film to a dry thickness of 5 μ to obtain a sample. The thus obtained samples were exposed in the same manner as in Example 1 and then subjected to sensitometry. The composition of the color developer used in the sensitometry was as follows:

Color developer (developed at 20°C. for 12 minutes):

Benzyl alcohol	3.8 ml.
Anhydrous sodium sulfite	2.0 g.
N-Ethyl-N-β-methanesulfonamido-ethyl-3-methyl-4-aminoaniline sulfate	5.0 g.
Sodium carbonate (monohydrate)	50.0 g.
Potassium bromide	1.0 g.
Caustic soda	0.6 g.
Water to make	1 liter

After the development, each sample was subjected to ordinary bleaching, fixing and water-washing treatment, and then measured in speed to green light and residual color (fog) to obtain the results set forth in Table 2, in which the relative speed is a speed to green light calculated by assuming as 100 that of the sample in which the combination of the control dyes I and II had been incorporated.

TABLE 2

Sample No.	Amount of exemplified compound incorporated	Relative speed	Residual color (fog)
10	(Control I) 20 mg. + (Control II) 20 mg.	100	0.05
11	(3) 30 mg. + (8) 10 mg.	120	0.03
12	(3) 10 mg. + (8) 30 mg.	120	0.04
13	(1) 30 mg. + (9) 10 mg.	130	0.04
14	(1) 10 mg. + (9) 30 mg.	140	0.05
15	(7) 30 mg. + (11) 10 mg.	110	0.03
16	(7) 10 mg. + (11) 30 mg.	130	0.03

From Table 2, it is understood that the light-sensitive silver halide photographic materials of the present invention are excellent green-sensitive color photographic materials which are not deteriorated in optical sensitizing property and less in residual color even when present together with a magenta coupler.

Example 3

A silver chlorobromide emulsion for photographic positives, containing 20 mole percent of silver bromide was subjected to second ripening to the optimum degree and then divided into several portions each 1 kg. in weight. Each divided emulsion was incorporated with a combination of the present compounds set forth in Table 3. Thereafter, 1-(2,4,6-trichlorophenyl)-3-(3-dodecyl-succinimidobenzamido)-5-pyrazolone as a magenta coupler was dissolved at an elevated temperature in a mixed solvent comprising di-n-butyl phthalate and ethyl acetate, and then dispersed in a gelatin solution by use of sodium alkylbenzenesulfonate, and a given amount of the resulting dispersion was added to the emulsion. Subsequently, the emulsion was incorporated with a hardener and a coating aid, coated on a film base and then dried to prepare a sample. Each of the thus prepared samples was exposed and subjected to color development in the same manner as in Example 2 to obtain a magenta color image. The relative speed and residual color (fog) of each sample were as set forth in Table 3, in which the relative speed is as defined previously.

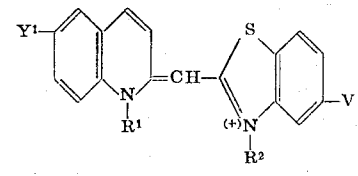
TABLE 3

Sample No.	Amount of exemplified compound incorporated (per kg. of emulsion)	Relative speed	Residual color (fog)
17	(Control I) 15 mg. + (Control II) 15 mg.	100	0.04
18	(1) 15 mg.+(14) 15 mg.	150	0.02
19	(1) 10 mg.+(14) 20 mg.	160	0.03
20	(4) 15 mg.+(9) 15 mg.	140	0.03
21	(4) 10 mg.+(9) 20 mg.	130	0.04

As is clear from Table 3, the samples according to the present invention were excellent in green sensitivity and residual color.

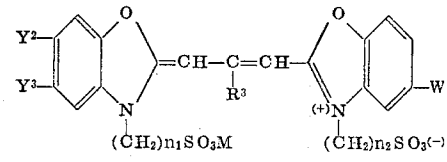
We claim:

1. A light-sensitive silver halide photographic material characterized by containing in the light-sensitive silver halide emulsion a combination comprising at least one monomethinecyanine dye of the formula,



(I)

wherein Y^1 is a hydrogen atom, a lower alkyl group or a lower alkoxy group; Z is S or Se; V is a hydrogen atom or a lower alkyl group; R^1 is a lower alkyl group which may contain a sulfo or hydroxy group; R^2 is a sulfoalkyl group or a carboxyalkyl group having one to four carbon atoms; X is an anion; and m is zero or one, and at least one oxacarbocyanine dye of the formula,

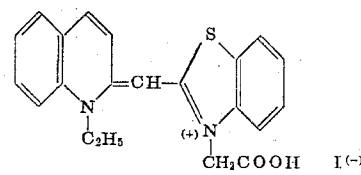


(II)

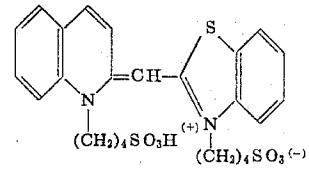
wherein Y^2 is a hydrogen atom or a lower alkyl group; Y^3 is a hydrogen atom, a lower alkyl group, a lower alkoxy group, a halogen atom or a phenyl group; W is a halogen atom or a phenyl group; R^3 is a lower alkyl group; M is a hydrogen atom or an alkali metal atom; and n_1 and n_2 are individually 2, 3 or 4.

2. A light-sensitive silver halide photographic material according to claim 1, wherein the compound of said formula (I) is one member selected from the group consisting of

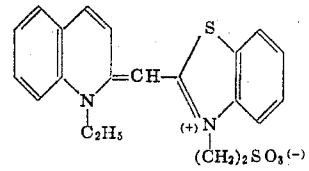
(1)



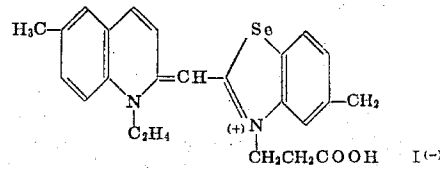
(2)



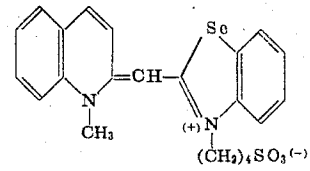
(3)



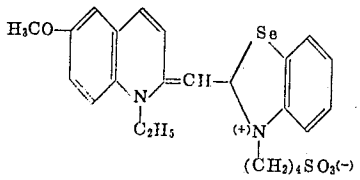
(4)



(5)

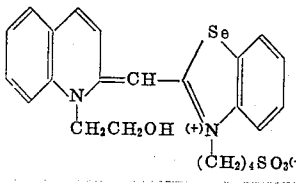


(6)



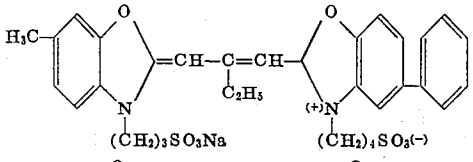
and

(7)

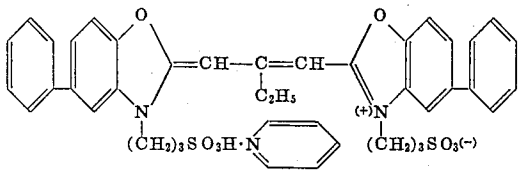


and the compound of said formula (II) is one member selected from the group consisting of

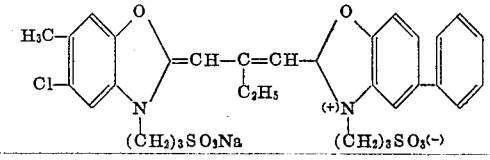
(8)



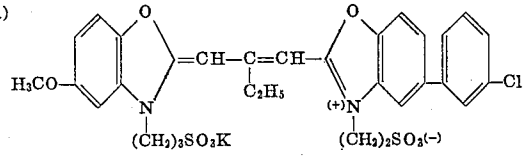
(9)



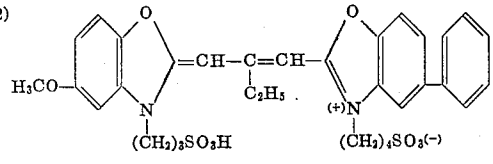
(10)



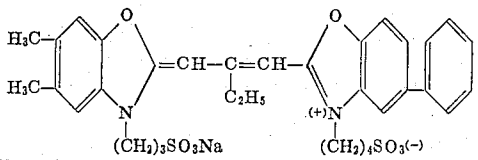
(11)



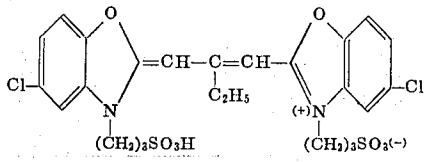
(12)



(13)



(14)



3. A light-sensitive silver halide photographic material according to claim 2, wherein the exemplified compound (2) and the exemplified compound (10) are used in combination.

4. A light-sensitive silver halide photographic material according to claim 2, wherein the exemplified compound (5) and the exemplified compound (12) are used in combination.

5. A light-sensitive silver halide photographic material according to claim 2, wherein the exemplified compound (6) and the exemplified compound (9) are used in combination.

6. A light-sensitive silver halide photographic material according to claim 2, wherein the exemplified compound (3) and the exemplified compound (8) are used in combination.

7. A light-sensitive silver halide photographic material according to claim 2, wherein the exemplified compound (1) and the exemplified compound (9) are used in combination.

8. A light-sensitive silver halide photographic material according to claim 2, wherein the exemplified compound (7) and the exemplified compound (11) are used in combination.

9. A light-sensitive silver halide photographic material according to claim 2, wherein the exemplified compound (1) and the exemplified compound (14) are used in combination.

10. A light-sensitive silver halide photographic material according to claim 2, wherein the exemplified compound (4) and the exemplified compound (9) are used in combination.

* * * * *