United States Patent [19]

Sato et al.

[11] **3,776,739**

[45] ***Dec. 4, 1973**

[54] **SPECTRALLY SENSITIZED SILVER HALIDE PHOTOGRAPHIC EMULSION**

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[*] Notice: The portion of the term of this patent subsequent to July 18, 1989, has been disclaimed.

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[21] Appl. No.: **115,550**

[30] **Foreign Application Priority Data**

Feb. 16, 1970 Japan 45/13284

[52] **U.S. Cl.** **96/137,** 96/139, 260/240.6

[51] **Int. Cl.** **G03c 1/18**

[58] **Field of Search** 96/137, 142, 139

[56] **References Cited**

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1,846,303	2/1932	Brooker	96/137
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Brooker et al., Journal American Chemical Society, Vol. 57, pages 2,480–2,488, (1935).

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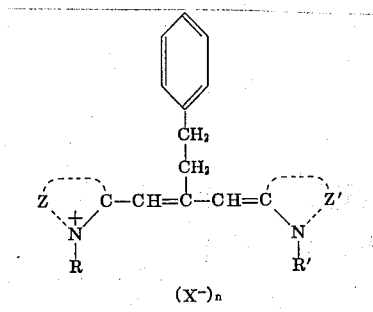
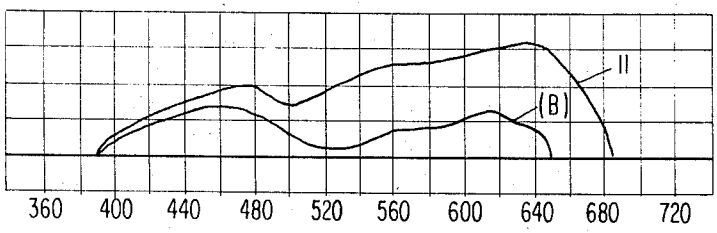
[57] **ABSTRACT**

A spectrally sensitized silver halide photographic emulsion containing at least one sensitizing dye represented by the following general formula



wherein Z and Z′, each represents the atomic group necessary to complete a benzothiazole nucleus, a benzoselenazole nucleus or a naphthothiazole nucleus, R and R′ each represents an alkyl group, a carboxyalkyl group or a sulfoalkyl group, at least one of said R and R′ being a carboxyalkyl or a sulfoalkyl group, X represents an anion and *n* is 0 or 1, is disclosed. The emulsion is highly sensitive to red light.

5 Claims, 1 Drawing Figure



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SPECTRALLY SENSITIZED SILVER HALIDE PHOTOGRAPHIC EMULSION

BACKGROUND OF THE INVENTION

1. Field of the Invention

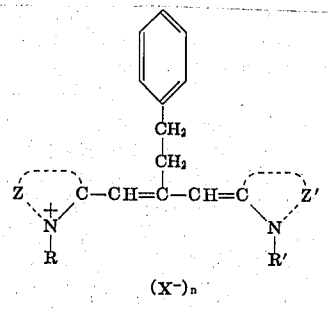
The present invention generally relates to a silver halide photographic emulsion containing a novel sensitizing dye. More particularly, the present invention relates to a silver halide photographic emulsion having a high sensitivity to red.

2. Description of the Prior Art

It is well known in the technical field of silver halide manufacture, emulsion manufacutre, that addition of a sensitizing dye to a silver halide photographic emulsion broadens the wave length region over which the emulsion is sensitized, thereby optically sensitizing the silver halide photographic emulsion. It is generally accepted that the spectral sensitivity is most often influenced by the chemical structure of the sensitizing dye, and particularly the maximum spectral sensitivity in the longer wave length region. This is presumed to be caused by sensitizing dye aggregation on the surface of silver halide grains, is apt to be influenced by the chemical structure or steric effects of substituents of the sensitizing dye. Accordingly, if a desired photosensitive wave length region is to be highly sensitized with a photographic light sensitive material, it is practically extremely important to employ such a sensitizing dye as having the desired selectivity.

SUMMARY OF THE INVENTION

The present invention provides a silver halide photographic emulsion which is highly sensitive to red. The present invention can be achieved by incorporating a novel sensitizing dye into a silver halide photographic emulsion. The novel sensitizing dye is represented by the following general formula (I):



$(X^-)_n$

wherein Z and Z′ represent the atomic groups necessary to complete a benzothiazole nucleus (for example, the nucleus of benzothiazole, 5-chlorobenzothiazole, 5-bromobenzothiazole, 5-methylbenzothiazole, 5,6-dimethylbenzothiazole, 5-phenylbenzothiazole, 5-methoxybenzothiazole, 5-ethoxybenzothiazole, 5-methoxycarbonylbenzothiazole, 5-hydroxybenzothiazole, 5-methyl-6-ethoxybenzothiazole, and the like), a benzoselenazole nucleus (for example, the nucleus of benzoselenazole, 5-chlorobenzoselenazole, 5-methylbenzoselenazole, 5-methoxybenzoselenazole, 5-hydroxybenzoselenazole, 5-methoxycarbonylbenzoselenazole, and the like) or a naphthothiazole nucleus (for example, the nucleus of β-naphthothiazole); wherein R and R′ each represents an alkyl group (for example, an ethyl group, an n-propyl group, and the like), a carboxyalkyl group (for example, a β-carboxyethyl group, a ν-carboxypropyl group, a δ-carboxybutyl group, a ω-carboxypentyl group, and the like), or a sulfoalkyl group, (for example, a ν-sulfopropyl group, a ν-sulfobutyl group, a δ-sulfobutyl group, and the like), at least one of R and R′ being a carboxyalkyl or sulfoalkyl group; wherein X represents an anion (for example, a chloride ion, a bromide ion, an iodide ion, a p-toluene sulfonate ion, an ethyl sulfonate ion and the like); and wherein *n* is 0 or 1 provided that when *n* is 0, the dye is an intramolecular salt.

BRIEF DESCRIPTION OF THE DRAWING

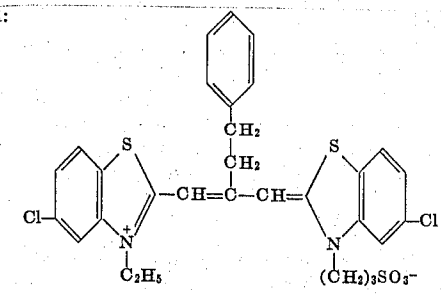
The accompanying drawing is a graphical representation of the spectral sensitization of a photographic emulsion incorporating a novel sensitizing dye of the present invention, Dye No. 11 described hereinafter and in the Examples, in comparison with a photographic emulsion incorporating a sensitizing dye, Dye B, described hereinafter and in the Examples but outside the scope of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

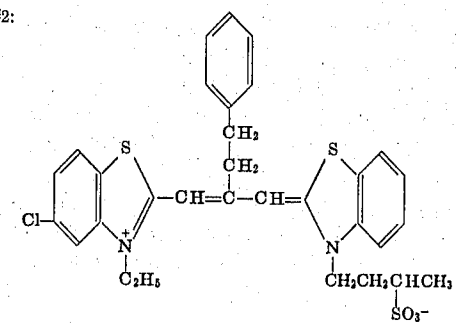
As defined in the above-described general formula (I), one of the characteristics of the sensitizing dyes employed in the present invention is that the dyes have a phenethyl group in their meso position, the substituent exerting an influence upon formation and properties of the J-aggregate of the dye and being particularly effective in sensitizing the wave length region of from 630 to 650 mμ.

Typical examples of novel sensitizing dyes represented by the above-described formula (I), employed in this invention, are shown below by way of exemplification.

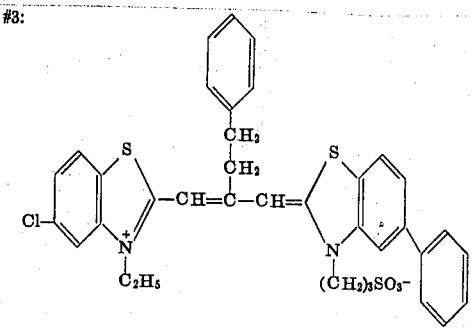
Dye #1:



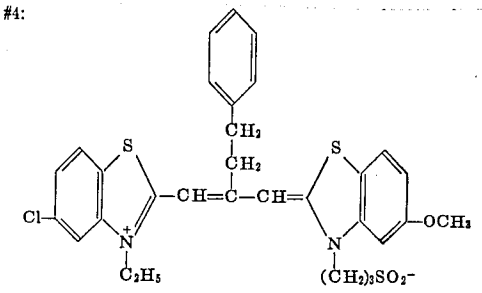
Dye #2:



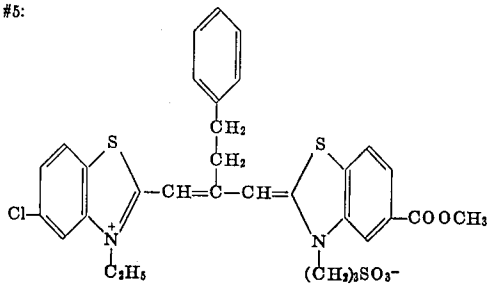
Dye #3:



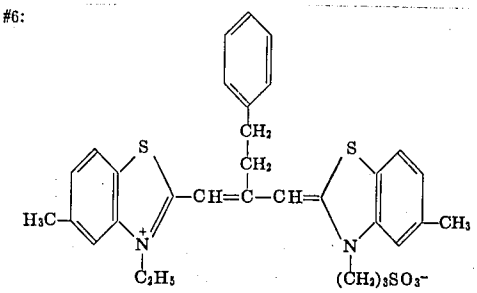
Dye #4:



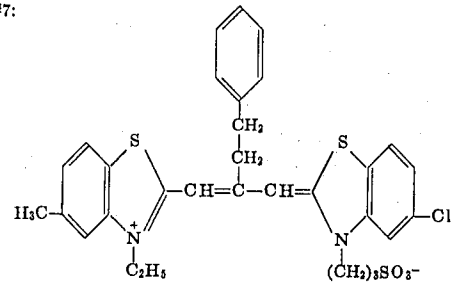
Dye #5:



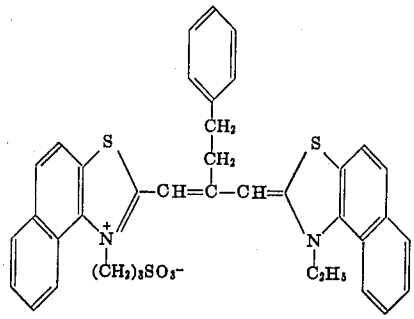
Dye #6:



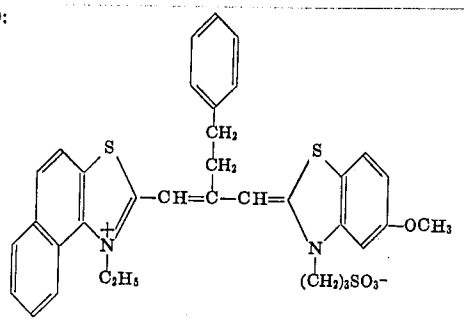
Dye #7:



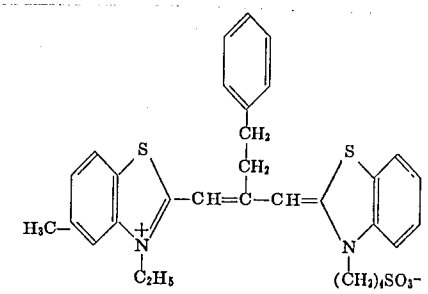
Dye #8:



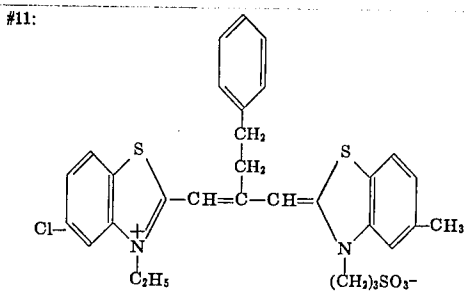
Dye #9:



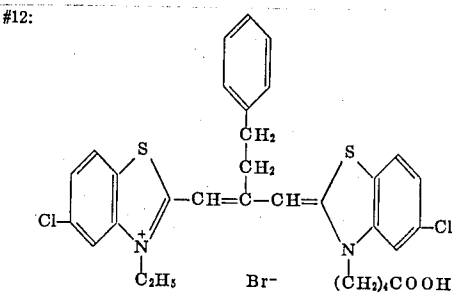
Dye #10:



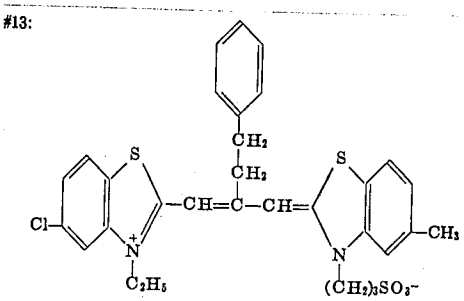
Dye #11:



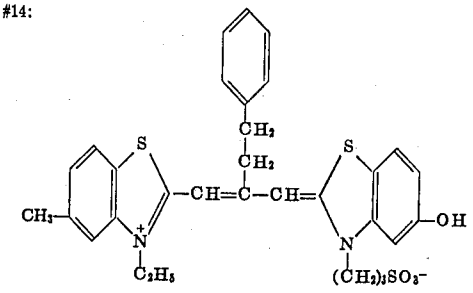
Dye #12:



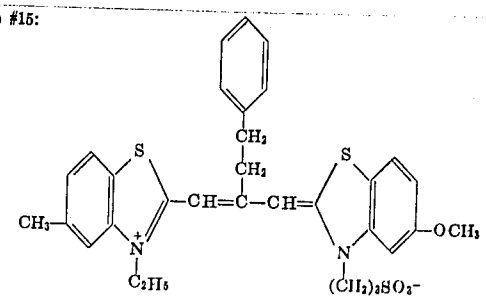
Dye #13:



Dye #14:

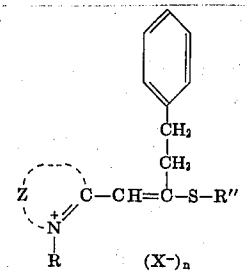


Dye #15:



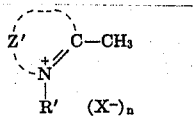
The novel sensitizing dyes of the general formula (i) employed in accordance with the present invention can be prepared in a conventional manner. For example, they may be readily synthesized by one skilled in the art in the manner described in U.S. Pat. No. 2,503,776, in German Patent No. 929,080, or in German Patent No. 1,072,765.

Thus, the novel sensitizing dyes represented by the general formula (I) can be prepared by reacting a compound represented by the following general formula (II):



(II)

wherein Z, R, X and *n* have the same meaning as defined in the above-described general formula (I), and R'' represents an alkyl group, such as a methyl and an ethyl group, with a compound represented by the following general formula (III):



(III)

wherein Z', R', X and *n* have the same meaning as defined in the above-described general formula (I). The reaction can be effected by heating the reactants under reflux in a suitable solvent, such as methanol, ethanol and isopropanol, in the presence of a basic condensing agent, such as triethylamine.

The physical properties of the typical examples of the novel sensitizing dyes of the general formula (I) presented hereinbefore are shown in Table 1 below.

TABLE 1

Dye No.	M.P.(°C)	MeOH λ max (nm)
1	281	559
2	275	558
3	238	562
4	277	563
5	280	558
6	269	558
7	203	556
8	232	584
9	297	577
10	257	555
11	258	564
12	246	558
13	281	558
14	298	564
15	268	563

The sensitizing dyes employed according to the present invention are capable of spectrally sensitizing a silver halide photographic emulsion. They are particularly effective in broadening the spectrally sensitizable region of a gelatino-silver halide photographic emulsion. They are also capable of sufficiently sensitizing a photographic emulsion containing a hydrophilic colloid other than gelatin, for example, agar collodion, water-soluble cellulose derivatives, polyvinyl alcohol and other synthetic or natural hydrophilic resins. They are further effective as sensitizing dyes for use in electrophotographs prepared by the zinc oxide method.

In the emulsion employed in accordance with the present invention, various kinds of the silver salts, for example, silver bromide and mixed silver halides, such as silver iodobromide, silver chlorobromide and silver chloroiodobromide, can be used.

In order to prepare the sensitized photographic emulsion of the present invention, one or more than one of the sensitizing dyes have only to be incorporated into a photographic emulsion in any conventional manner. In practice, usually the dyes are dissolved in a suitable solvent, such as methanol and ethanol, and the resulting solution is added into the photographic emulsion. The amount of the sensitizing dye incorporated into the emulsion can be varied over a wide range of from 5 to 200 mg/kg of the emulsion containing 0.5 mole of silver halide, depending upon the effect desired.

Furthermore, it is possible to apply hyper-sensitization or super-sensitization to the photographic emulsion of the present invention in a conventional manner, as described in, e.g., C.E. Mees and T.H. James, *The Theory of the Photographic Process*, Third Edition, p. 252, 253–256, The MacMillan Company.

On manufacturing the photographic emulsion in accordance with the present invention, it is also possible to incorporate into the emulsion, in a conventional manner, generally used additives, such as sensitizers, stabilizers, toning agents, film hardening agents, surface active agents, antifogging agents, plasticizers, development-accelerators, color-developing agents, and fluorescent whitening agents.

The photographic emulsion according to the present invention may be coated in a conventional manner on a suitable support, such as a glass sheet, a cellulose derivative film, a synthetic resin film, and a baryta-coated paper.

The present invention will be further explained in greater detail by reference to the following examples. It is to be understood, however, that the specific examples given herein are only illustrative and the present invention is not intended to be limited thereby.

EXAMPLES

The sensitizing dyes of the invention exemplified above were added into gelatino-silver iodobromide emulsions (AgI : AgBr = 7 moles : 93 moles) to prepare the corresponding silver halide photographic emulsions. The emulsions were then coated on bases of cellulose triacetate followed by drying, the thus coated emulsion thereafter being exposed to light through Fuji No. 7 filter, a red filter manufactured by Fuji Photo Film Co., Ltd. and capable of passing therethrough only light having a wave length longer than 580 nm) followed by development wherein, as a developer there was employed a liquid having the composition as shown in the following Table 2.

TABLE 2

Metol	2 g
Sodium Sulfite	100 g
Hydroquinone	5 g
Borax	2 g

Water added to make the total volume to 1 liter.

In the following Table 3, the sensitivity to red and the maximum sensitization wave length results with the sensitizing dyes of the invention exemplified hereinbe-

fore and sensitizing dyes used for comparison, each being added to the abovedescribed silver iodobromide, are shown.

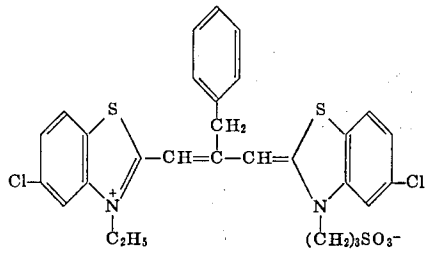
TABLE 3

Ex. No.	Dye No.	Amount of the Dye Added (10^{-5} mol/kg emulsion)	Emulsion	Wavelength where maximum sensitization obtained (nm)	Relative sensitivity to red
1	1	8	AgBr/I	638	900
2	2	8	do	634	820
3	3	8	do	626	920
4	4	8	do	640	900
5	5	8	do	628	850
6	6	8	do	625-630	800
7	7	8	do	632-634	850
8	8	8	do	650	700
9	9	8	do	645	900
10	10	8	do	620	810
11	11	6	do	644	1750
12	12	8	do	635	800
13	13	8	do	634	850
14	14	8	do	620-625	700
15	15	8	do	638	650
Comparative Test Nos.					
1'	A*	8	AgBr/I	660	540
2'	B*	10	do	620	100
3'	C*	8	do	628	580

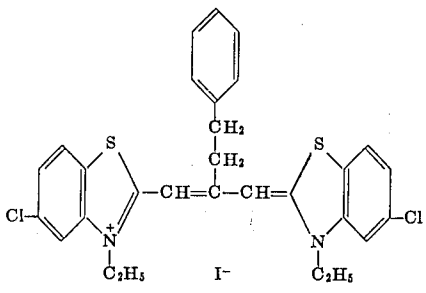
* For comparison purposes

The sensitizing dyes used for comparison have the following formulas:

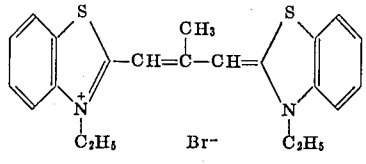
Comparative Sensitizing Dye (A):



Comparative Sensitizing Dye (B):



Comparative Sensitizing Dye (C):

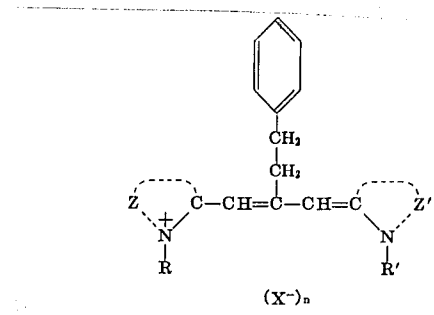


The sensitivity to red was expressed as relative sensitivity to red with respect to that estimated as **100** for Sensitizing Dye B which was obtained by its exposure to light using Fuji 4 filter (red filter).

From the above data, it can be seen that the silver halide photographic emulsion of the present invention provides superior photographic properties. e.g., higher red sensitivity, to the silver halide photographic emulsion containing a sensitizing dye outside the scope of the present invention.

What is claimed is:

1. A silver halide photographic emulsion containing at least one sensitizing dye represented by the following general formula

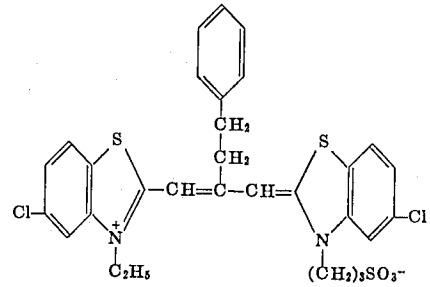


wherein Z and Z' each represent the atomic group necessary to complete a nucleus selected from the group consisting of a benzothiazole nucleus, a benzoselenazole nucleus, and a naphthothiazole nucleus; wherein R and R' each is selected from the group consisting of an alkyl group, a carboxyalkyl group, and a sulfoalkyl group; wherein at least one of R and R' is selected from the group consisting of a carboxyalkyl group and a sulfoalkyl group; wherein X is an anion; and wherein *n* is 0 or 1.

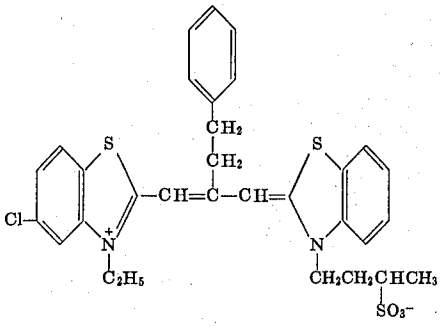
2. A silver halide photographic emulsion as claimed in claim **1**, wherein Z and Z' are selected from the atomic groups necessary to complete a benzothiazole, a 5-chlorobenzothiazole, a 5-bromobenzothiazole, a 5-methylbenzothiazole, a 5, 6-dimethylbenzothiazole, a 5-phenylbenzothiazole, a 5-methoxybenzothiazole, a 5-ethoxybenzothiazole, a 5-methoxycarbonylbenzothiazole, a 5-hydroxybenzothiazole, a 5-methyl-6-ethoxybenzothiazole, a benzoselenazole, a 5-chlorobenzoselenazole, a 5-methylbenzoselenazole, a 5-methoxybenzoselenazole, a 5-hydroxybenzoselenazole, a 5-methoxycarbonylbenzoselenazole, and a β-naphthothiazole nucleus; and wherein R and R' are selected from the group consisting of an ethyl, an n-propyl, a β-carboxyethyl, a ν-carboxypropyl, a δ-carboxybutyl, a ω-carboxypentyl, a ν-sulfopropyl, a ν-sulfobutyl, and a δ-sulfobutyl group.

3. A silver halide photographic emulsion as claimed in claim **1**, wherein said sensitizing dye is selected from the group consisting of

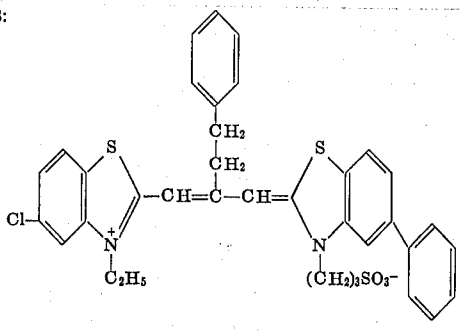
Dye #1:



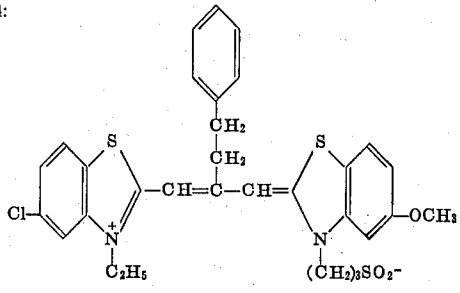
Dye #2:



Dye #3:



Dye #4:



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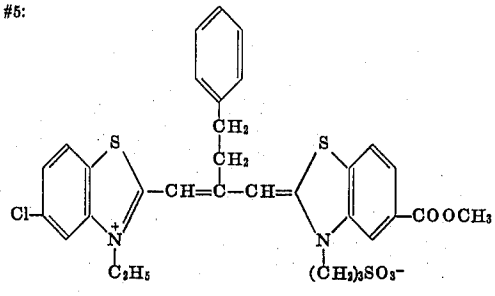

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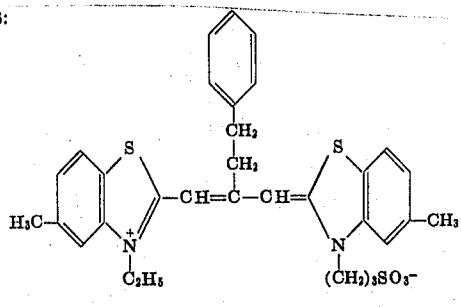

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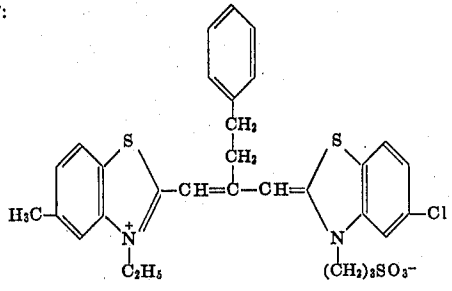
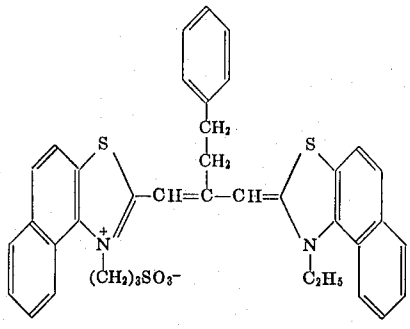
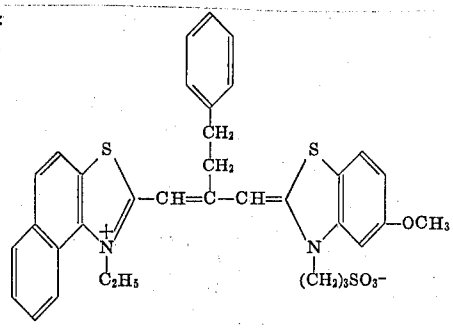


Dye #8:



Dye #9:



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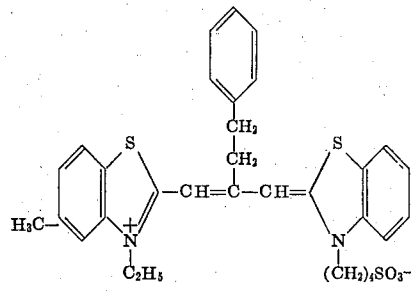

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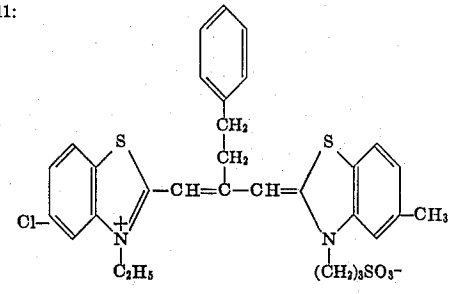

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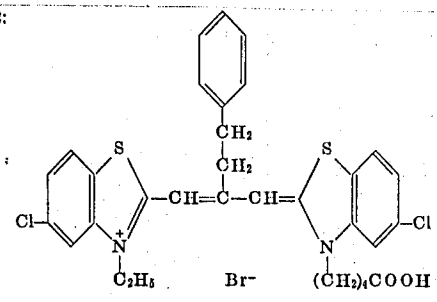

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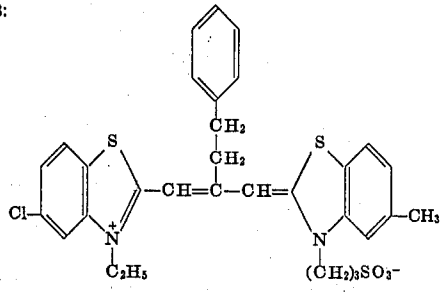
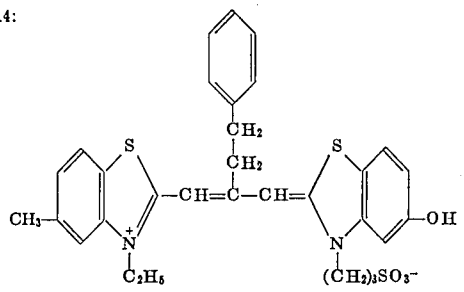


Dye #14:



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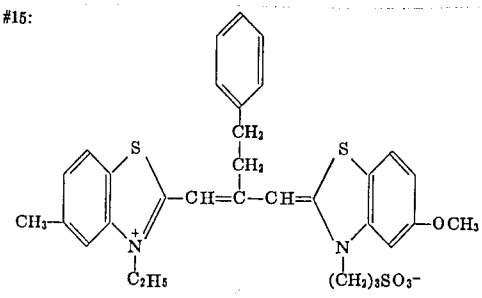

4. A silver halide photographic emulsion as claimed in claim 1, wherein the amount of the sensitizing dye ranges from 5 to 200 mg of dye per kg of emulsion containing 0.5 mole of silver halide.

5. A photographic light-sensitive material comprising a support having thereon at least one layer containing the silver halide emulsion as claimed in claim 1.

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