United States Patent

[11] 3,632,349

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[73] Assignee **Fuji Photo Film Co., Ltd.**
Kanagawa, Japan

[32] Priority **Apr. 9, 1969**
[33] **Japan**
[31] **44/27421**

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[54] **SILVER HALIDE SUPERSENSITIZED PHOTOGRAPHIC EMULSION**
11 Claims, 1 Drawing Fig.

[52] **U.S. Cl.** **96/123,** 96/124, 96/127, 96/137
[51] **Int. Cl.** **G03c 1/28**
[50] **Field of Search** 96/123, 124

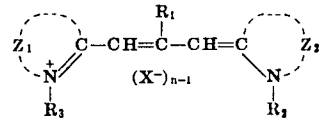
[56] **References Cited**

UNITED STATES PATENTS

2,704,720	3/1955	Jones	96/123
3,432,303	3/1969	Jones et al.	96/124

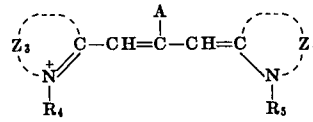
Primary Examiner—J. Travis Brown
Attorney—Sughrue, Rothwell, Mion, Zinn & Macpeak

ABSTRACT: A silver halide photographic emulsion containing at least one sensitizing dye represented by the following formula I:



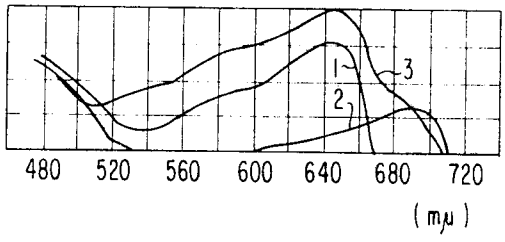
(I)

wherein R_1 is an alkyl group having from one to four carbon atoms; R_2 and R_3 are individually selected from the group consisting of an alkyl group, an allyl group and an alkyl group substituted by a hydroxyl group, an alkoxyl group, a carboxyl group, a sulfo group, a carboxyalkoxyl group or a sulfoalkoxyl group; Z_1 and Z_2 are the same or different atomic groups necessary to complete a benzothiazole nucleus of a benzoselenazole nucleus; n is 1 or 2 and X^- is an acid anion group; and at least one sensitizing dye represented by the following formula II:



(II)

wherein A is a thienyl group, a furyl group or a thienyl group substituted by a halogen atom, an alkyl group or an alkylcarboxyl group; R_4 and R_5 are individually selected from the group consisting of an alkyl group, an aryl group and an alkyl group substituted by a hydroxyl group, an alkoxyl group, a carboxyl group, a sulfo group, a carboxyalkoxyl group or a sulfoalkoxyl group; at least one of R_4 and R_5 being a sulfosubstituted alkyl group; Z_3 is an atomic group necessary to complete a naphthothiazole nucleus or a naphthoselenazole nucleus, and Z_4 is an atomic group necessary to complete a naphthothiazole nucleus, a naphthoselenazole nucleus, a benzothiazole nucleus or a benzoselenazole nucleus.



WAVE LENGTH

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ATTORNEYS

SILVER HALIDE SUPERSENSITIZED PHOTOGRAPHIC EMULSION

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a spectrally sensitized silver halide photographic emulsion and more particularly, to an emulsion whose spectral sensitivity in the red region is raised by the use of a combination of at least two kinds of sensitizing dyes.

2. Description of the Prior Art

It has long been known that, in order to extend the light-sensitive wavelength region of a light-sensitive material further to the long wavelength side, one adds some sensitizing dye to the silver halide emulsion. This is termed spectral sensitization. The spectral sensitization effect depends upon the chemical structure of the sensitizing dye employed, its state in emulsion and various properties of the emulsion such as the crystal habit of the silver halide, the halogen composition, the silver ion concentration and the hydrogen ion concentration. It is also affected by fog inhibitors coexistent in the emulsion, stabilizers, flocculating agents, hardeners, binders and plasticizers.

In the case of a color sensitive material of the incorporated type, particularly those in which a coupler is incorporated, these additives often act so as to lower the spectral sensitivity. In many light-sensitive materials, two or more sensitizing dyes are used in order to sensitize to a predetermined wavelength region according to their use. In many cases, however, the sensitization produced by the use of two or more sensitizing dyes is less than the sum of the sensitizations of the components. This is known as antisensitization. On the other hand, sometimes the use of two or more sensitizing dyes in special combination gives a sensitization greater than the sum of the individual effects. This is known as supersensitization. A severe selection is required for such a combination of two or more sensitizing dyes having a supersensitizing action. Since even a slight difference in chemical structure has a large effect on the supersensitization, it is a view common to all photographic engineers that a combination of sensitizing dyes showing supersensitizing action cannot readily be expected from the chemical structure only of the dyes. It has been very difficult to find a combination of two or more sensitizing dyes showing a supersensitizing action.

A color sensitive material is ordinarily composed of at least three light-sensitive emulsion layers: a blue-sensitive emulsion layer, a green-sensitive emulsion layer and a red-sensitive emulsion layer. The distribution of spectral sensitivity of each emulsion layer is a principal factor in determining the color reproduction characteristics of the light-sensitive material. In order to obtain a suitable color reproduction, in general, the spectral light-sensitive wavelength regions of the blue, green and red-sensitive emulsion layers, respectively, must be separated sufficiently. Above all, the red-sensitive emulsion must have a high sensitivity in the red region and a low sensitivity in the green region, because a dye sensitizing throughout the whole visible region is generally used therefor. In order to obtain a true color reproduction, the maximum sensitizing wavelength should be within a range of from 640 to 650 mμ and the sensitivity of longer wavelengths should be up to at least 690 mμ to which the visible sensitivity extends. Moreover, the sensitizing dye used in the red-sensitive emulsion layer must be prevented from diffusing into another adjacent emulsion layer and sensitizing the same. In the case of a high sensitivity color light-sensitive material, care should be taken to avoid the lowering of a high spectral sensitivity with the passage of time and while being allowed to stand in a state of liquid emulsion.

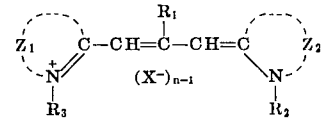
It is therefore an object of the present invention to provide a silver halide emulsion wherein the maximum sensitizing wavelength is not longer than 650 mμ, the spectral sensitivity extends to 680 to 690 mμ in a low sensitivity and the red sensitivity is raised by the supersensitization.

It is another object of the present invention to provide an improved silver halide photographic emulsion wherein the red sensitivity is not given to an adjacent emulsion layer through diffusion when used as a red-sensitive emulsion layer of a color sensitive material.

SUMMARY OF THE INVENTION

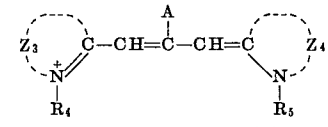
The above-mentioned objects of the present invention can be accomplished by incorporating in a silver halide photographic emulsion a combination of at least one of the sensitizing dyes represented by the following general formula I and at least one of the sensitizing dyes represented by the following general formula II:

General Formula I



wherein R_1 is an alkyl group having one to four carbon atoms, such as methyl and ethyl groups; R_2 and R_3 are individually an alkyl group such as a methyl, ethyl or propyl group, an allyl group or a substituted alkyl group such as 2-hydroxyethyl, 2-methoxyethyl, carboxymethyl, 2-carboxyethyl, 3-carboxypropyl, 4-carboxybutyl, 3-sulfopropyl, 4-sulfobutyl, 3-sulfoisobutyl, 2-carboethoxyethyl, 2-(3-sulfopropoxy)ethyl, 2[2-(3-sulfopropoxy)]ethoxyethyl and 2-hydroxy-1-sulfopropyl groups; Z_1 and Z_2 are the same or different atomic groups necessary for forming a benzothiazole or benzoselenazole nucleus; n is 1 or 2 X^- is an acid anion group such as halide, rhodanate, perchlorate, p-toluene sulfonate, benzene-sulfonate, ethylsulfate, methylsulfate ion, etc., and

General Formula II



wherein A is a thienyl group, a furyl group or a substituted thienyl group such as 2,5-dichloro-3-thienyl, 5-methyl-2-thienyl or 2-methyl-5-carboxy-3-thienyl; R_4 and R_5 are individually an alkyl group, an allyl group or an alkyl group substituted by a group selected from the group consisting of hydroxy, alkoxy, carboxy, sulfo, carboxy alkoxy and sulfoalkoxy, at least one of R_4 and R_5 being a substituted alkyl group containing a sulfo group; Z_3 is an atomic group necessary for forming a naphthothiazole or a naphthoselenazole nucleus and Z_4 is an atomic group necessary for forming a naphthothiazole, naphthoselenazole, benzothiazole or benzoselenazole nucleus.

BRIEF DESCRIPTION OF THE DRAWING

The FIGURE shows the sensitization effects of employing a dye of formula I alone, a dye of formula II alone and a combination of dyes of formulas I and II, respectively.

DETAILED DESCRIPTION OF THE INVENTION

The important features of the present invention are: (1) in the compound represented by the general formula II, at least one of the two heterocyclic nuclei of the cyanine dye is a naphthoselenazole or a naphthothiazole nucleus, (2) there is at least one sulfo-substituted alkyl group on the resonating terminal nitrogen atom in the heterocyclic nucleus and (3) there is either an aryl group, a thienyl group, a furyl group or a substituted thienyl group in the meso position.

There are many cyanine dyes capable of giving characteristics similar to the cyanine dyes of the present invention having an aryl group at the meso position. The sensitizing dye

represented by general formula II shows a very weak spectral sensitizing action only when used alone, but a remarkably high spectral sensitivity when used together with the sensitizing dye represented by general formula I.

Another feature of the present invention is that the maximum sensitizing wavelength is not migrated to longer than the maximum sensitizing wavelength obtained by the sensitizing dye represented by the general formulas, rather there is a tendency of color dilution, a weak sensitivity within the wavelength region 680–690 mμ, a high spectral sensitivity in the red region. The present invention is thus different in this respect from that described in Japanese Pat. Publication No. 4933/1968. In accordance with the present invention, furthermore, the particular dye employed is prevented from diffusing into an adjacent emulsion layer whereby the red sensitivity is not given, and accordingly the color reproduction is improved.

The spectral sensitivity obtained by the use of a combination of the sensitizing dye represented by general formula I and the sensitizing dye represented by general formula II resists the hindering action of a coupler of the incorporated type.

The sensitizing dye represented by general formula I is a carbocyanine dye whose J-band appears easily. The benzothiazole nucleus or benzoselenazole nucleus may be substituted by a halogen atom, a phenyl group, an alkyl group or a hydroxyl group so that the J-band may appear easily or a suitable spectral sensitivity distribution may be given.

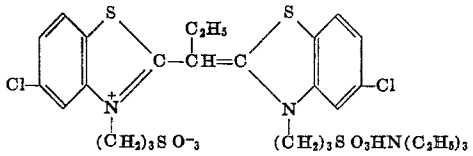
The sensitizing dyes used in the present invention are added to the silver halide emulsion separately or in admixture in the form of a solution in water or in a water-soluble organic solvent such as methanol, ethanol, acetone or pyridine. The amount added and the order of addition to the silver halide emulsion may be varied as desired. In general, the amount of the sensitizing dye added is preferably from 1×10^{-6} to 1×10^{-3} mole per mole of silver halide and the weight ratio of sensitizing dye II to sensitizing dye I is from 100:1 to 1:10, preferably from 20:1 to 1:1.

Any of the following may be used as the silver halide emulsion in the present invention: silver chloride, silver chlorobromide, silver bromide and silver iodobromide. The sensitizing dyes of the present invention may be incorporated into the silver halide emulsion together with a fog inhibitor, a stabilizer, a chemical sensitizer, a hardener, a coupler, a plasticizer, a photographic dye and a coating agent.

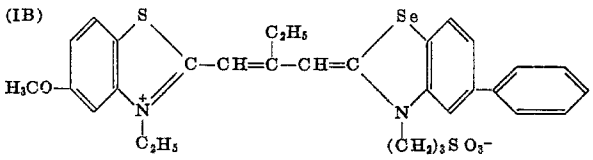
The thus-obtained silver halide photographic emulsion having the foregoing composition may be applied to a suitable support, for example, a cellulose derivative film, polyethylene terephthalate film, other plastic films, baryta paper, resin coated paper, synthetic paper or a glass sheet.

Examples of the sensitizing dyes used in the present invention are shown below, and are merely illustrative in nature:

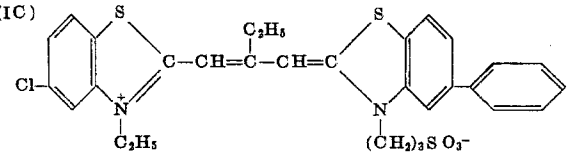
(IA)



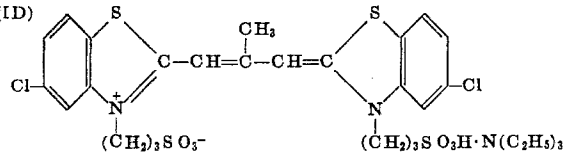
(IB)



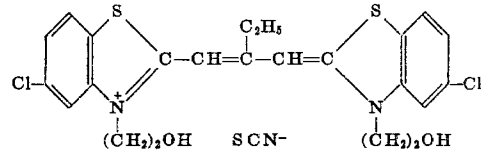
(IC)



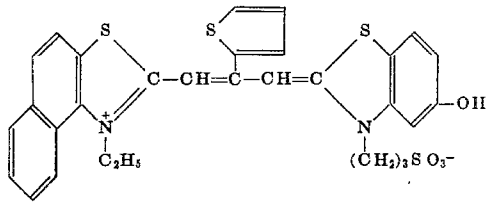
(ID)



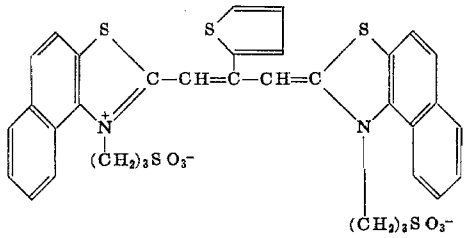
(IE)



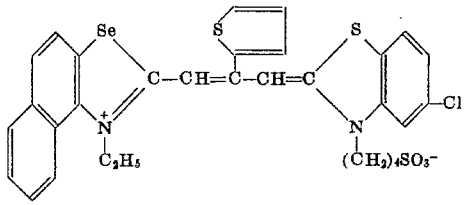
(IIA)



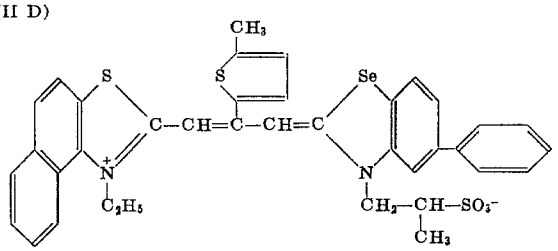
(IIB)



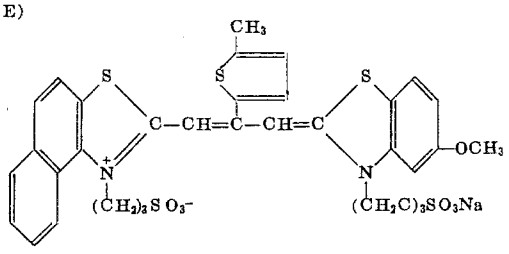
(II C)



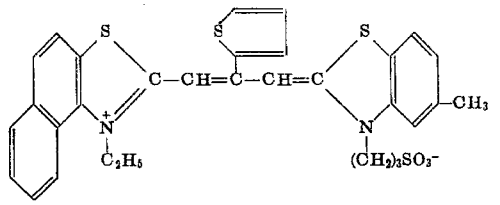
(II D)



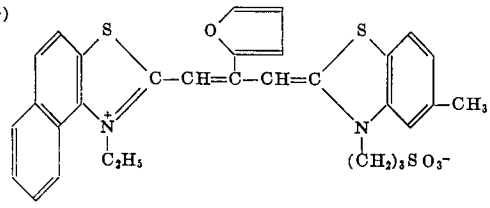
(II E)



(II F)



(IIG)

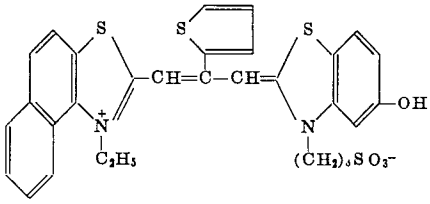


The sensitizing dye of general formula I used in the present invention may be synthesized by any known method, for example, that disclosed in U.S. Pat. No. 2,503,776 or German Pat. No. 929,080.

The sensitizing dye of general formula II may be synthesized by any known method, for example, that disclosed in U.S. Pat. No. 2,060,383, U.S. Pat. No. 2,756,227 or U.S. Pat. No. 2,503,776.

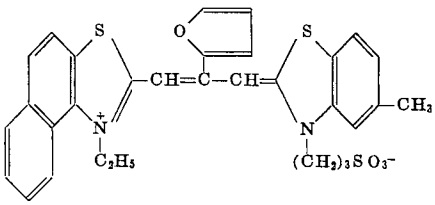
Methods of synthesis of typical sensitizing dyes of the present invention are shown below:

Synthesis of dye (IIA)



0.5 g. of 4,5-benzo-3-ethyl-2-(alpha-thiothienoyl)methylenebenzothiazoline and 0.4 g. of methyl p-toluenesulfonate were reacted for 1 hour by heating and fusing at 110° C. The reaction product is mixed with 0.4 g. of anhydro-5-hdyroxy-2- methyl-3-(3-sulfopropyl)benzothiazolium hydroxide and reacted for 1 hour and 30 minutes in 30 ml. of ethanol and 1 ml. of triethylamine while heating and refluxing. The precipitated crystal is filtered and recrystallized from a mixed solvent of methanol and chloroform to give 0.5 g. of a dye melting at 284° C. (II A). Spectral absorption maximum wavelength 608 mμ (in methanol).

Synthesis of dye (IIG)



0.5 g. of 4,5-benzo-3-ethyl-2-(alpha-throfuroyl)methylenebenzothiazoline and 0.4 g. of methyl p-toluenesulfonate are reacted for 1 hour by heating and fusing at 110° C. The reaction product is mixed with 0.4 g. of anhydro 2,5-dimethyl-3-(sulfopropyl)benzothiazolium hydroxide and reacted for 1 hour in 30 ml. of ethanol and 1 ml. of triethylamine while heating and refluxing. The precipitated crystal is filtered and recrystallized from a mixed solvent of methanol and chloroform to give 0.4 g. of a dye (II G) melting at 282° C. Spectral absorption maximum wavelength 607 mμ (in methanol).

The following examples are given in order to further illustrate the present invention and are not intended to limit the same.

EXAMPLE 1

Five hundred grams of a silver iodobromide gelatin emulsion (silver iodobromide content 4.0 mole percent) prepared in a conventional manner was taken and rendered molten in a thermostat at 40° C. As shown in table 1, a predetermined amount of the sensitizing dye represented by general formula I and a predetermined amount of the sensitizing dye represented by general formula II were mixed in solution and added thereto with agitation.

The emulsion was allowed to stand in the thermostat at 37° C. while stirring for 10 minutes, then uniformly coated onto a glass sheet support in a proportion of 7.0 ml. per cabinet size, set and dried to obtain a light-sensitive sample. The sample was cut and subjected to light-wedge exposure using a red light from a light source having a color temperature of 5,400° K. obtained by adapting a Davis-Gibson conversion filter to a light source having a color temperature of 2,666° K. and using a K-7 filter (made by Fuji Photo Film Co., Ltd.) permitting wavelengths longer than about 600 mμ.

The exposed sensitive sample was developed at 20° C. for 10 minutes with a developer having the following composition, stopped, fixed and washed with water to obtain a strip. Measurement of the density thereof was carried out by the use of an S-type densitometer made by Fuji Photo Film Co., Ltd. to determine the relative red sensitivity. The optical density point at which the sensitivity was determined was a point of (fog density +0.10). The results are shown in table 1.

Composition of Developer	
water (50° C.)	750 ml.
metol	2 g.
anhydrous sodium sulfite	100 g.
hydroquinone	5 g.
borax	2 g.
water to	1,000 ml.
pH=8.70±0.10	

Sensitizing dye	Amount used, ml. (mole conc.)	Sensitizing dye	Amount used, ml. (mole conc.)	Rel. red sensitivity	Fog	$\lambda S_{max.}$ mμ	Note
1 A	10 (1×10^{-3})			85	0.11	650	
	20			100	0.13	650	Curve (1) in figure.
		II A	1 (5×10^{-4})	27	0.09	685	
			20	37	0.12	685	
1 A	20 (1×10^{-3})		5	166	0.17	650	
	20		10	200	0.17	650	Curve (3) in figure.
		II B	1 (5×10^{-4})	30	0.12	695	Curve (2) in figure.
			2	30	0.14	695	
1 A	20 (1×10^{-3})		5	141	0.12	645	
	20		10	141	0.12	645	
		II D	10 (5×10^{-4})	21	0.10	685	
			20	25	0.10	685	
1 A	20 (1×10^{-3})		5	111	0.09	650	
	20		10	123	0.09	650	
		II E	10	21	0.08	680	
			20	20	0.12	680	
1 A	20 (1×10^{-3})		5 (5×10^{-4})	148	0.15	650	
	20		10	148	0.15	655	
		II F	10	21	0.08	680	
			20	27	0.09	680	
1 A	20 (1×10^{-3})		5 (5×10^{-4})	126	0.10	645	
	20		10	140	0.11	645	

Sensitizing dye	Amount used, ml. (mole conc.)	Sensitizing dye	Amount used, ml. (mole conc.)	Rel. red sensitivity	Fog	$\lambda S_{max.}$ mμ	Note
1 B	20 (5×10^{-3})			92	0.11	640	
	40			95	0.12	640	
	40	II A	5 (5×10^{-4})	110	0.18	640	
	40		10	115	0.18	640	
1 C	20 (5×10^{-4})			80	0.10	638	
	40			85	0.12	638	
	40	II D	5 (5×10^{-4})	100	0.16	635	
	40		10	105	0.15	635	
1 D	10 (1×10^{-3})			113	0.10	645	
	20			113	0.15	645	
		II A	5 (5×10^{-4})	132	0.16	690	
			10	125	0.10	690	

The light-sensitive emulsion sample half exposed was cut and exposed using a reflection type grating spectograph, followed by a series of developing processings to obtain a spectrogram. The results are shown in the accompanying graph for comparison. Curve 1 is a curve obtained by using 20 ml. of a solution of (I A) having a mole concentration of 5×10^{-3} curve 2 is a curve obtained by using 1 ml. of a solution of (II B) having a mole concentration of 5×10^{-4}, and curve 3 is a curve obtained by jointly using (I A) and (II B). As is evident from the graph, the supersensitizing effect is marked.

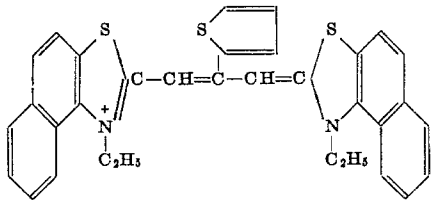
EXAMPLE 2

One thousand grams of a silver iodobromide gelating emulsion (silver iodobromide content 6 mole percent) prepared in a conventional manner was taken and rendered molten in a thermostat at 37° C. As in example 1, a predetermined amount of sensitizing dye was added thereto, stirring adequately and allowed to stand at 37° C. for 60 minutes. Sensitizing dye A shown below was used for comparison purposes in addition to the sensitizing dyes of the present invention.

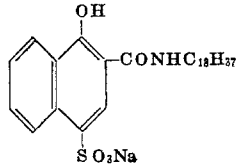
Then 200 ml. of a 5 percent aqueous solution of cyan coupler B having the structure shown below was added thereto and stirred. A surfactant was then added to the resulting emulsion and the emulsion was coated onto a cellulose triacetate film to obtain a red-sensitive color photographic material.

The photographic material was subjected to light-wedge exposure in a manner similar to example 1, then to development at 20° C. for 12 minutes with a color forming developer containing a N,N'-diethylaminoparaaminoaniline derivative, first fixing, bleaching, second fixing and water washing to obtain a negative cyan image. Measurement of the red filter density was carried out by the use of a red filter to obtain a relative red sensitivity. The results are shown in table 2.

Sensitizing dye A for comparison



Cyan coupler B



Composition of Developer

N,N'-diethylaminoparaaminoaniline sulfate	2.0 g.
sodium sulfite	20 g.
sodium carbonate (monohydrate)	50 g.
hydroxylamine hydrochloride	1.5 g.
potassium bromide	1.0 g.
water to	1,000 ml.

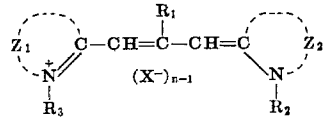
Sensitizing dye	Amount used ml. (mole conc.)	Sensitizing dye	Amount used ml. (mole conc.)	Rel. red sensitivity	Fog	$\lambda S_{max.}$
(1 E)	20 (5×10^{-4})			85	0.10	650
	40			100	0.10	
	80			105	0.10	
	40	(II B)	5 (5×10^{-4})	166	0.10	650
	40		10	170	0.11	
		(II B)	10	25	0.15	695
			20	25	0.16	
			40	25	0.17	
		(A)	10 (5×10^{-4})	(*)	0.14	(*)
			20	(*)	0.15	
			40	(*)	0.15	
	40	(A)	5	87	0.14	650
	40		10	75	0.14	

*Spectrally sensitized very little.

It will be understood from these results that the sensitizing dyes of the present invention have excellent properties as compared with sensitizing dye A.

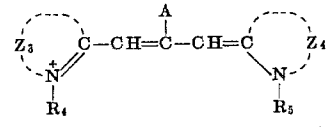
What is claimed is:

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



(I)

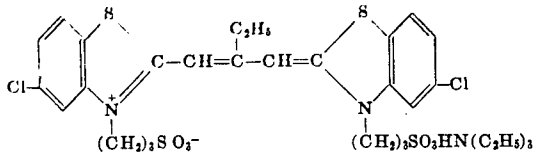
wherein R_1 is an alkyl group having from one to four carbon atoms; R_2 and R_3 are individually selected from the group consisting of an alkyl group, an allyl group and an alkyl group substituted by a hydroxyl group, an alkoxyl group, a carboxyl group, a sulfo group, a carboxyalkoxyl group, or a sulfoalkoxyl group; Z_1 and z_2 are the same or different atomic groups necessary to complete a benzothiazole nucleus or a benzoselenazole nucleus; n is 1 or 2 and X^- is an acid anion group; and at least one sensitizing dye represented by the following formula II:



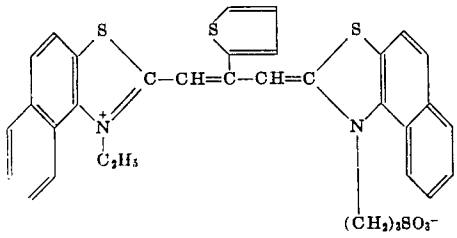
(II)

wherein A is a thienyl group, a furyl group or a thienyl group substituted by a halogen atom, an alkyl group or an alkyl carboxyl group; R_4 and R_5 are individually selected from the group consisting of an alkyl group, an aryl group and an alkyl group substituted by a hydroxyl group, an alkoxyl group, a carboxyl group, a sulfo group, a carboxyalkoxyl group or a sulfoalkoxyl group; at least one of R_4 and R_5 being a sulfo-substituted alkyl group; Z_3 is an atomic group necessary to complete a naphthothiazole nucleus or a naphthoselenazole nucleus, and Z_4 is an atomic group necessary to complete a naphthothiazole nucleus, a naphthoselenazole nucleus, a benzothiazole nucleus or a benzoselenazole nucleus.

2. A silver halide photographic emulsion as in claim 1, wherein said sensitizing dyes represented by formulas I and II are:

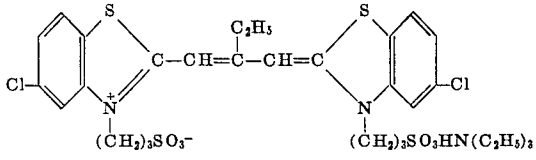


and

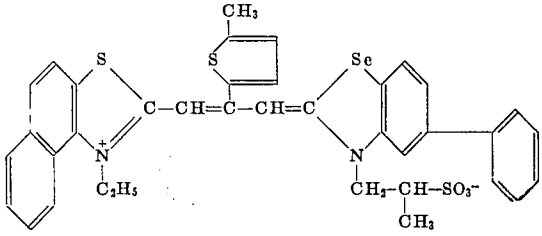


respectively.

3. A silver halide photographic emulsion as in claim 1, where said sensitizing dyes represented by formulas I and II are:

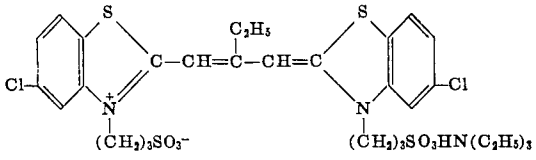


and

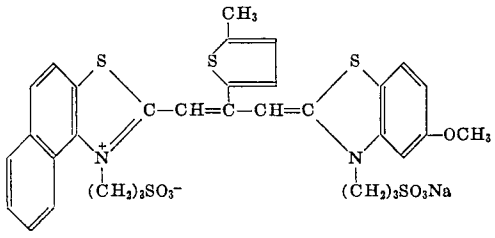


respectively.

4. A silver halide photographic emulsion as in claim 1, where said sensitizing dyes represented by formulas I and II are:

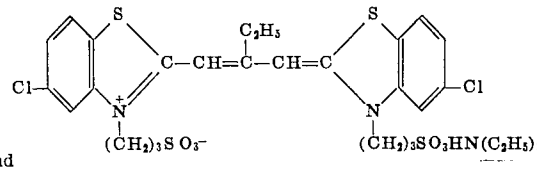


and

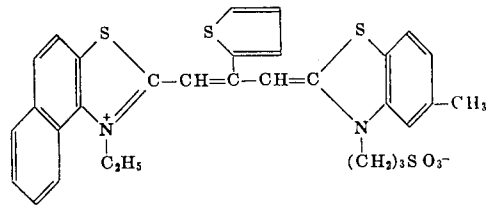


respectively.

5. A silver halide photographic emulsion as in claim 1, where said sensitizing dyes represented by formulas I and II are:

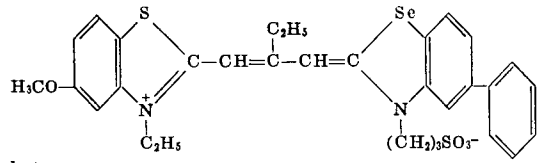


and

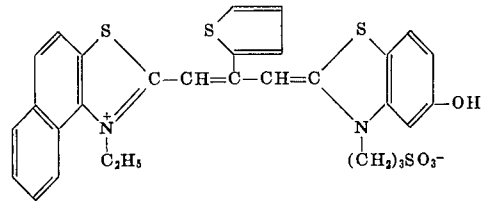


respectively.

6. A silver halide photographic emulsion as in claim 1, where said sensitizing dyes represented by formulas I and II are:

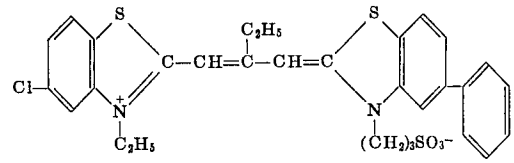


and

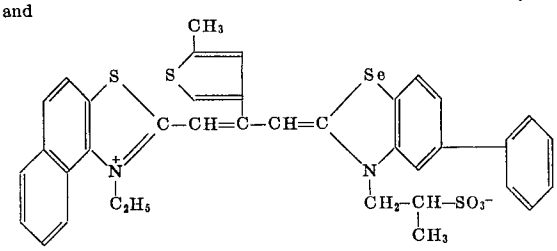


respectively.

7. A silver halide photographic emulsion as in claim 1, where said sensitizing dyes represented by formulas I and II are:

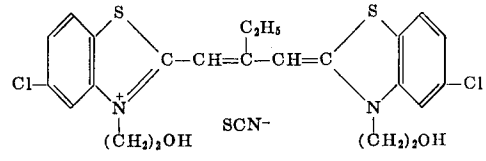


and

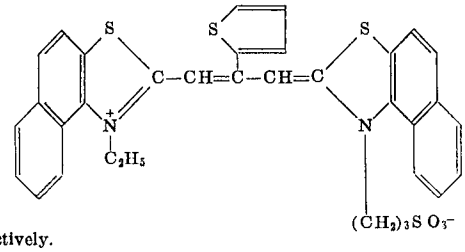


respectively.

8. A silver halide photographic emulsion as in claim 1, where said sensitizing dyes represented by formulas I and II are:



and



respectively.

9. A silver halide photographic emulsion as in claim 1, wherein the amount of sensitizing dye added to said emulsion varies from 1×10^{-6} to 1×10^{-3} mole per mole of silver halide, and wherein the weight ratio of said dye of formula II to said dye of formula I varies from 100:1 to 1:10.

10. A silver halide photographic emulsion as in claim 9, wherein said weight ratio varies from 20:1 to 1:1 .

11. A color sensitive material comprising a support having thereon at least one layer containing the photographic silver halide emulsion as in claim 1.

* * * * *