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3,666,480

SPECTRALLY SENSITIZED SILVER HALIDE PHOTOGRAPHIC EMULSION

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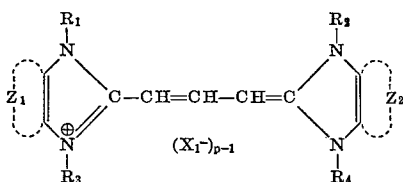
Int. Cl. G03c 1/14

U.S. Cl. 96—124

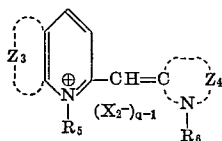
9 Claims

ABSTRACT OF THE DISCLOSURE

A spectrally sensitized silver halide photographic emulsion containing at least one sensitizing dye represented by the following first Formula:



wherein R_1 , R_2 , R_3 and R_4 each represent alkyl groups, at least one of said R_3 and R_4 being an alkyl group having a sulfo group; Z_1 and Z_2 represent the non-metallic atomic groups necessary to complete a benzimidazole nucleus; X_1^- represents an acid anion and p represents an integer of 1 or 2, p being 1 when said dye forms an intermolecular salt; and at least one sensitizing dye represented by the following second Formula:



wherein Z_3 represents the atomic group necessary to complete a quinoline nucleus; Z_4 represents the non-metallic atomic group necessary to complete a benzothiazole or benzoselenazole nucleus substituted by a carboxylic acid, an alkoxycarbonyl, a carbamoyl, or an acyl group; R_5 and R_6 represent alkyl groups, at least one of said R_5 and R_6 being an alkyl group having a sulfo group; X_2^- represents an acid anion and q has the same meaning as p .

BACKGROUND OF THE INVENTION

Field of the invention

This invention relates to a spectrally sensitized silver halide photographic emulsion, in particular, one which is supersensitized in the green region.

Description of the prior art

It is well known that spectral sensitization is a very important technique employed in the making of a silver halide photographic emulsion, in particular, a color photosensitive material. The spectral sensitivity depends on the chemical structure and property of the sensitizing dye used and the property of the silver halide used, for example, halogen composition, crystal habit, chemical ripening, pAg and pH. The spectral sensitivity, however, also depends on the various additives to the emulsion, many of which decrease the spectral sensitivity. In the case of an emulsion used in the making of an incorporated type color photographic material, the sensitivity is decreased by the introduction of a coupler. This effect

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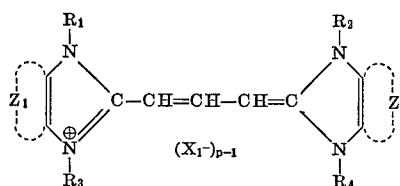
is a large obstacle in the making of photographic material.

The distribution of spectral sensitivity in the green region in which human eyesight sensitivity is high is very important for the color reproduction of a color photosensitive material. Therefore, many efforts have been made directed toward spectral sensitization in the green region to obtain a suitable spectral sensitivity distribution as well as a high sensitivity. For instance, United States Pat. No. 2,701,198 discloses a method of sensitization comprising the combination of a benzimidazolocarbocyanine dye and a pseudocyanine dye. Japanese patent publication Nos. 4936/68 and 22884/68 disclose the combination of a benzimidazolocarbocyanine dye and a benzoxacarbocyanine dye. However, these methods still have great disadvantages. For example, in the method disclosed in United States Pat. No. 2,701,198, the sensitivity is lowered remarkably by the coexistence of the coupler and the dye contamination is increased. In the method disclosed in Japanese patent publication No. 4936/68, there is much dye contamination and the sensitivity is low in the relatively short wavelength region of 510–530 $m\mu$ of the green region as evidenced by Japanese patent publication 22884/68.

SUMMARY OF THE INVENTION

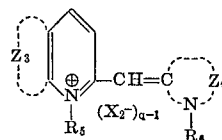
It is the principal object of this invention to provide a spectrally sensitized silver halide photographic emulsion in which the sensitivity in the relatively short wavelength region of 510–530 $m\mu$ of the green region is raised and in which there is no increase of dye contamination and no lowering of sensitivity due to the coexistence of a coupler. This object can be accomplished by the use of a supersensitized silver halide photographic emulsion wherein at least one sensitizing dye represented by the following General Formula I and at least one sensitizing dye represented by the following General Formula II is added to the emulsion:

General Formula I



in which R_1 , R_2 , R_3 and R_4 represent alkyl groups, at least one of R_3 and R_4 being an alkyl group having a sulfo group; Z_1 and Z_2 represent the non-metallic atoms necessary to complete a benzimidazole nucleus; X_1^- represents an acid anion group and p represents an integer of 1 or 2, p being 1 when said dye forms an intermolecular salt.

General Formula II



in which Z_3 represents the atomic group necessary to complete a quinoline nucleus; Z_4 represents the non-metallic atomic group necessary to complete a benzothiazole or benzoselenazole nucleus substituted by a carboxylic acid, an alkoxycarbonyl, a carbamoyl such as N-ethylcarbamoyl, or an acyl group; R_5 and R_6 represent alkyl groups, at least one R_5 and R_6 being an alkyl group having a sulfo group; X_2^- represents an acid anion group; q having the same meaning as p .

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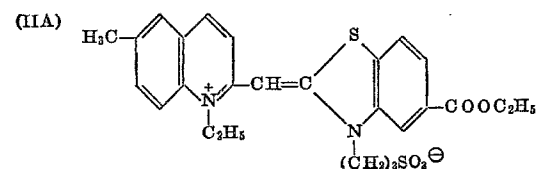
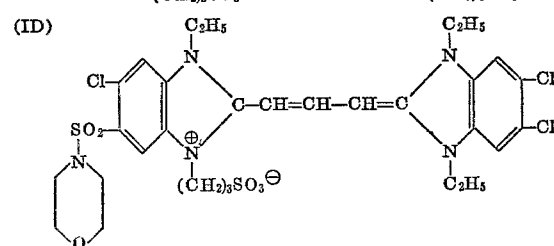
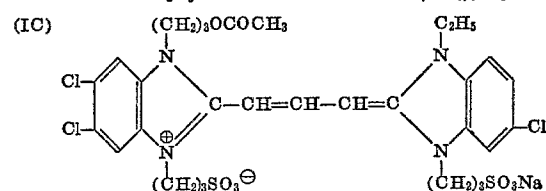
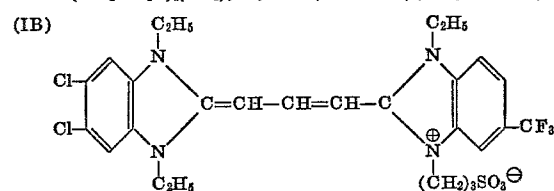
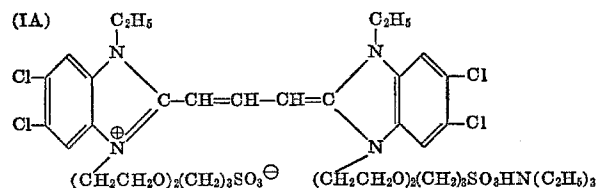
DESCRIPTION OF THE PREFERRED EMBODIMENTS

According to this invention, the spectrally sensitized silver halide photographic emulsion can advantageously be used in combination with the oxacarbocyanine dye disclosed in Japanese patent publication No. 4936/68 or with the hemicyanine dye disclosed in Belgian Patent No. 724,467.

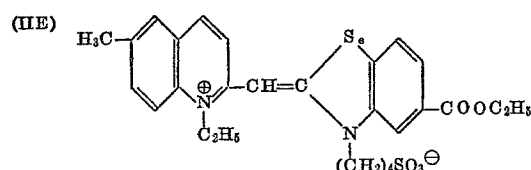
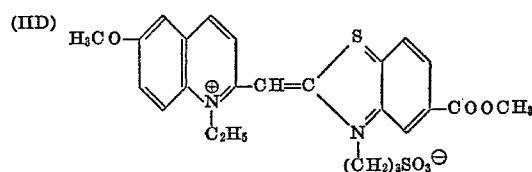
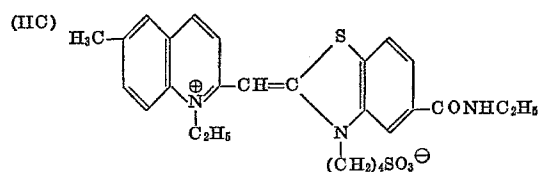
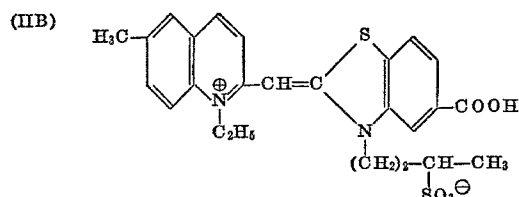
In R_1 , R_2 , R_3 , R_4 and R_5 , the alkyl groups may be, for example, methyl, ethyl propyl, acetoxypentyl, hydroxyethyl, allyl, benzyl, γ -sulfopropyl, γ -sulfobutyl, δ -sulfobutyl, 2-(3-sulfopropoxy) ethyl, 2-[2-(3-sulfopropoxy) ethoxy] ethyl or 2-hydroxy-1-sulfopropyl groups. Examples of X_1 and X_2 are chlorine, bromine, iodine, perchlorate, thiocyanate, p-toluene sulfonate, benzenesulfonate, methyl sulfonate and ethyl sulfate ions.

One feature of the invention lies in the substituent of the Z_4 -forming nucleus in Formula II. The substituent of the invention is useful for raising the sensitivity in the 515–530 $m\mu$ range in connection with the property of the dye J aggregate and to obtain a suitable spectral sensitivity. The dye of Formula I is the well-known benzimidazolcarbocyanine. In particular, the nucleus substituent of said benzimidazole includes those mentioned in Japanese patent publication Nos. 4936/68, 22884/68, 2530/69 and 16589/69.

Examples of the compounds of this invention are shown below:



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The compounds of Formula I can readily be synthesized by known methods, such as those disclosed in United States Pat. Nos. 2,912,329 and 2,778,823 and Japanese patent publication Nos. 7828/63, 27166/67, 4931/68, 13823/68, 14497/68, 16589/69, etc.

The compounds of Formula II can also readily be synthesized by known methods such as those disclosed in United States Patent No. 2,503,776. A typical method for the synthesis of compound IIA is as follows: 850 mg. of 6-methyl-2-ethylmercapto-1-ethylquinolinium ethyl sulfate and 800 mg. of anhydro-5-carbomethoxy-2-methyl-3-(γ -sulfopropyl)-benzothiazolium hydroxide are dissolved in 160 ml. of ethyl alcohol, to which is added 3.5 ml. of triethylamine, and heated for 4 hours with refluxing. After the reaction, the solvent is removed and the residue is treated with ether and then with acetone to yield a crude crystal. When this crude crystal is recrystallized from ethyl alcohol, 400 mg. of an orange crystal having a melting point of 300° C. and a

$$\lambda_{\text{max}}^{\text{MeOH}} \text{ of } 485 \text{ m}\mu$$

is obtained. The Other sensitizing dyes of this invention can be synthesized in a similar manner.

The characteristics of the sensitizing dyes mentioned as typical examples of Dye type II are shown below:

Dye No.	M.P. (° C.)	$\lambda_{\text{max}}^{\text{MeOH}}$ m μ
IIA	300 or more	485
IIB	do	490
IIC	do	488
IID	do	492
IIE	do	492

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The dye used in this invention may be added to the emulsion in the form of a solution in water or in a water-soluble organic solvent such as methanol, ethanol, pyridine, acetone or Cellosolve. The sensitizing dyes represented by Formulae I and II may be added as individual solutions or as a mixed solution. Dissolving may be effected by ultrasonic wave agitation. The amount of each dye may be varied with the emulsion employed. Ordinarily, the amount of both dyes is preferably from 1×10^{-6} mole to 1×10^{-3} mole per 1 mole of silver halide. The weight proportion of the dye of Formula I to the dye of Formula II varies from 10:1 to 1:2, and preferably from 4:1 to 2:1. This proportion may also be varied depending on the use of other additives in the emulsion.

The silver halide emulsions which may be used are, for example, silver iodobromide, silver bromide and silver chlorobromide. In particular, a silver iodobromide emulsion is advantageous to use, because its particle size is not particularly restricted. Gelatino-silver halide emulsions are mainly used, but binders other than gelatin may, of course, be used, for example, polyvinyl alcohol, alginate polymers, polyvinyl imidazole, polyvinylpyrrolidone and mixtures thereof with gelatin.

The silver halide emulsion of the present invention is coated onto a suitable support, depending on its use, for example, baryta paper, cellulose triacetate film, polyethylene terephthalate film, plastic films, resin-coated paper or synthetic paper.

The following examples illustrate the present invention in more detail, and are not intended to limit the same.

EXAMPLES

50 g. of 1 - phenyl-3-[3-(2,4-ditertiaryamylphenoxyacetamide)benzoamide]-5-pyrazolone dissolved with heating in 100 ml. of dibutyl phthalate was added to 1000 ml. of a 10% aqueous solution of gelatin, to which 50 ml. of a 5% aqueous solution of sodium alkylbenzenesulfonate was then added. This was emulsified by a high speed revolving mixer. The resulting emulsion is called a "coupler dispersion."

1 kg. of a silver iodobromide emulsion prepared in a conventional manner (amount of silver: 0.25 mole; iodine content: 4.0 mole percent) was placed in a beaker and dissolved in a bath at 40° C. Predetermined amounts of the sensitizing dyes as shown in Table I were added there-

TABLE I

Example No.	Dye used	Amount used, ml. (mol conc.)	Dye used	Amount used, ml. (mol conc.)	Relative yellow filter sensitivity	Fog	Maximum Sensitizing wavelength (mμ)
1	(IA)	40(5×10^{-4})			100	0.15	580
		80			100	0.16	583
		40	(IIA)	60(1×10^{-3})	200	0.15	575, 514
		40	(IIA)	120	169	0.13	
			(IIA)	60	35	0.11	
			(IIA)	120	40	0.12	515, 530
		40	(IIB)	60	169	0.13	
		40	(IIB)	120	169	0.14	
			(IIB)	60	35	0.11	
			(IIB)	120	40	0.12	522
3		40	(IIC)	60	105	0.14	580, 515
		40	(IIC)	120	132	0.15	
			(IIC)	60	31	0.10	—515
			(IIC)	120	31	0.11	
4	(IB)	20(5×10^{-4})			93	0.14	570
		40			126	0.15	572
		40	(IIA)	60	200	0.13	568, 513
		40	(IIA)	120	142	0.14	
		40	(IIB)	60	178	0.15	570, 515
		40	(IIB)	120	127	0.15	
		40	(IIE)	60	135	0.22	570, 530
		40	(IIE)	120	135	0.25	
			(IIE)	60	31	0.16	530
			(IIE)	120	35	0.18	
7	(IC)	20(5×10^{-4})			89	0.18	578, —
		40			79	0.20	
		40	(IIA)	60	132	0.18	578, 510
		40	(IIA)	120	100	0.15	
8	(ID)	20			89	0.17	565, —
		40			89	0.18	
		40	(IID)	60	112	0.22	565, 530
		40	(IID)	120	112	0.25	
			(IID)	60	35	0.13	530
			(IID)	120	40	0.14	

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to with agitation and allowed to stand for 10 minutes. 400 g. of the magenta coupler dispersion was then added with agitation and allowed to stand for 1 hour. The resulting emulsion was applied to a support of cellulose triacetate film to give a dry film thickness of 7 microns on the base. A sample of green-sensitive photographic material was thus obtained.

The sample was cut into strips and subjected to light wedge exposure through a yellow filter of No. K-12 (trademark) using a sensitometer having a light source color temperature of 5400° K. It was then developed at 20° C. for 12 minutes with the following developer composition:

	G.
N,N-diethyl-p-aminoaniline sulfate	2.0
Sodium sulfite	2.0
Sodium carbonate (monohydrate)	50.0
Hydroxylamine hydrochloride	1.5
Potassium bromide	1.0
Water to make 1 liter.	

pH 10.8 ± 0.1 .

Thereafter, the sample was passed through a first fixing solution, a bleaching solution and a second fixing solution and washed with water to obtain a magenta image. After drying, the green filter density was measured with an S-type (trademark) densitometer manufactured by Fuji Photo Film Co., Ltd. Thus, a characteristic curve was obtained from which the sensitivity at the optical density "fog+0.20" was determined, is shown in Table 1.

	G.
Composition of bleaching solution:	
Red prussiate	100
Potassium bromide	20
Water to make 1 liter.	

pH 6.9 ± 0.3 .

Composition of fixing solution:

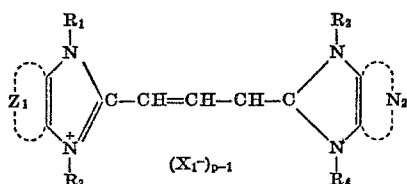
	g--	200
Hypo		
Sodium sulfite	g--	20
Acetic acid (28%)	ml--	45
Boric acid	g--	7.5
Potassium alum	g--	20
Water to make 1 liter.		

pH 4.5 ± 0.2 .

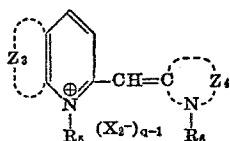
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What is claimed is:

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



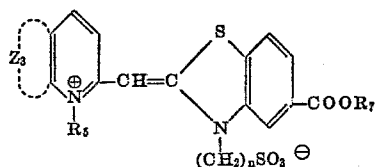
wherein R_1 , R_2 , R_3 and R_4 each represent alkyl groups, at least one of said R_3 and R_4 being an alkyl group having a sulfo group Z_1 and Z_2 represent the non-metallic atomic groups necessary to complete a benzimidazole nucleus; X_1^- represents an acid anion and p represents an integer of 1 or 2, p being 1 when said dye forms an intermolecular salt; and at least one sensitizing dye represented by the following second formula:



wherein Z_3 represents the atomic group necessary to complete a quinoline nucleus; Z_4 represents the non-metallic atomic group necessary to complete a benzothiazole or benzoselenazole nucleus substituted by a carboxylic acid, an alkoxy carbonyl, a carbamoyl, or an acyl group; R_5 and R_6 represent alkyl groups, at least one of said R_5 and R_6 being an alkyl group having a sulfo group; X_2^- represents an acid anion and q has the same meaning as p .

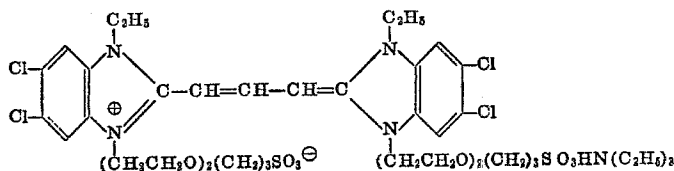
2. An emulsion as in claim 1 wherein said alkyl group of R_1 , R_2 , R_3 , R_4 , R_5 and R_6 is methyl, ethyl, propyl, acetoxypentyl, hydroxyethyl, allyl, benzyl, γ -sulfopropyl, γ -sulfobutyl, δ -sulfobutyl, 2-(3-sulfopropoxy)ethyl, 2-[2-(3-sulfopropoxy)ethoxy]ethyl or 2-hydroxy-1-sulfopropyl.

3. The spectrally sensitized silver halide photographic emulsion of claim 1, wherein the sensitizing dye represented by the second formula is:



wherein R_5 and Z_3 have the same meaning as in claim 1, wherein R_7 represents a methyl or ethyl group, and wherein n represents 2, 3 or 4.

4. A spectrally sensitized silver halide photographic emulsion containing a sensitizing dye represented by the formula:

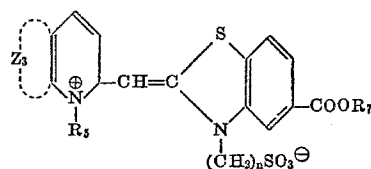


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and at least one sensitizing dye represented by the following formula:

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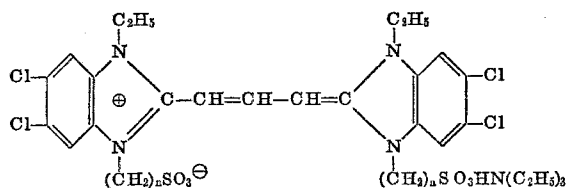


wherein R_5 , R_7 , Z_3 and n have the same meaning as in claim 3.

5. A spectrally sensitized silver halide photographic emulsion containing a sensitizing dye represented by the formula:

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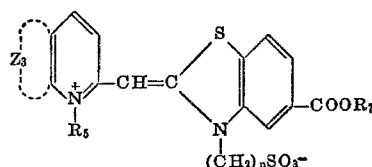
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wherein n is an integer from 1 to 5, and at least one sensitizing dye represented by the following formula:

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wherein R_5 , R_7 , Z_3 and n have the same meaning as in claim 3.

6. The emulsion of claim 1 further containing a magenta coupler.

7. The emulsion as in claim 1 wherein the sensitizing dyes represented by the first and second formulae are incorporated in said silver halide emulsion in an amount of from 1×10^{-6} mole to 1×10^{-3} mole per 1 mole of silver halide in said emulsion.

8. The emulsion as in claim 1 wherein the weight ratio of the sensitizing dye represented by the first formula to the sensitizing dye represented by the second formula varies from 10:1 to 1:2.

9. A photographic light-sensitive element comprising a

support having thereon at least a layer containing the silver halide emulsion of claim 1.

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J. TRAVIS BROWN, Primary Examiner

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