June 6, 1972 KEISUKE SHIBA ET AL 3,667,960

SPECTRALLY SUPER SENSITIZED SILVER HALIDE
PHOTOGRAPHIC EMULSION
Filed March 27, 1970

FIG. 1

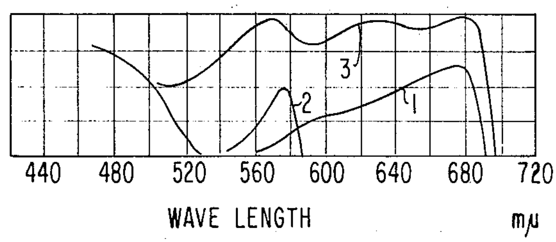


FIG. 2

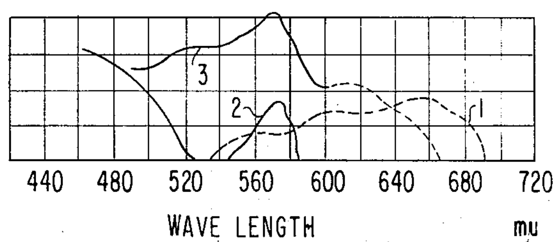


FIG. 3

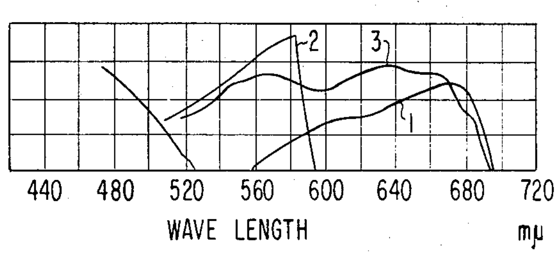
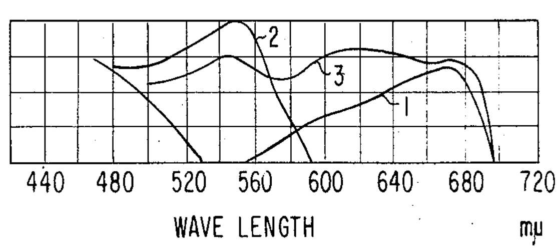


FIG. 4



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ATTORNEYS

3,667,960

SPECTRALLY SUPERSENSITIZED SILVER HALIDE PHOTOGRAPHIC EMULSION

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Filed Mar. 27, 1970, Ser. No. 23,122
Claims priority, application Japan, Mar. 27, 1969, 44/23,320
Int. Cl. G03c *1/14*
U.S. Cl. 96—124 15 Claims

ABSTRACT OF THE DISCLOSURE

Supersensitization of silver halide photographic emulsions by employing a combination of specific sensitizing dyes, one containing a heterocyclic nucleus selected from the group cosisting of naphthoselenazole and naphthoxazole and the other of which containing a 2-quinoline nucleus. The particular combination of spectral sensitizing dyes employed provide a high degree of supersensitization over the entire visible range.

BACKGROUND OF THE INVENTION

(1) Field of the invention

This invention relates to a spectrally sensitized silver halide photographic emulsion.

(2) Description of the prior art

Light-sensitive photographic material must be sensitive over the entire wave length sensed by human eyesight and possess a suitable spectral sensitivity distribution. Spectral sensitization of silver halide photographic emulsions, that is, the addition of a sensitizing dye thereto to enlarge its wave length sensitivity range is well known. Generally, light-sensitive photographic material must be spectrally sensitized over the entire visible range. Further, high green sensitivity is especially required so that the sensitivity of the material closely corresponds to human eyesight. Furthermore, two or more sensitizing dyes are generally used to obtain a silver halide photographic emulsion possessing superpanchromatic spectral sensitization and high sensitivity in the green range. In many cases, however, the spectral sensitivity obtained by using two or more sensitizing dyes in combination is lower than that obtained with the individual dyes.

The spectral sensitizing action is affected by the chemical structure of the sensitizing dye and the properties of the silver halide emulsion used, for example, the hydrogen ion concentration, silver ion concentration, crystal habit of the silver halide fine crystals, grain diameter and halogen composition. It is also markedly affected by the particular fog inhibitor, stabilizer, sensitizer, hardener, binder, precipitant, plasticizer, color former and photographic dye employed in the emulsion. Many of such materials act so as to weaken the spectral sensitization obtained.

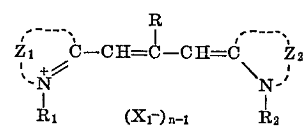
In some cases, however, the spectral sensitization obtained with a given sensitizing dye is synergistically strengthened by using it in combination with another selected sensitizing dye or organic compound preferably an aromatic organic compound. Such action is known as supersensitization. Sensitizing dyes used for superpanchromatic spectral sensitization have the ability to absorb long wave length light and generally result in a large desensitizing action. The spectral sensitization efficiency obtained by using such dyes is therefore often low. This is a disadvantage in the obtaining of a silver halide photographic emulsion having high spectral sensitivity.

Therefore, utilization of supersensitization has been desired, in particular, with sensitizing dyes to be used for superpanchromatic spectral sensitization. The proper selection of dye combinations having supersensitizing action is extremely difficult and entirely empirical, since seemingly meaningless differences in chemical structure between sensitizing dyes often have large influences upon the supersensitizing action.

SUMMARY OF THE INVENTION

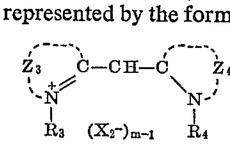
It is the principal object of the invention to provide a silver halide emulsion having high sensitivity substantially over the whole visible range, that is, both superpanchromatically and spectrally and, in which the spectral sensitivities of not only the red range, but also the green range, are favorably affected by supersensitization.

The above object can be accomplished by employing, in a silver halide photographic emulsion, a combination of at least (a) one of a sensitizing dye represented by the formula



(I)

in which R is hydrogen or a lower alkyl group, such as a methyl or ethyl group; R_1 and R_2 are each a lower alkyl group, such as methyl, ethyl and propyl groups, an aryl group or a substituted lower alkyl group, such as Y-lower alkyl, wherein Y is hydroxy, lower alkoxy, carboxy, sulfo, sulfo-lower alkoxy (as examples of such groups may be mentioned 2 - hydroxyethyl, 2 - methoxyethyl, carboxymethyl, 3 - carboxypropyl, 4 - carboxybutyl, 3-sulfobutyl, 3 - sulfopropyl, 4 - sulfobutyl, 2 - (3 - sulfopropoxy)ethyl, and 2-hydroxy propyl); at least one or R_1 and R_2 being a substituted alkyl group; Z_1 is an atomic group necessary to complete a naphthothiazole, naphthoselenazole or naphthoxazole nucleus; Z_2 is an atomic group necessary to complete a naphthothiazole, benzothiazole, naphthoselenazole, benzoselenazole, naphthoxazole or benzimidazole nucleus; X_1^- is an acid anion group, such an a halogen ion (Cl, Br, etc.), perchlorate, p-toluenesulfonate, benzenesulfonate, ethylsulfate, methylsulfate, rhodanide ion etc., and n is 1 or 2, the dye being an intermolecular salt when n is 1, and (b) at least one of a cyanine dye represented by the formula



(II)

in which R_3 and R_4 are each as recited above for R_1 and R_2; Z_3 is an atomic group necessary to complete a 2-quinoline nucleus, optionally substituted by a lower alkyl group, an alkoxy group, a hydroxyl group or a halogen atom; Z_4 is an atomic group necessary to complete a 2-quinoline nucleus, a non-substituted benzothiazole nucleus, a benzothiazole nucleus substituted by a lower alkyl group, such as methyl or ethyl, a phenyl group or a halogen atom, a non-substituted benzoselenazole nucleus or a benzoselenazole nucleus substituted by a lower alkyl group, a phenyl group or a halogen atom; X_2^- is an acid anion group such as a halogen ion (Cl, Br, etc.), perchlorate, p-toluene sulfonate, benzenesulfonate, ethylsulfate, methylsulfate, rhodanide ion etc.; and m is 1 or 2, the dye being an intermolecular salt when m is 1.

DETAILED DESCRIPTION OF THE INVENTION

The essential feature of the sensitizing dye represented by Formula I is that at least one of the two heterocyclic nuclei is a heterocyclic nucleus selected from the group consisting of naphthothiazole, naphthoselenazole and naphthoxazole nuclei. This sensitizing dye is capable of providing spectral sensitivity at sufficiently long wave lengths. However, the sensitivity obtained using either dye alone is not always sufficient. In cases where both of R_1 and R_2 in Formula I are alkyl or aryl groups, in particular, desensitization is severe and contrast is sharply reduced. This is also the case when R of Formula I is an aryl group, such as phenyl or substituted phenyl, thenyl, thienyl, substituted thienyl or furyl. The use of the two dyes in combination, however, provides marked sensitization in the red range as well as high contrast. If both R_1 and R_2 of Formula I are unsubstituted alkyl or aryl groups, there is also a tendency towards supersensitization, but less than that of the present invention. Where at least one R_1 and R_2 is a substituted alkyl group, in particular, if substituted by a hydrophilic substituent, such as hydroxyl, carboxyl or sulfo, the supersensitizing action is obtained to a remarkable degree. Above all, an alkyl group substituted by a sulfo group is desirable. The well-known dyes belonging to the group represented by Formula I, such as those disclosed in British Patent 1,137,084 and U.S. Patent 3,177,210, provide a marked supersensitizing action when incorporated into a silver halide photographic emulsion in combination with the sensitizing dye represented by Formula II .When R of Formula I is an aryl group, there is a slight tendency towards supersensitization but not nearly to the extent obtained in the case of employing those compounds represented by Formula II of the present invention. Another disadvantage of any supersensitization obtained with the combination of sensitizing dyes wherein R_1 and R_2 of the Formula I compound are both unsubstituted alkyl or aryl groups with the sensitizing dye represented by Formula II is that there is obtained an unevenness of application to the silver halide emulsion and thus stable supersensitization is difficult, if not impossible, to achieve.

A feature of the chemical structure of the sensitizing dye represented by Formula II is the presence of at least one 2-quinoline nucleus. Another feature consists in that Z_4 represents an atomic group necessary to complete either a 2-quinoline nucleus or an unsubstituted or lower alkyl group-, phenyl group- or halogen atom-substituted benzothiazole nucleus or benzoselenazole nucleus. Not only does the sensitizing dye represented by Formula II provide high red sensitivity through its remarkable supersensitization to the sensitizing dye represented by Formula I, but, also, sensitivity in the green region of the former is itself raised. In those cases where in the heterocyclic nucleus represented by Z_4 of Formula II is a benzothiazole or benzoselenazole nucleus having an electron donating substituent, such as an alkoxy or hydroxyl group, the green sensitivity is lowered to some extent when used in combination with the sensitizing dye of Formula I. This, of course, is an undesirable tendency with regard to attaining the object of the present invention. Some sensitizing benzimidazolocarbocyanine and oxacarbocyanine dyes also have a similar tendency when used in combination with the sensitizing dyes of Formula I. That is to say, red sensitivity is increased by the combined use over that obtained by using the dye of Formula I alone, but green sensitivity is somewhat lowered by the use of the combination.

The important characteristic of the present invention is to obtain high sensitivity and contrast, not only in the red range but also the green range by using, in combination, at least one of the sensitizing dyes represented by Formula I and at least one of the sensitizing dyes represented by Formula II.

The sensitizing dyes used in the present invention may be dissolved in water or a water-soluble organic solvent such as methanol, ethanol, acetone, methyl Cellosolve or pyridine and added to a silver halide emulsion in admixture or individually. Ultrasonic wave agitation or stirring may be applied in the solubilization of the sensitizing dyes. The method of addition, amounts added and order of addition may be varied as desired. The amounts added may range preferably from 1×10^{-6} mol to 5×10^{-4} mol per 1 mol of silver halide, the ratio of the sensitizing dye represented by Formula II to that of Formula I being 100:1 to 1:10, in particular, 10:1 to 1:2.

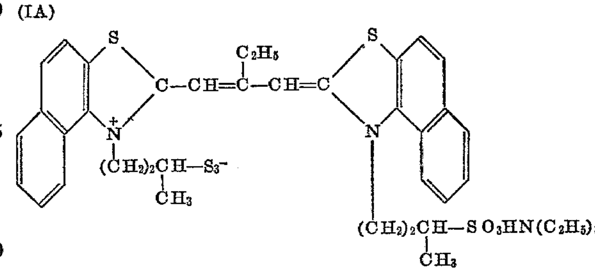
Illustrative of the conventional silver halide emulsions which may be used in the present invention are silver iodobromide, silver bromide, silver chlorobromide, silver chloride and silver chloroiodobromide emulsions and the like. To these emulsions may be applied conventional chemical sensitization as well as the usual additives such as fog inhibitors, stabilizers, sensitizers, surfactants, hardeners, plasticizers and photographic dyes and the like.

The emulsions may be coated onto any suitable support, such as a cellulose derivative film, polyethylene terephthalate film, polycarbonate film, plastic film, baryta paper, resin coated paper, synthetic paper, resin laminated paper, glass sheets and the like.

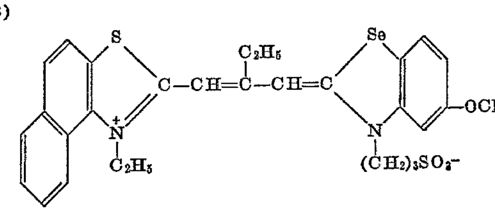
Examples of the sensitizing dyes which may be used in the present invention are set forth below without intending to limit the invention to those materials specifically exemplified. Other such dyes which would be suitable for use in accordance with the present invention will readily occur to those skilled in this art.

Sensitizing dyes represented by general formula I

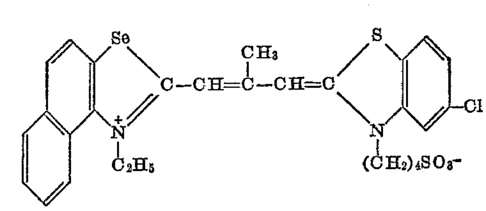
(IA)



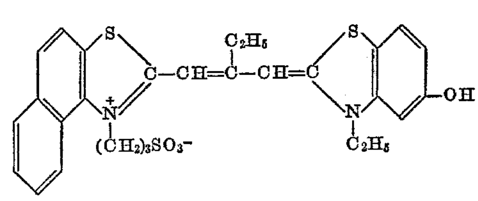
(IB)



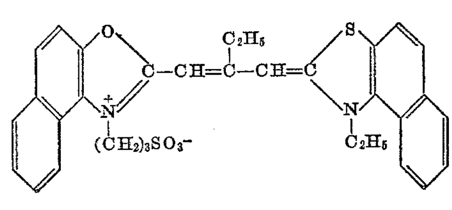
(IC)



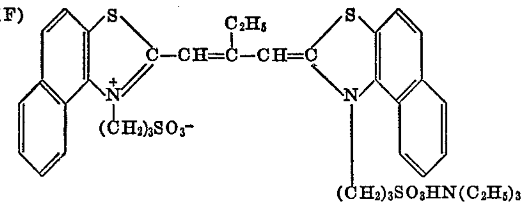
(ID)



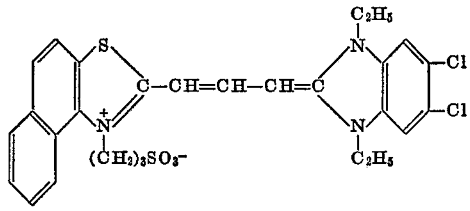
(IE)



(IF)

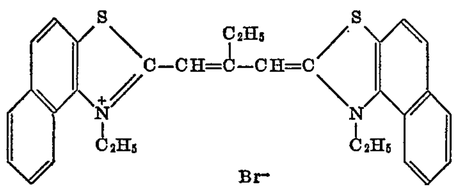


(IG)



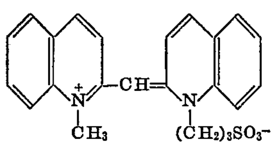
Sensitizing dye for comparison

(A)

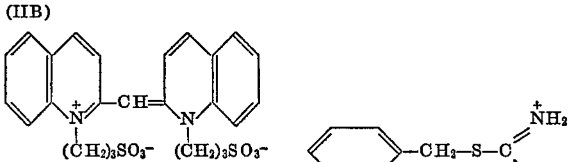


Sensitizing dyes represented by general formula II

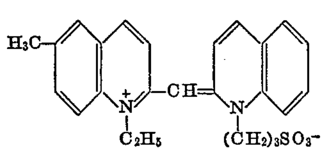
(IIA)



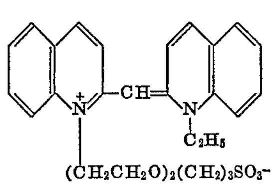
(IIB)



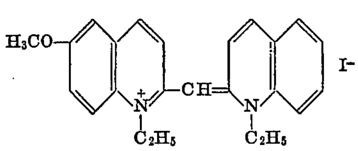
(IIC)



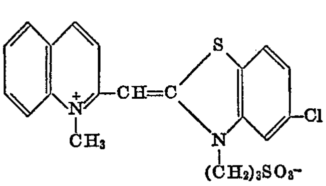
(ID)



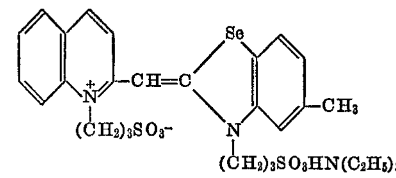
(IE)



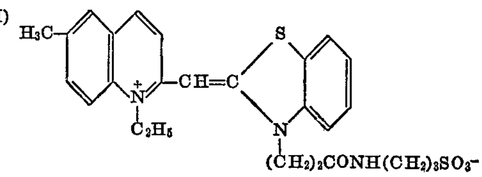
(IF)



(IG)

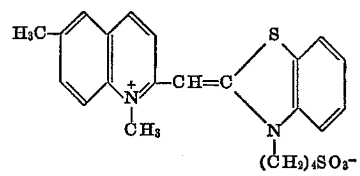


(IIH)

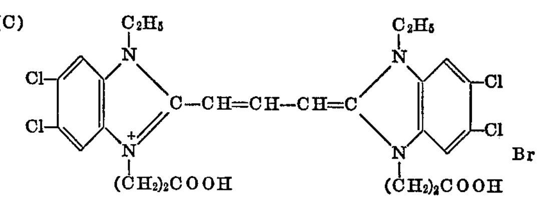


Sensitizing dyes for comparison

(B)



(C)



The sensitizing dyes represented by Formulas I and II can readily be synthesized by well-known methods, for example, as disclosed in U.S. Pat. No. 2,504,776, British Pat. No. 742,112, German Pat. No. 1,072,765 and Japanese patent publication Nos. 23,467/65, 1,412/65, 27,-166/67 and 27,167/67.

The following examples will illustrate the invention in more detail without limiting the same.

Examples 1–11.—500 g. of a silver iodobromide photographic emulsion (iodine content: 4.0 mol percent) prepared in known manner and subjected to chemical ripening was melted in a beaker and maintained at 40° C. The sensitizing dyes represented by Formulas I and II were respectively dissolved in methanol in given concentrations. Certain amounts of the sensitizing dye solutions as shown in Tables 1 and 2 were respectively dissolved in methanol in given concentrations. Certain amounts of the sensitizing dye solutions as shown in Tables 1 and 2 were respectively taken in test tubes, added to the emulsion, mixed and stirred. After 10 minutes, 7 ml. of each emulsion was taken, coated onto a glass sheet of cabinet size, set and dried to provide a test sample.

The resulting sample was cut into two pieces, one of which was then subjected to light wedge exposure through a yellow filter (K–12 (trademark), made by Fuji Photo Film Co.) and a red filter (K–7 (trademark)) using an actinometer, the color temperature of which had been converted into 5400° K. by applying a Davis-Gibson converting filter to a light source of color temperature 2666° K., and another of which was subjected to light wedge exposure for 1/50 second using as a light source a monochromatic light near the maximum absorption wave length in the green range obtained by the use of the sensitized dye represented by the general Formula II (mainly corresponding to the J-band). The maximum absorption wave length (λ mμ) used is shown in the table.

The exposed sample was developed at 20° C. for 10 minutes with a developer having the following composition, passed through a stopping solution and fixing solution and washed with water to obtain a strip, the density of which was measured by the use of an S-type densitometer made by Fuji Photo Film Co. The yellow filter sensitivity (S_Y), red filter sensitivity (S_R) and sensitivity to a monochromatic light of a predetermined wave length (S_λ) were determined. The standard point of optical density used for determining the sensitivity was the point of (fog+0.20).

The "relative sensitivity" in Table 1 is a value determined by taking the sensitivity of S_Y, S_R and S_λ to be 100 in the case of adding 20 ml. of the dye (I A) in No. 1.

Composition of the developer employed:

Water (50° C.)—750 ml.
Metol—2 g.
Anhydrous sodium sulfite—100 g.
Hydroquinone—5 g.
Borax—2 g.
Water to make 1000 ml.

The experiment as shown in Table 2 was carried out in order to further clarify the characteristics of the sensitizing dyes used in the present invention. The "relative sensitivity" in Table 2 is determined by setting of 100 for a value S_Y, S_R and S_λ in the case of adding 20 ml. of the dye (IF) in No. 1 of Table 2.

TABLE 1

Number	Dye	Amount used, ml. (mol. conc.)	Dye	Amount used, ml. (mol. conc.)	Relative sensitivity S_Y	S_R	$\lambda m\mu$	S_λ	Fog
1	(IA)	10 (5×10^{-4})	-	-	110	110	570	108	0.16
		20	-	-	110	100	-	100	0.18
		40	-	-	80	85	-	100	0.19
2	(IA)	20	(IIA)	10 (1×10^{-3})	282	282	575	466	0.18
		20		20	322	250	-	564	0.19
		20		40	398	142	-	1,000	0.12
3	(IA)	-	(IIA)	10 (1×10^{-3})	60	(*)	575	115	0.10
		-		20	76	(*)	-	300	0.12
		-		40	88	(*)	-	230	0.12
4	(IA)	20	(IIB)	20 (1×10^{-3})	282	190	575	1,020	0.18
		20		40	390	240	-	1,600	0.19
		-		20 (1×10^{-3})	42	(*)	-	179	0.13
		-		40	47	(*)	-	282	0.17
5	(IA)	20	(IIC)	40 (5×10^{-4})	332	234	575	470	0.18
		20		80	338	200	-	560	0.22
		-		20	45	(*)	-	71	0.12
		-		40	50	(*)	-	370	0.14
		-		80	60	(*)	-	500	0.17
6	(IA)	20	(IID)	40 (4×10^{-4})	220	141	580	1,180	0.22
		20		80	240	132	-	1,120	0.34
		-		20	25	(*)	-	117	0.22
		-		40	20	(*)	-	110	0.35
		-		80	18	(*)	-	107	0.38
7	(IA)	2	(IIF)	20 (1×10^{-3})	200	200	530	1,010	0.16
		20		40	310	230	-	1,250	0.17
		20		80	280	278	-	1,200	0.17
		-		20	30	(*)	-	120	0.14
		-		40	32	(*)	-	125	0.14
8	(IA)	20	(IIH)	20 (1×10^{-3})	200	230	530	1,200	0.16
		20		40	234	332	-	1,350	0.18
		-		20	35	(*)	530	141	0.16
		-		40	45	(*)	-	175	0.18
9	(ID)	20 (5×10^{-4})	(IIA)	-	42	30	-	(*)	0.16
		40		-	50	43	-	(*)	0.17
		20		20 (1×10^{-3})	282	50	575	1,200	0.18
		20		40	500	70	-	1,350	0.18
10	(IB)	20 (5×10^{-4})	(IIC)	-	100	85	575	(*)	0.17
		40		-	126	126	-	(*)	0.18
		20		20 (1×10^{-3})	470	167	-	850	0.18
		20		40	332	99	-	010	0.19
11	(IE)	20 (5×10^{-4})	(IIC)	-	200	117	575	325	0.15
		40		-	282	132	-	430	0.17
		80		-	330	142	-	500	0.18
		20		20 (1×10^{-3})	490	166	-	1,250	0.17
		20		40	564	166	-	1,350	0.19
12	(IG)	20 (5×10^{-4})	(IIG)	-	282	142	540	230	0.16
		40		-	350	153	-	355	0.18
		20		20 (1×10^{-3})	450	176	-	1,000	0.19
		20		40	530	166	-	1,250	0.20
13	(IC)	20 (5×10^{-4})	(IIE)	-	80	110	590	70	0.14
		40		-	98	105	-	120	0.16
		20		20 (1×10^{-3})	750	125	-	300	0.32
		20		40	800	125	-	450	0.42

*No value is given because the sensitivity or contrast is too low.

TABLE 2

Number	Dye	Amount used, ml. (mol. conc.)	Dye	Amount used, ml. (mol. conc.)	Relative sensitivity S_Y	S_R	λ mμ	Sλ	Fog
1	(IF)	10 (5×10^{-4})			105	100			0.15
		20			100	100	575	100	0.15
		40			90	95			0.17
	(A)	5 (1×10^{-4})			93	71		126	0.15
		10			118	100		166	0.19
		20			118	87		160	0.24
2	(IF)	20	(IIA)	10 (1×10^{-3})	282	282	575	468	0.18
		20		20	332	282		660	0.17
		20		40	440	200		1,000	0.12
3	(A)	20	(IIA)	10 (1×10^{-3})	200	98		450	0.18
		20		20	282	85		660	0.22
		20		40	332	71		1,000	0.22
4			(B)	10 (2×10^{-3})	166	(*)	550	950	0.11
				20	224	(*)		1,050	0.12
				40	270	(*)		1,170	0.13
5			(C)	20 (5×10^{-4})	166	(*)	580	900	0.11
				40	141	(*)		850	0.12
6	(IF)	20	(B)	20 (2×10^{-3})	166	142	550	600	0.12
		20			220	166		700	0.12
7		20	(C)	20 (5×10^{-4})	140	91	580	760	0.12
		20		40	152	68		560	0 13

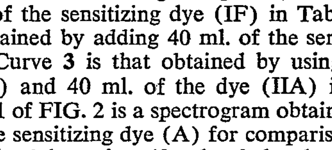
*See footnote at end of Table 1.

On the other hand, the non-exposed sample was subjected to light wedge exposure using a reflection type refractive lattice spectrograph (GR-2 (trademark), made by Narumi Co.) and then to development in the same manner as above to obtain a wedge spectrogram.

Curve **1** of FIG. 1 is a spectrogram obtained by adding 20 ml. of the sensitizing dye (IF) in Table 2, Curve **2** is that obtained by adding 40 ml. of the sensitizing dye (IIA) and Curve **3** is that obtained by using 20 ml. of the dye (IF) and 40 ml. of the dye (IIA) in combination. Curve **1** of FIG. 2 is a spectrogram obtained by using 10 ml. of the sensitizing dye (A) for comparison, Curve **2** is that obtained by using 40 ml. of the dye (IIA) and Curve **3** is that obtained by using 10 ml. of the dye (A) and 40 ml. of the dye (IIA) in combination. Similarly, Curves **1**, **2** and **3** of FIG. 3 are spectrograms obtained by using 20 ml. of the dye (IF), 20 ml. of the sensitizing dye (C) for comparison and 20 ml. of the dye (C) and 20 ml. of the dye (IF) in combination, respectively and Curves **1**, **2** and **3** of FIG. 3 are spectrograms obtained by using 20 ml. of the dye (IF), 40 ml. of the dye (B) and 20 ml. of the dye (IF) and 40 ml. of the dye (B) in combination, respectively. It can be readily seen that, in the case of FIG. 1, for example, the sensitivity obtained by using the dyes (IF) and (IIA) in combination, is supersensitization over the entire sensitive wave length region as compared with that obtained by using the dye (IF) or (IIA) along. Similar results may be observed with regard to the other figures.

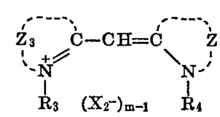
What is claimed is:

1. A silver halide photographic emulsion containing a supersensitizing combination, comprising at least one sensitizing dye represented by the formula:



(I)

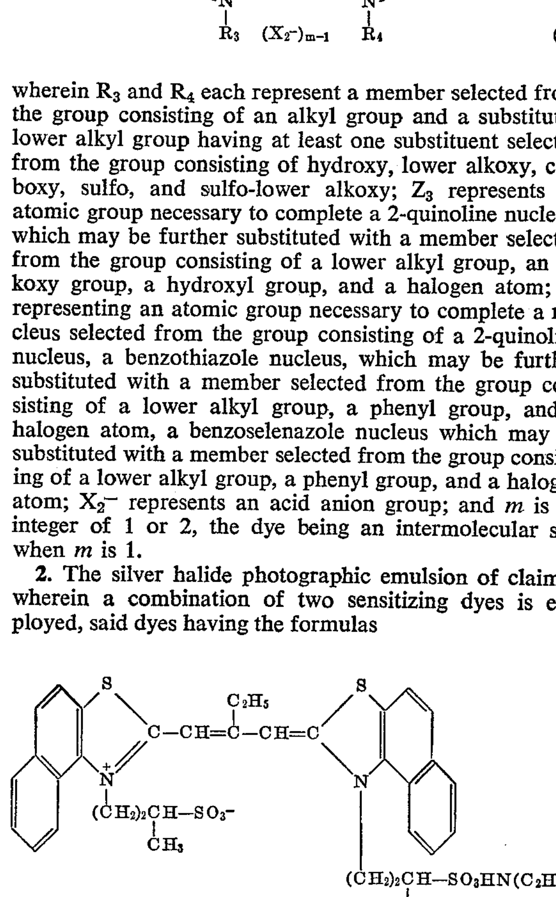
wherein R represents a member selected from the group consisting of an alkyl group of from 1 to 4 carbon atoms and a hydrogen atom; R_1 and R_2 each represent a member selected from the group consisting of a lower alkyl group and a substituted lower alkyl group having at least one substituent selected from the group consisting of a sulfo radical and a carboxy radical, at least one of R_1 and R_2 being a substituted lower alkyl group; Z_1 represents an atomic group necessary to complete a nucleus selected from the group consisting of a naphthothiazole, a naphthoselenazole and a naphthoxazole; Z_2 represents an atomic group necessary to complete a nucleus selected from the group consisting of a naphthothiazole, a benzothiazole, a naphthoselenazole, a benzoselenazole, a naphthoxazole, and a benzoselenazole; X_1^- represents an acid anion group; and n is an integer of 1 or 2, the dye being an intramolecular salt when n is 1, and at least one sensitizing dye of the formula (II)



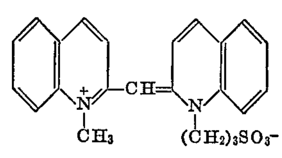
(II)

wherein R_3 and R_4 each represent a member selected from the group consisting of an alkyl group and a substituted lower alkyl group having at least one substituent selected from the group consisting of hydroxy, lower alkoxy, carboxy, sulfo, and sulfo-lower alkoxy; Z_3 represents an atomic group necessary to complete a 2-quinoline nucleus, which may be further substituted with a member selected from the group consisting of a lower alkyl group, an alkoxy group, a hydroxyl group, and a halogen atom; Z_4 representing an atomic group necessary to complete a nucleus selected from the group consisting of a 2-quinoline nucleus, a benzothiazole nucleus, which may be further substituted with a member selected from the group consisting of a lower alkyl group, a phenyl group, and a halogen atom, a benzoselenazole nucleus which may be substituted with a member selected from the group consisting of a lower alkyl group, a phenyl group, and a halogen atom; X_2^- represents an acid anion group; and m is an integer of 1 or 2, the dye being an intermolecular salt when m is 1.

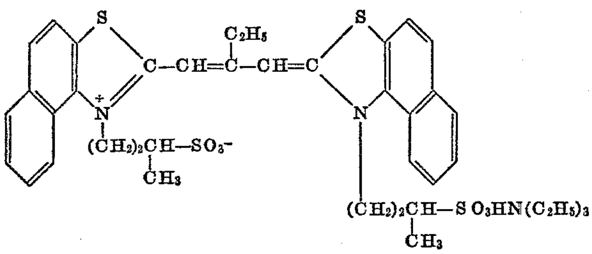
2. The silver halide photographic emulsion of claim **1** wherein a combination of two sensitizing dyes is employed, said dyes having the formulas



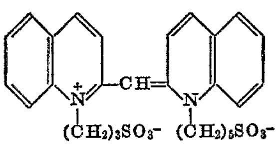
and

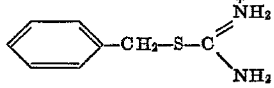


3. A silver halide photographic emulsion as claimed in claim **1**, where a sensitizing dye of formula



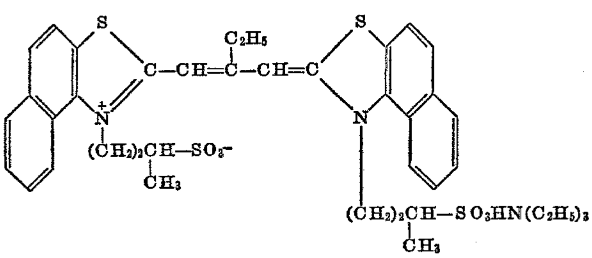
and a sensitizing dye of formula



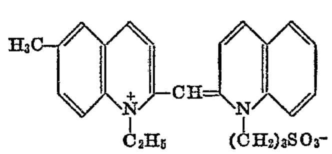


are incorporated in combination.

4. A silver halide photographic emulsion as claimed in claim **1**, where a sensitizing dye of formula

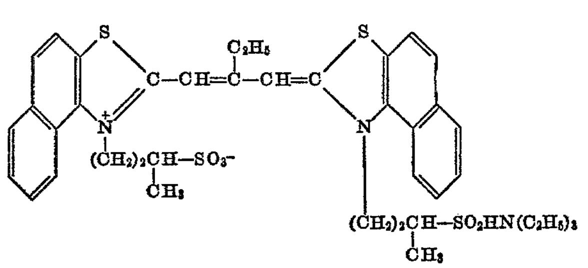


and a sensitizing dye of formula

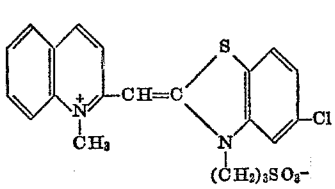


are incorporated in combination.

5. A silver halide photographic emulsion as claimed in claim **1**, where a sensitizing dye of formula

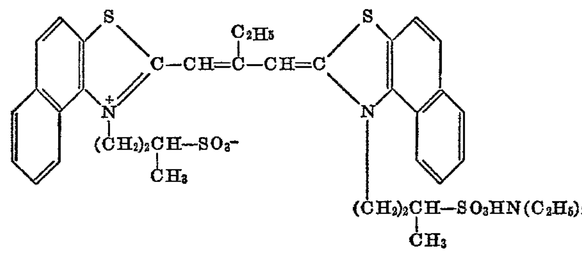


and a sensitizing dye of formula

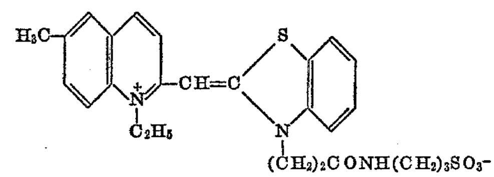


are incorporated in combination.

6. A silver halide photographic emulsion as claimed in claim **1**, where a sensitizing dye of formula

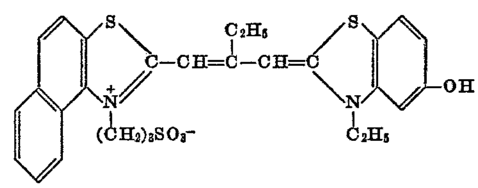


and a sensitizing dye of formula

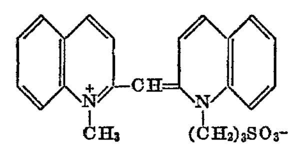


are incorporated in combination.

7. A silver halide photographic emulsion as claimed in claim **1**, where a sensitizing dye of formula

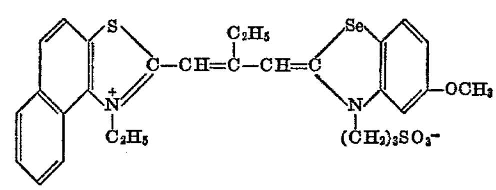


and a sensitizing dye of formula

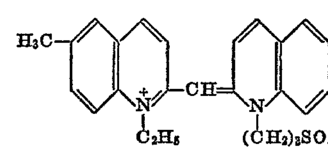


are incorporated in combination.

8. A silver halide photographic emulsion as claimed in claim **1**, where a sensitizing dye of formula

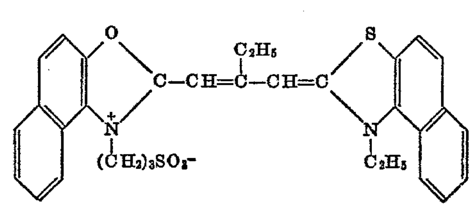


and a sensitizing dye of formula

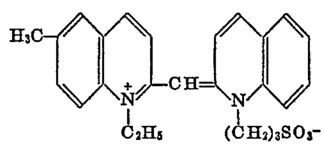


are incorporated in combination.

9. A silver halide photographic emulsion as claimed in claim **1**, where a sensitizing dye of formula

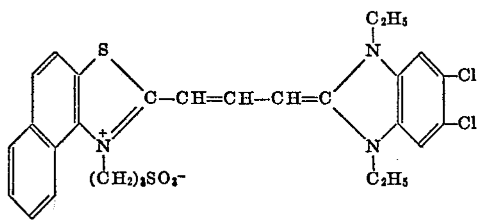


and a sensitizing dye of formula

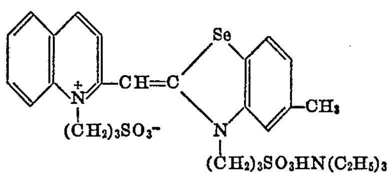


are incorporated in combination.

10. A silver halide photographic emulsion as claimed in claim **1**, where a sensitizing dye of formula

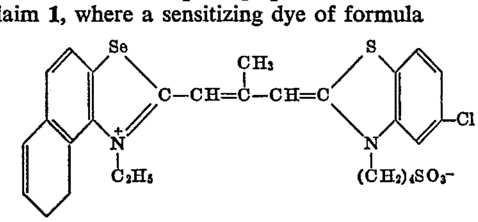


and a sensitizing dye of formula

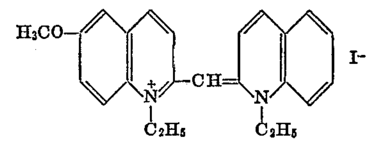


are incorporated in combination.

11. A silver halide photographic emulsion as claimed in claim **1**, where a sensitizing dye of formula



and a sensitizing dye of formula



are incorporated in combination.

12. A photographic light-sensitive element comprising a support having thereon at least one layer containing a silver halide photographic emulsion as recited in claim **1**.

13. The silver halide photographic emulsion of claim **1**, wherein said dyes may be present in an amount of from 1×10^{-6} mol to 5×10^{-4} mol per mol of silver halide.

14. The silver halide photographic emulsion of claim **1**, wherein the ratio of the sensitizing dye represented by Formula II to that of Formula I ranges from 100:1 to 1:10.

15. The silver halide photographic emulsion of claim **14**, wherein said ratio ranges from 10:1 to 1:2.

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U.S. Cl. X.R.

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