

fig. 1

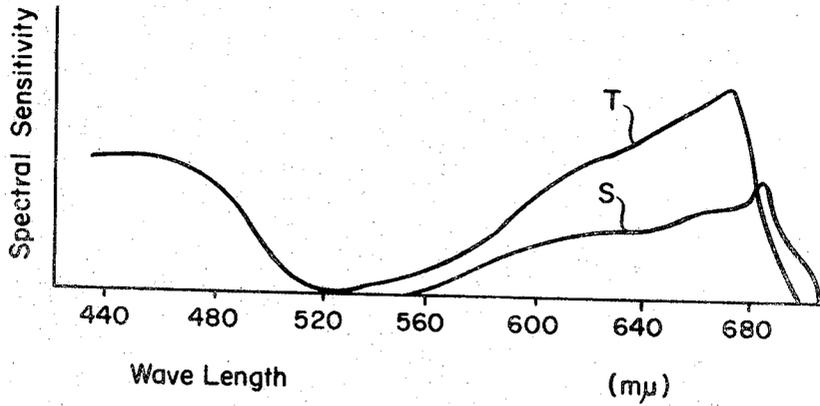


fig. 2

INVENTORS
Keisuke Shiba
Akira Sato

BY
Stephen, Rothwell, Mason, Limco & Associates
ATTORNEYS

PHOTOGRAPHIC SUPERSENSITIZED SILVER HALIDE EMULSIONS

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a photographic silver halide emulsion which has been spectrally sensitized, and more particularly, to a photographic silver halide emulsion in which the spectral sensitivity of the red-sensitive region has been increased by using a combination of at least two types of sensitizing dyes.

2. Description of the Prior Art

One well known sensitizing technique used in the preparation of photographic light sensitive elements involves incorporating a sensitizing dye in a photographic silver halide emulsion, whereby the silver halide emulsion is spectrally sensitized or the light-sensitive wavelength region is altered to encompass a longer wave length.

The extent of spectral sensitization depends upon the chemical structure of the sensitizing dye used, the properties of the silver halide emulsion, such as the type of silver halide employed in the emulsion, the crystal habits and the crystal system of the silver halide, the silver ion concentration, the pH of the silver halide emulsion, and the like.

Further, the extent of spectral sensitization is also influenced by additives which are usually incorporated in a silver halide emulsion, such as, stabilizers, antifoggants, wetting agents, precipitants, and other various agents for improving the physical properties of the emulsion layer. Generally, however, the spectral sensitivity of a silver halide emulsion sensitized by a sensitizing dye will be reduced.

In photographic light-sensitive elements, at times only one sensitizing dye is employed for sensitizing a desired spectral wavelength region, but usually a combination of two or more sensitizing dyes will be employed for this purpose. However, the sensitivity obtained by a combination of sensitizing dyes is usually lower than that obtained by using separate sensitizing dyes. This phenomenon is generally called "antisensitization."

However, in certain specific cases, the spectral sensitivity obtained when using a combination of two or more sensitizing dyes is markedly higher than that obtained by using the sensitizers separately. This situation is called "super-sensitization." It is known, in "super-sensitization," that the chemical structures of the sensitizing dyes must be rigorously selected in view of each other, as a slight variation of the structures will remarkably influence "super-sensitization" by the dyes. Unfortunately, the effect of any one combination of sensitizing dyes cannot be easily anticipated from their mere chemical structures. Thus, the basic problem in the area spectral sensitization has been finding combinations of two or more sensitizing dyes which will show the desired super-sensitizing qualities.

A multilayer color photographic light sensitive element used in a subtractive color process usually has a blue-sensitive emulsion layer, a green-sensitive emulsion layer, and a red-sensitive emulsion layer. In particular, in a multilayer color photographic camera element for subtractive color processes, the spectral sensitivity distribution of each light-sensitive emulsion layer is an important factor in determining the color reproducing properties of the color photographic element.

In general, to obtain suitable color reproducing properties, the spectral light-sensitive wave length regions of the blue-sensitive emulsion layers, green-sensitive emulsion layers, and red-sensitive emulsion layers must be adequately separated from each other. Since panchromatic sensitizing dyes are employed in a red-sensitive emulsion, it is necessary that the spectral sensitivity of the green-sensitive region be as low as possible, while the spectral sensitivity of the red-sensitive region be increased as much as possible.

However, in the red-sensitive emulsion, it is desirable that the maximum sensitizing wavelength be no longer than 670 m. In addition, the sensitizing dyes incorporated into the red-

sensitive emulsion layer must not diffuse into adjacent emulsion layers, and thereby sensitize the adjacent layers.

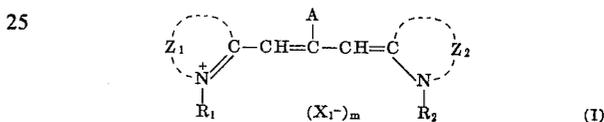
Furthermore, when a high speed color photographic light sensitive element is involved, the spectral sensitivity of each individual light-sensitive emulsion layer must be very high, and the sensitivity must not be lowered as time passes.

In the case of a multilayer color photographic element for subtractive color process which contains couplers in the emulsion layers, the spectral sensitivity of each light-sensitive emulsion must not be reduced by the presence of the coupler when the emulsion is handled or stored in the liquid state.

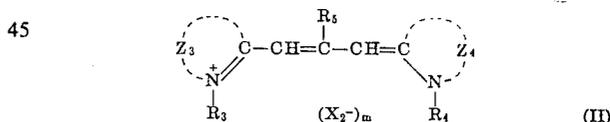
SUMMARY OF THE INVENTION

It has been found that a photographic silver halide emulsion in which the spectral sensitivity of the red-sensitive region has been increased may be produced by using a combination of at least two types of sensitizing dyes. Specifically, at least one carbocyanine dyes represented by general formula (I) and at least one carbocyanine dye represented by general formula (II) are utilized in the combination.

A carbocyanine dye represented by general formula (I) may be represented as follows:



wherein Z_1 represents an atomic group necessary for forming a member selected from the group consisting of a naphthothiazole ring and a naphthoselenazole ring; Z_2 represents an atomic group necessary for forming a member selected from the group consisting of a naphthothiazole ring, a naphthoselenazole ring, a benzothiazole ring, and a benzoselenazole ring; R_1 and R_2 each represents a member selected from the group consisting of an alkyl group and a substituted alkyl group; A represents a member selected from the group consisting of a phenyl group and a substituted phenyl group; X_1^+ represents an anion; and n is 0 or 1; said dye forming an intramolecular salt when n is 0. A carbocyanine dye represented by general formula (II) may be illustrated as follows:



wherein Z_3 and Z_4 each represents an atomic group necessary for forming a member selected from the group consisting of a benzothiazole ring and a benzoselenazole ring; R_3 and R_4 each represents a member selected from the group consisting of an alkyl group and a substituted alkyl group; R_5 represents a lower alkyl group; X_2^+ represents an anion; and m is 0 or 1; said dye forming an intramolecular salt when m is 0.

Accordingly, it is an object of the present invention to provide a photographic silver halide emulsion in which the red sensitivity has been increased by super-sensitization, without shifting the maximum sensitizing wavelength to a wavelength which is too long to be acceptable.

Another object of this invention is to provide a photographic silver halide emulsion capable of preventing panchromatic sensitizing dyes used in the red-sensitive emulsion layer from diffusing into adjacent emulsion layers, thereby imparting red sensitivity thereto.

BRIEF DESCRIPTION OF THE DRAWING

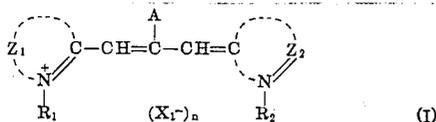
FIGS. 1 and 2 of the accompanying drawings illustrate the spectrosensitivity curves obtained for various dye samples.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

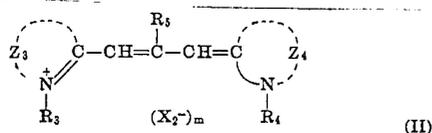
The objects of this invention can be attained by incorporating into a photographic silver halide emulsion a combination

3

of at least one carbocyanine dye (hereinafter called "sensitizing dye 1") represented by general formula I



wherein Z_1 represents an atomic group necessary for the formation of a naphthothiazole ring or a naphthoselenazole ring; Z_2 represents an atomic group necessary for the formation of a naphthothiazole ring, a naphthoselenazole ring, a benzothiazole ring, or a benzoselenazole ring; R_1 and R_2 each represents an alkyl group or a substituted alkyl group; A represents a phenyl group or a substituted phenyl group; X_1^- represents an anion; and n is 0 or 1 (said dye forming an intramolecular salt when n is 0); and at least one carbocyanine dye (hereinafter called "sensitizing dye 2") represented by general formula II



wherein Z_3 and Z_4 each represent an atomic group necessary for the formation of a benzothiazole ring or a benzoselenazole ring; R_3 and R_4 each represents an alkyl group or a substituted alkyl group; R_5 represents a lower alkyl group; X_2^- represents an anion; and m is 0 or 1; said dye forming an intramolecular salt when m is 0.

In the above formula, A is defined to be a phenyl group or a substituted phenyl group. Illustrative substituents for the substituted phenyl group are: a carboxyl group, a sulfonic acid group, a sulfoalkoxy group, a halogen atom, an alkyl group, an alkoxy group, an oxy group, and the like. Illustrative examples of R_1 , R_2 , R_3 and R_4 are: a methyl group, an ethyl group, a propyl group, a 2-hydroxyethyl group, a 2-methoxyethyl group, a carboxymethyl group, a 2-carboxyethyl group, a 3-carboxypropyl group, a 4-carboxybutyl group, a 2-sulfoethyl group, a 3-sulfopropyl group, a 4-sulfobutyl group, a 3-sulfoisobutyl group, a 2-carboethoxyethyl group, an aralkyl group, an allyl group, i.e., a vinyl methyl group, and the like.

The benzothiazole ring or the benzoselenazole ring (among the rings represented by Z_1 or Z_2) may have substituents such as: a halogen atom, a phenyl group, a sulfophenyl group, a sulfoalkoxy group, a carboalkoxy group, a sulfonic acid group or an alkyl group at the 5- and/or the 6-position thereof.

As mentioned above Z_3 and Z_4 represent an atomic group necessary in the formation of a benzothiazole ring or a benzoselenazole ring, and these rings may be substituted by an alkyl group, a phenyl group or a halogen atom.

Illustrative of the anions represented by X_1^- or X_2^- are chlorine ions, bromine ions, iodine ions, perchloric acid ions, p-toluene sulfonic acid ions, ethyl sulfate ions, and the like.

The main feature of the present invention is that sensitizing dye 1 acts as a super-sensitizer to sensitizing dye 2.

Sensitizing dye 1 has a substituted or unsubstituted phenyl group at the meso-position thereof, and further, at least one of the two heterocyclic rings of the cyanine dye is a naphthothiazole ring or a naphthoselenazole ring. This unique chemical structure is believed to be most important to the synergistic effect obtained.

When sensitizing dye 1 is used alone, the red sensitivity of the silver halide emulsion obtained is lower than that obtained by using sensitizing dye 2 alone. However, when sensitizing dye 1 is incorporated in a silver halide emulsion together with sensitizing dye 2, an extremely high red sensitivity, much greater than that obtained when using sensitizing dye 2 alone is obtained due to a super-sensitization. This is the most important feature of the present invention.

Another important feature of the present invention is that when sensitizing dye 2 is used together with sensitizing dye 1,

4

which acts as a super-sensitizer, the maximum sensitizing wavelength of sensitizing dye 2 does not substantially shift to a longer wavelength.

These properties are extremely useful in improving the color reproduction qualities of color photographic light-sensitive elements.

The inventors have already found that a mesoalkyl-substituted naphtho-thia-carbocyanine dye has a super-sensitizing action to some of the sensitizing dyes represented by general formula I (cf. U.S. application, Ser. No. 592,292, now U.S. Pat. No. 3,522,052).

Sensitizing dye 1 of the present invention has many merits. A smaller amount of dye 1 than of the aforesaid mesoalkyl-substituted naphtho-thia-carbocyanine dye can provide a higher red sensitivity, and further, the amounts thereof may be varied in a considerably wider range. In addition, the maximum sensitizing wavelength is not shifted to an unacceptable longer wavelength.

Sensitizing dye 1 of this invention has a comparatively flat spectral sensitivity distribution over the whole red-sensitive region, and the green sensitivity thereof is comparatively low.

Moreover, sensitizing dye 1 of this invention when incorporated into a red-sensitive emulsion layer, will scarcely diffuse into adjacent emulsion layers and impart red sensitivity thereto. Hence the use of this dye improves effectively the formation of color mixing to such an extent that practically no color mixing will occur.

When sensitizing dye 1 is incorporated into a photographic silver halide emulsion together with the other sensitizing dye according to the present invention, the harmful effects of any coupler present in the silver halide emulsion on spectral sensitivity are reduced.

Generally, it has been believed that carbocyanine sensitizing dye having a phenyl group or a substituted phenyl group at the meso-position thereof will only give low sensitivity, due to steric hindrance. Directly opposite to this belief, when sensitizing dye 1, having a phenyl group or a substituted phenyl group at the meso-position thereof, is incorporated, as a super-sensitizer, in a photographic silver halide emulsion, together with the other sensitizing dye, as in this invention, an extremely high red-sensitivity is unexpectedly obtained and there is no shift of the maximum sensitizing wavelength to a longer wavelength.

Sensitizing dye 2, represented by general formula II, is a carbocyanine dye which tends to provide a J-band and which has a spectral sensitivity mainly at the red-sensitive region, that is, in the region of from 590 $m\mu$ to 680 $m\mu$. The heterocyclic ring thereof may be substituted with an alkyl group, a phenyl group, a halogen atom and the like, to provide a proper spectral sensitivity distribution.

The sensitizing dyes used in the present invention can be dissolved in a water-soluble organic solvent such as methanol, ethanol, acetone, pyridine and the like, and the sensitizing dyes of this invention may be incorporated in a silver halide emulsion as an organic solvent solution of two or more dyes, or as an organic solvent solution of each separate dye. Of course, according to the purpose for which the final product is desired, the order of addition of the sensitizing dyes, the ratio of the amounts of sensitizing dyes, the proportions of the sensitizing dyes to silver halide emulsion used, and the like may be varied.

As the silver halide emulsion employed in the present invention, there are silver chlorobromide emulsions, silver bromide emulsions, silver iodobromide emulsions, silver chloride emulsions, silver chloriodobromide emulsions and the like. Into the silver halide emulsions described above there may be incorporated in addition to the sensitizing dyes of this invention additives which are usually employed, such as, stabilizers, antifoggants, agents for improving the physical properties of emulsion films, plasticizers, couplers and wetting agents. The silver halide emulsion of this invention may be applied to proper supports, such as, cellulose derivative films, plastic films, or baryta papers.

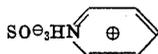
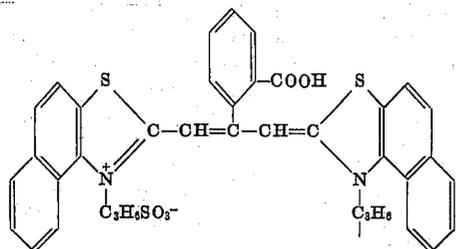
A few examples of the sensitizing dyes used in the present invention will be illustrated below, but it should be understood

5

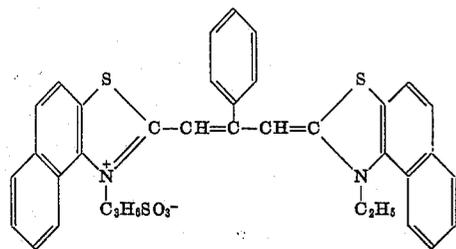
6

that the dyes of this invention are not to be limited only to those set out.

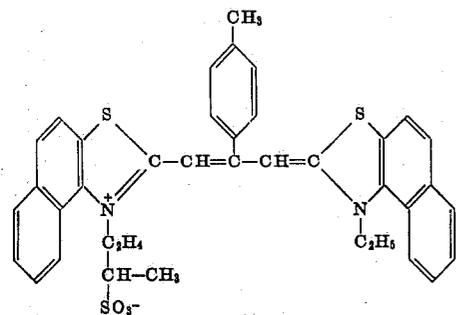
(IA)



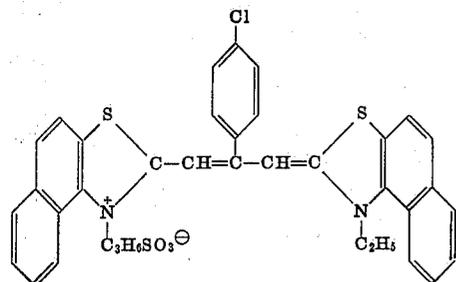
(IB)



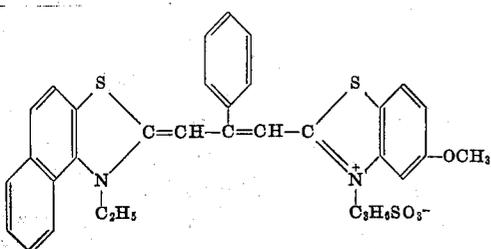
(IC)



(ID)

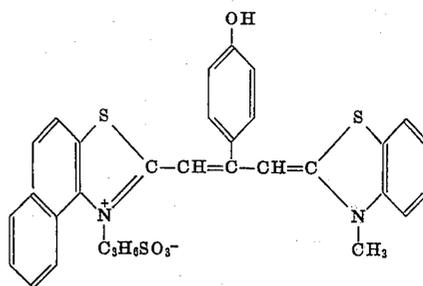


(IF)



(IG)

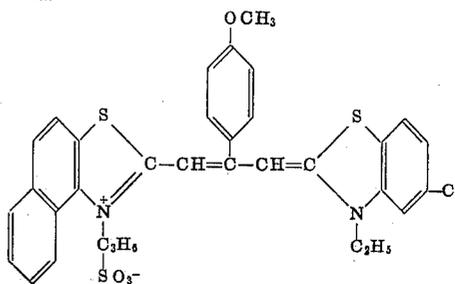
5



10

(IJ)

15

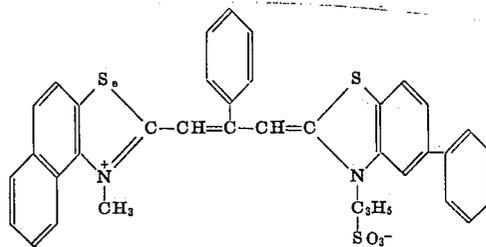


20

25

(IK)

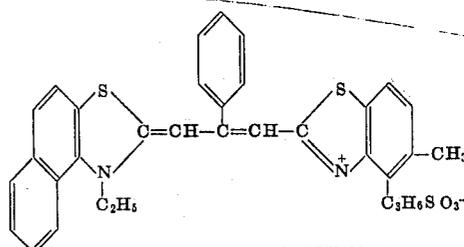
30



35

(IL)

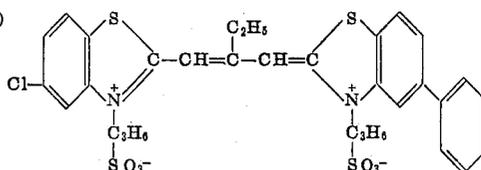
40



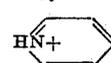
45

(IIA)

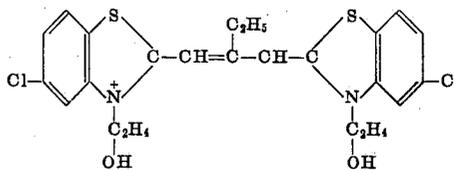
50



55



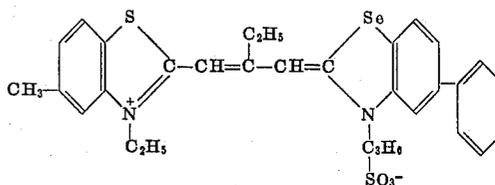
60 (IIB)



65

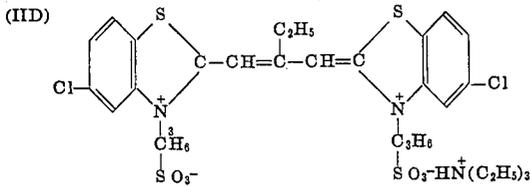
(IIC)

70



75

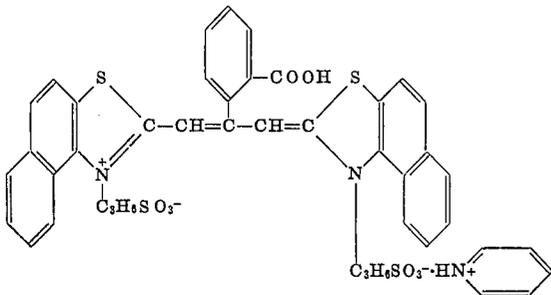
7



The sensitizing dyes represented by general formulas I and II may be prepared by known methods such as those described in U.S. Pat. Nos. 2,226,156 and 2,503,776.

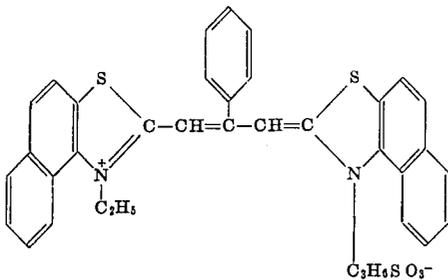
Examples of typical sensitizing dyes used in the present invention will be explained below.

Preparation 1: Sensitizing dye I-A



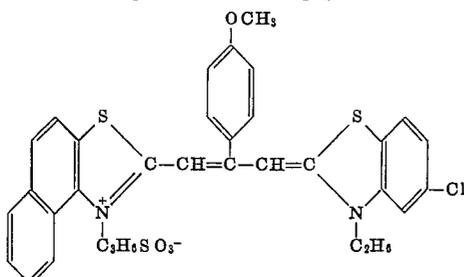
A mixture of 3 g. of anhydro-4,5-benzo-2-methyl-3-(3-sulfopropyl) benzothiazolium hydroxide and 3.5 g. of phthalic anhydride was reacted in 10 ml. of pyridine, under refluxing, by heating for 10 minutes. The crystal formed was recovered by filtration, washed with methanol with heating, and then recrystallized from a mixed solvent of methanol and chloroform to provide 0.9 g. of dye I-A, having a melting point of 223° C. The wavelength of the maximum spectral absorption of this sensitizing dye in methanol was 603 m μ .

Preparation 2: Sensitizing dye I-B



A mixture of 3 g. of 4,5-benzo-3-(3-sulfopropyl)-2-thio-benzoyl-methylenebenzothiazoline and 2 g. of methyl p-toluenesulfonate was reacted for 90 minutes at 110° C. The reaction product was mixed with 3.1 g. of anhydro-4,5-benzo-2-methyl-3-(3-sulfopropyl)benzothiazolium hydroxide, 150 ml. of ethanol, 50 ml. of methanol, and 3 ml. of triethylamine and the system was reacted with refluxing for 1 hour. The crystals thus formed were recovered by filtration and recrystallized from a mixed solvent of methanol and chloroform to provide 2.8 g. of sensitizing dye I-B, having a melting point of 289° C. The wavelength of the spectral absorption maximum of the dye, in methanol, was 602 m μ .

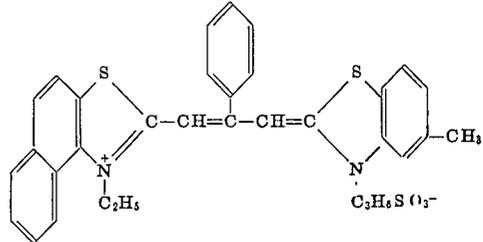
Preparation 3: Sensitizing dye I-J



8

A mixture of 1 g. of 5-chloro-3-ethyl-2-p-methoxythiobenzoyl-methylene benzothiazoline and 0.7 g. of p-toluene sulfonic acid was reacted under refluxing at 110° C. for 1 hour. The reaction product was mixed with 0.9 g. of anhydro-4,5-benzo-2-methyl-3-(3-sulfopropyl)benzothiazolium hydroxide, 30 ml. of ethanol, and 0.8 ml. of triethylamine, and the mixture thus formed was reacted under refluxing for 1 hour. The crystals thus formed were filtered and recrystallized from a mixed solvent of methanol and chloroform to provide 1.6 g. of dye I-J, having a melting point of 292° C. The wavelength of the spectral absorption maximum of the dye, in methanol, was 586 m μ .

Preparation 4: Sensitizing dye I-L



A mixture of 1 g. of 4,5-benzo-3-(3-sulfopropyl)-2-thio-benzoylmethyl benzothiazoline and 0.7 g. of methyl p-toluene sulfonate was reacted for 90 minutes at 110° C., and the reaction product was mixed with 0.9 g. of anhydro-2,5-dimethyl-3-(3-sulfopropyl)benzothiazolium hydroxide, 30 ml. of ethanol and 0.8 ml. of triethylamine followed by reacting, with refluxing, for 1 hour. The crystals thus formed were filtered and recrystallized from a mixed solvent of methanol and chloroform to provide 1.5 g. of dye I-L having a melting point greater than 300° C. The wavelength of the spectral absorption maximum of the dye, in methanol, was 586 m μ .

Some practical aspects of the invention will be shown by the following examples.

Example 1

A gelatino silver halide emulsion (100 g.), prepared in a conventional manner, was melted in a beaker at 40° C. Then, a predetermined amount of a methanol solution of sensitizing dye 1, having a known concentration, and a known amount of a methanol solution of sensitizing dye 2, having a known concentration, were added to the emulsion and stirred.

The system was then allowed to stand for 10 minutes in a thermostat-equipped bath maintained at 37° C. The system was then stirred, and the emulsion was uniformly applied to a glass plate at a thickness of 7.0 ml. per cabinet size (area), and set and dried to provide a light-sensitive emulsion layer.

By using a D.G. conversion filter, a light having a color temperature of 5400° K. was obtained from a light source having a color temperature of 2666° K. By using a Fuji No. 7 Filter (made by the Fuji Photo-Film Co.) which transmitted only light having a wavelength longer than about 600 m μ , a red light was obtained, and the light-sensitive emulsion layer prepared as above was exposed to the red light using an optical wedge.

Thereafter, the exposed emulsion layer was developed for 10 minutes at 20° C. in a developer having the following composition:

Water (50° C.)	750 ml.
Metol	2 g.
Sodium Sulfite (anhydrous)	100 g.
Hydroquinone	5 g.
Borax	2 g.
Further water to make 1,000 ml.	
pH, 8.70±0.10.	

The developed light-sensitive plate was further processed in a stopping bath and a fixing bath, and then washed with water. The density of the thus processed sample was measured using a S-Type Densitometer (made by the Fuji Photo-Film Co.) in order to determine red sensitivity. The optical density, which was utilized to determine the sensitivity, was calculated by

using the fog density plus 0.10. The red sensitivities of the various samples are shown in table 1 below.

In FIG. 2, curve S represents the spectral sensitivity curve obtained by using 2 ml. of the comparative sensitizing dye A at

TABLE 1

No.	Sensitizing dye used: molar concentration cc. (amount/ml.) of dye	Sensitizing dye used: molar concentration cc. (amount/ml.) of dye	Relative red sensitivity	Fog	Maximum sensitizing wave length(m μ)		
1	(I-A) (8×10^{-4} mol.)	(I-B) (2×10^{-4})	2	85	0.13	640	
			4	85	0.15	640	
			6	100	0.15	640	
			4	141	0.15	640	
			4	141	0.15	640	
			4	152	0.12	640	
			1	50	0.12	680	
			2	50	0.13	680	
			4	42	0.12	680	
			2	(I-A) (8×10^{-4} mol.)	(I-C) (2×10^{-4})	4	145
4	147	0.12				640	
4	160	0.13				640	
1	50	0.12				680	
2	50	0.12				682	
4	56	0.12				682	
3	(II-B) (4×10^{-4})	(I-A) (4×10^{-4})				2	97
			4	100	0.12	660	
			6	100	0.15	660	
			4	100	0.15	660	
			4	132	0.17	660	
			4	141	0.13	658	
			4	141	0.11	658	
			1	8	0.12	640	
			2	10	0.15	650	
			4	12	0.15	650	
4	(II-B) (4×10^{-4})	(I-D) (2×10^{-4})	4	0.4	200	0.13	650
			4	0.8	200	0.12	650
			4	1.6	200	0.12	650
	(II-B) (4×10^{-4})	(I-D) (2×10^{-4})	4	0.4	25	0.10	680
			4	0.8	38	0.10	680
			4	1.6	50	0.12	680
5	(II-C) (4×10^{-4})	(I-K) (2×10^{-4})	2	85	0.12	640	
			4	85	0.12	643	
			6	122	0.14	643	
			4	0.4	132	0.14	643
			4	0.8	132	0.13	643
			4	1.6	118	0.12	643
			4	0.4	16	0.15	656
			4	0.8	25	0.15	656
			4	1.6	35	0.16	656

A fresh light-sensitive emulsion produced in accordance with this invention was prepared by the procedure described above, and applied to a glass plate to form a light-sensitive emulsion layer. The light-sensitive emulsion layer thus formed was subjected to spectral exposure by means of a reflection-type grating spectrograph and developed as described above. The spectral sensitivity of the thus prepared sample was measured to provide a spectral sensitivity curve.

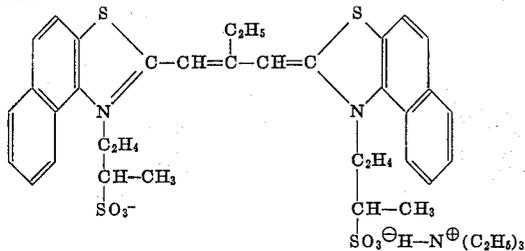
In FIGS. 1 and 2 of the accompanying drawings, the spectral sensitivity curves obtained are shown for various samples.

Curve P in FIG. 1 represents the spectral sensitivity curve obtained by using 4 ml. of sensitizing dye II-B, at a molar concentration of 4×10^{-4} moles per 100 g. of emulsion; curve Q represents the spectral sensitivity curve obtained by using 2 ml. of sensitizing dye I-A, at a molar concentration of 4×10^{-4} moles per 100 g. of emulsion; and curve R represents the spectral sensitivity curve obtained using 2 ml. of sensitizing dye I-A and 4 ml. of sensitizing dye II-B, in the proportions described in the first section of this paragraph.

From the results shown in FIG. 1, it is clear that by the incorporation of sensitizing dye I-A into the emulsion, a super-sensitization is obtained.

The procedures outlined above were repeated using a conventional sensitizing dye (dye A) which had no phenyl group at the meso-position thereof instead of sensitizing dye I. The spectral sensitivity curves of the various prepared samples utilizing dye A are shown in FIG. 2.

Sensitizing dye A may be represented by the following formula:

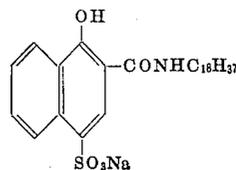


a molar concentration of 4×10^{-4} moles of dye per 100 g. of the emulsion. Curve T represents the results obtained when using 4 ml. of sensitizing dye II-B, and 2 ml. of sensitizing dye A, in the aforesaid concentrations per 100 g. of emulsion.

It is clear from the results shown in FIGS. 1 and 2 that when a combination of sensitizing I-A and sensitizing dye II-B was employed, a remarkable super-sensitization was obtained, the spectral absorption maximum wavelength was 658 m μ ., and light-sensitive portions in the longer wavelength area were less; whereas, when a combination of sensitizing dye A and sensitizing dye II-B was employed, the super-sensitizing effect was lower than that illustrated by the present invention, the absorption maximum wavelength was about 670 m μ ., and considerable light-sensitive portions were present in the longer wave area.

Example 2

A gelatino silver iodobromide emulsion (100 g.) prepared by conventional means was fused in a beaker at 37° C. The sensitizing dyes of this invention were added to the emulsion as in example 1, and the mixture was stirred and allowed to stand for 60 minutes at 37° C. Thereafter, 20 ml. of a 5 percent aqueous alkali solution of a cyan coupler having the following formula:



was added to the silver halide emulsion and stirred. After adjusting the pH of the emulsion to 6.5 with citric acid and adding a hardening agent, a surface active agent, and a wetting agent, the resulting silver halide emulsion was applied directly to a film support, and dried to provide a red-sensitive color photographic film.

The red-sensitive color photographic film thus prepared was subjected to a wedge exposure, or spectral exposure as in example 1, and developed for 10 minutes at 20° C. in a color developer containing, as a color developing agent, a N,N'-diethylamino-p-aminoaniline derivative. The light-sensitive film thus developed was subjected to primary fixing, bleaching, secondary fixing, and washing, to provide a negative cyan image. The red density of the cyan image was measured to provide a relative red sensitivity, the results being shown in table 2.

TABLE 2

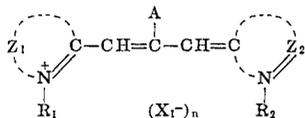
Run No.	Sensitizing dye used: molar concentration cc. (amount/ml.) of dye	Sensitizing dye used: molar concentration cc. (amount/ml.) of dye	Relative red sensitivity	Fog length (mμ)	Maximum sensitizing wave	
..... (II-D) (8×10 ⁻⁴)..... (I-E) (2×10 ⁻⁴).....	2	0.4	97	0.10	650
		4	0.8	100	0.12	658
		6	1.6	100	0.12	660
		4	0.4	282	0.13	660
		4	0.8	250	0.15	660
		4	1.6	260	0.14	660
		8	8	50	0.12	670
7..... (II-D) (8×10 ⁻⁴)..... (I-F) (2×10 ⁻⁴).....	4	0.4	232	0.12	660
		4	0.8	232	0.10	660
		4	1.6	200	0.15	660
		4	2	37	0.12	670
		4	4	42	0.15	670
		4	8	31	0.15	670
		8..... (II-D) (8×10 ⁻⁴)..... (I-G) (2×10 ⁻⁴).....	4	0.4	142
4	0.8			232	0.13	660
4	1.6			232	0.13	660
4	2			31	0.12	660
4	4			31	0.12	660
4	8			25	0.12	660
9..... (II-D) (8×10 ⁻⁴)..... (I-J) (2×10 ⁻⁴).....			4	0.4	232
		4	0.8	250	0.13	662
		4	1.6	200	0.15	662
		4	2	50	0.12	667
		4	4	50	0.12	670
		4	8	60	0.14	670
		10..... (II-D) (8×10 ⁻⁴)..... (I-L) (2×10 ⁻⁴).....	4	0.4	232
4	0.8			282	0.12	658
4	1.6			200	0.12	655
4	2			50	0.12	670
4	4			60	0.15	670
4	8			60	0.15	670

The composition of the color developer used in the above experiment was as follows:

N,N'-diethylamino-p-aminoaniline sulfate	2.0 g.
Sodium sulfite	20 g.
Sodium carbonate (mono-hydrate)	50 g.
Hydroxyl amine hydrochloride	1.5 g.
Potassium bromide	1.0 g.
Water to make 1000 ml.	
pH, 10.8±0.1	

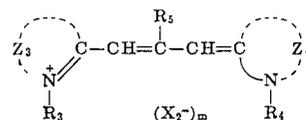
What is claimed is:

1. A photographic silver halide emulsion containing at least one carbocyanine dye represented by general formula (I)



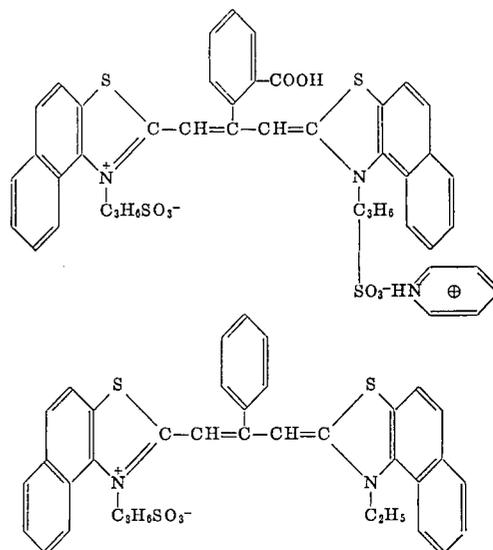
A wherein Z₁ represents an atomic group necessary for forming a member selected from the group consisting of a naphthothiazole ring and a naphthoselenazole ring; Z₂ represents an atomic group necessary for forming a member selected from the group consisting of a naphthothiazole ring, a naphthoselenazole ring, a benzothiazole ring, and a benzoselenazole ring; R₁ and R₂ each represent a member selected from the group consisting of an alkyl group and a substituted alkyl group selected from the class consisting of a hydroxyalkyl group, an alkoxyalkyl group, a sulfo radical-containing alkyl group, a carboxy radical-containing alkyl group, an aralkyl group and an allyl group, as is used in the carbocyanine dye art; A represents a member selected from the group consisting of a phenyl group and a substituted phenyl group wherein said substituent is selected from the class consisting of a carboxyl-, a sulfonic acid-, a sulfoalkoxy-, a

halogen-, an alkyl-, an alkoxy- and an oxy group; X₁⁻ represents an anion; and n is 0 or 1; said dye forming an intramolecular salt when n is 0; and at least one carbocyanine dye represented by the general formula (II)

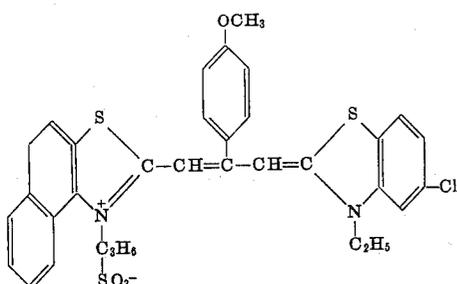
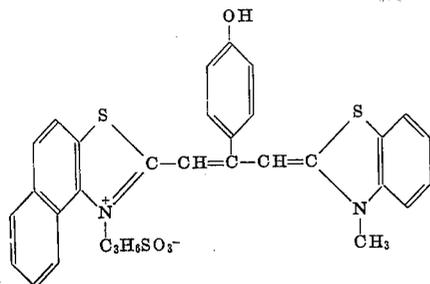
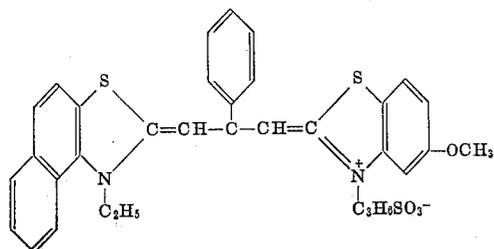
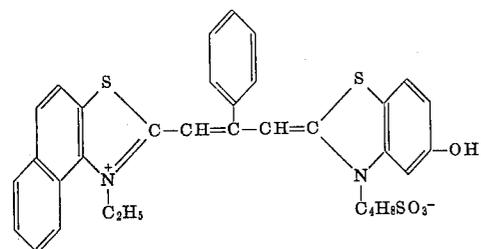
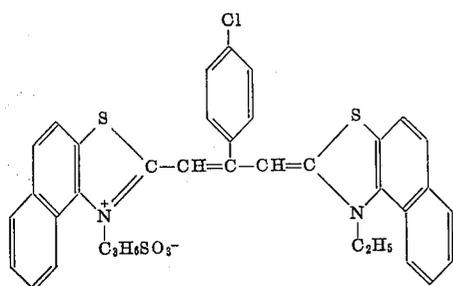
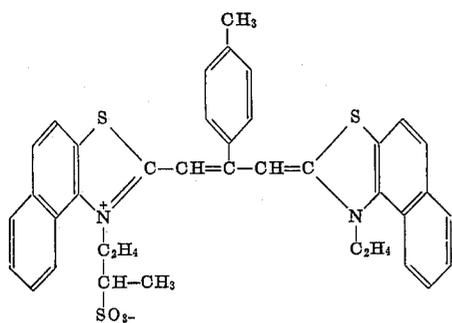


awherein Z₃ and Z₄ each represents an atomic group necessary for forming a member selected from the group consisting of a benzothiazole ring and a benzoselenazole ring; R₃ and R₄ have the same meaning as defined for R₁ and R₂ above, at least one of said R₁, R₂, R₃ and R₄ being selected from the class consisting of a sulfo radical-containing alkyl group and a carboxy radical-containing alkyl group; R₅ represents a lower alkyl group; X₂⁻ represents an anion; and m is 0 or 1; said dye forming an intramolecular salt when m is 0.

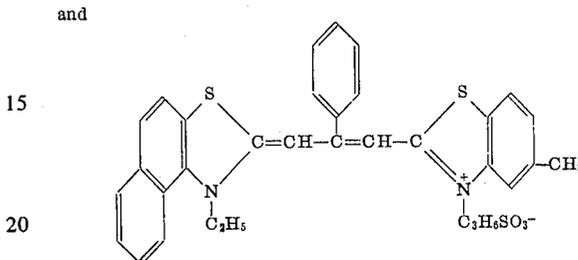
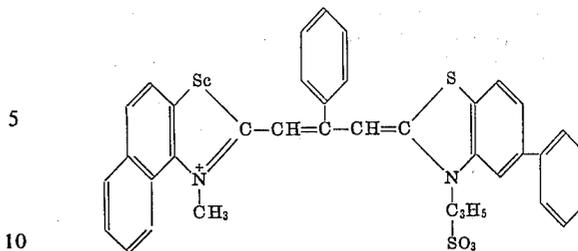
2. A photographic silver halide emulsion as claimed in claim 1 wherein the carbocyanine dye represented by general formula (I) is a compound selected from the group consisting of:



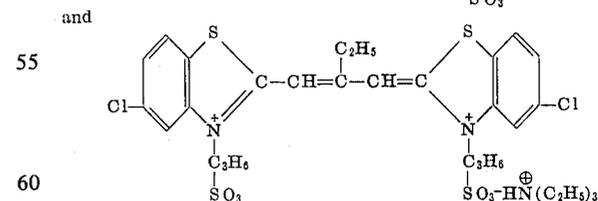
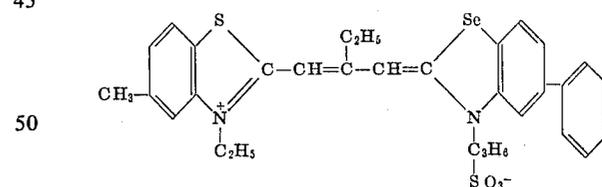
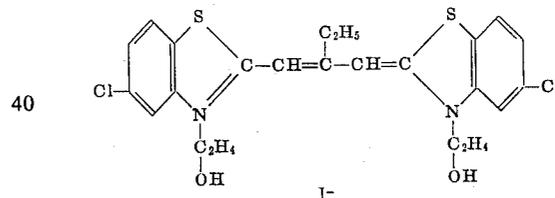
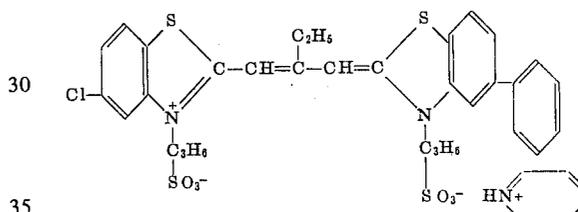
13



14



3. A photographic silver halide emulsion as claimed in claim 1, wherein the carbocyanine dye represented by general formula (II) is a compound selected from the group consisting of:



4. A photographic silver halide emulsion as defined in claim 1 wherein R_1 , R_2 , R_3 and R_4 are selected from the group consisting of a methyl group, an ethyl group, a propyl group, a 2-hydroxyethyl group, a 2-methoxyethyl group, a carboxymethyl group, a 2-carboxyethyl group, a 3-carboxypropyl group, a 4-carboxybutyl group, a 2-sulfoethyl group, a 3-sulfopropyl group, a 4-sulfobutyl group, a 3-sulfoisobutyl group, a 2-carboethoxyethyl group, an aralkyl group and a vinylmethyl group.

5. A photographic silver halide emulsion as in claim 1 wherein X_1^{1-} and X_2^{1-} are selected from the group consisting of chlorine ions, bromine ions, iodine ions, perchloric acid ions, p-toluene sulfonic acid ions and ethyl sulfate ions.

6. A photographic silver halide emulsion as claimed in claim

I wherein in said combination there is no substantial shifting of the maximum sensitizing wavelength to a longer wavelength, and said sensitizing dye of formula (II) has a spectral sensitivity over substantially the whole red-sensitive region at 590 m μ to 680 m μ .

5

10

15

20

25

30

35

40

45

50

55

60

65

70

75