United States Patent

[11] 3,615,635

[72] Inventors **Keisuke Shiba;**
Akira Sato, both of Kanagawa, Japan

[21] Appl. No. **779,022**
[22] Filed **Nov. 26, 1968**
[45] Patented **Oct. 26, 1971**

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

[32] Priority **Nov. 27, 1967**
[33] **Japan**
[31] **42/76071**

---

[54] **SILVER HALIDE PHOTOGRAPHIC EMULSION**
4 Claims, 2 Drawing Figs.

[52] **U.S. Cl.** **96/126,**
96/102, 96/104, 96/106
[51] **Int. Cl.** **G03c 1/28**
[50] **Field of Search** 96/104,
102, 94, 106; 260/240.8, 240.6

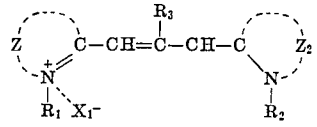
[56] **References Cited**

UNITED STATES PATENTS

3,173,791	3/1965	Kaleda	96/104
3,264,110	8/1966	Depoorter et al.	96/106
3,268,334	8/1966	DePoorter et al.	260/240.6 X
3,397,060	8/1968	Schwan et al.	96/104

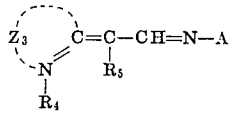
Primary Examiner—William D. Martin
Assistant Examiner—Theodore G. Davis
Attorney—Sughrue, Rothwell, Mion, Zinn & Macpeak

ABSTRACT: Silver halide photographic emulsion comprising at least one sensitizing dye represented by general formula I:

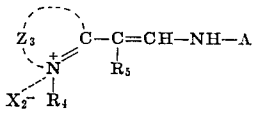


and at least one organic heterocyclic compound selected from the formulas represented by the general formulas II and III, wherein

general Formula II is:



and general Formula III is:



The substituent moieties shown in the above groups are described in the specification.

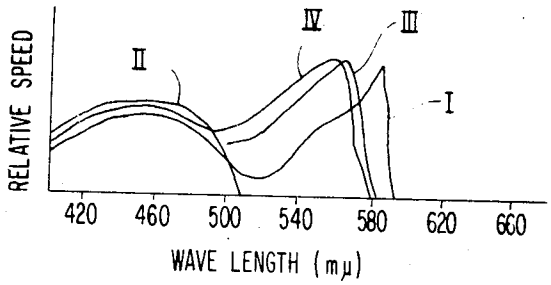


FIG. 1

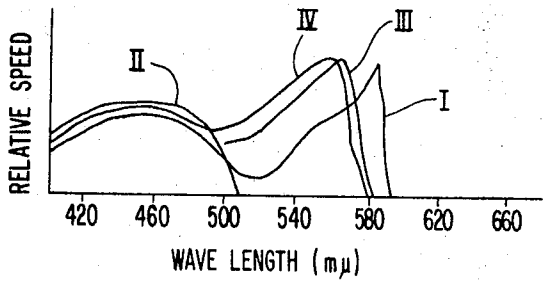
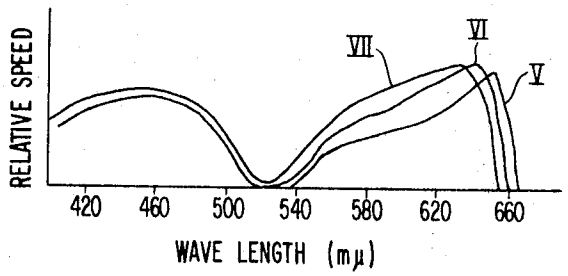


FIG. 2



INVENTORS
KEISUKE SHIBA
AKIRA SATO
BY
Leighton, Rothwell, Mion, Zinn & Macpeak
ATTORNEYS

SILVER HALIDE PHOTOGRAPHIC EMULSION

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a spectrally sensitized silver halide photographic emulsion and more particularly to a super-sensitized silver halide emulsion containing at least one organic heterocyclic compound, having a high spectral sensitivity and a suitable spectral sensitivity distribution.

2. Description of the Prior Art

It is well known that in making a photographic light-sensitive material a sensitizing dye is added to a silver halide photographic emulsion to thereby expand its spectral wavelength region towards the long wave length side, i.e., a spectral sensitizing technique is performed.

Spectral sensitivity is affected by the chemical structure of a sensitizing dye and by various properties of an emulsion, such as the halogen composition of the silver halide; crystal habit; crystal system; silver ion concentration; and the pH of the emulsion. The spectral sensitivity is also affected by additives present in an emulsion, such as a stabilizer, an antifoggant, a coating agent, a floculating agent, agents for modifying the physical properties of a film. In many cases, the spectral sensitivity of the film is lowered thereby.

A further technique has been known for making a light-sensitive material wherein two or more sensitizing dyes, or a sensitizing dye and an organic heterocyclic compound, are used in combination. In such a combination, there is often obtained a spectral sensitivity which is lower than either individual component. This is known as antisensitization. In certain special cases, however, the spectral sensitivity obtained by the use of a sensitizing dye in combination with one or more sensitizing dyes or organic heterocyclic compounds is "superadditively" increased, much beyond the results obtained by the use of a single sensitizing dye. This is known as supersensitization.

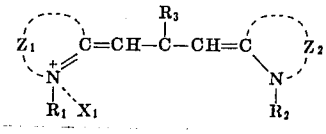
It is also well known that the selection of the materials for such combinations of sensitizing dyes and organic heterocyclic compounds is critical, since supersensitization is markedly affected by a slight difference in the chemical structure of components. Thus, a suitable combination of a sensitizing dye or organic heterocyclic compound having a supersensitization effect is not predictable from chemical structural formula alone. An important problem is spectral sensitizing techniques is to find suitable combinations of sensitizing dyes and organic heterocyclic compounds which will give a supersensitizing action.

Ordinarily, a multilayer color light-sensitive material for subtractive color processes comprises a blue-sensitive emulsion layer, green-sensitive emulsion layer and red-sensitive emulsion layer. In the case of a multilayer color light-sensitive material for use in subtractive color process (used in cameras in particular), the distribution of the spectral sensitivity of emulsion layer is the main factor in determining the color reproducing character of the color light-sensitive material. It is required that a green-sensitive emulsion layer have a sensitivity which is as high as possible, that the maximum spectral sensitivity not occur in the long wavelengths and that a high spectral sensitivity be present only in the green region. It is known that, for example, 5,5'-6,6'-tetrachlorobenzimidazolocarbocyane (represented by the general formula I) shows a strong maximum in its spectral sensitivity based upon the J-absorption band at 583–585 millimicrons. However, this is not preferred from the angle of color reproduction.

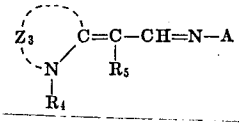
In the case of a red-sensitive emulsion layer, it must lower the spectral sensitivity in the green region while raising the spectral sensitivity in the red region, because a panchromatic sensitizing dye is generally used. Moreover, the maximum wavelength of the spectral sensitivity is preferably not at the longer wavelength side, for example, longer than 670 millimicrons. The requirement of a red-sensitive emulsion is to have a high spectral sensitivity in the narrow red region.

SUMMARY OF THE INVENTION

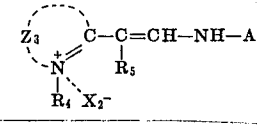
A silver halide photographic emulsion comprising at least one sensitizing dye represented by general formula 1:



wherein Z_1 and Z_2 are atoms necessary to complete a heterocyclic ring selected from the group consisting of a benzimidazole ring, a benzothiazole ring, a naphthothiazole ring and a benzoselenazole ring; R_1 and R_2 are a member selected from the group consisting of an unsubstituted alkyl group, a substituted alkyl group, a monovalent aliphatic unsaturated hydrocarbon group and an aralkyl group; R_3 is a member selected from the group consisting of a hydrogen atom and an alkyl group, said R_3 being a hydrogen atom when Z_1 and Z_2 are atoms forming benzimidazole ring; and X_1 is an anion group and at least one organic heterocyclic compound selected from the formulas represented by general formula II and II, wherein general formula II is:



wherein Z_3 is the atoms necessary to complete a heterocyclic ring selected from the group consisting of a benzimidazole ring and a naphthoimidazole ring; R_4 is a member selected from the group consisting of an unsubstituted alkyl group, a substituted alkyl group, a monovalent aliphatic unsaturated hydrocarbon group and an aralkyl group; R_5 is a member selected from the group consisting of a hydrogen atom and an alkylene group necessary to complete a ring when R_4 and R_5 are bonded to form the ring; and A is a member selected from the group consisting of an unsubstituted phenyl group and a substituted phenyl group and general formula III is



wherein X_2^1 is an anion group and A, Z_3, R_4 and R_5 have the same meaning as in general formula II.

It is the principal object of the present invention to provide a spectral sensitizing technique whereby the spectral sensitization of an ortho-chromatic sensitizing dye can be raised in a sufficiently narrow green region, while the spectral sensitization of a panchromatic sensitizing dye can be raised in sufficiently narrow red region.

BRIEF DESCRIPTION OF THE DRAWING

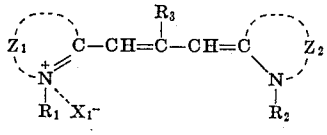
FIGS. 1 and 2 illustrate the spectral sensitivity curves resulting from the cases of utilizing a sensitizing dye alone and also in combination with an organic heterocyclic compound.

DETAILED DESCRIPTION OF THE INVENTION

The object of the invention can be accomplished by adding to a silver halide photographic emulsion at least one sensitiz-

ing dye represented by general formula I, and at least one organic heterocyclic compound represented by the general formula II, or, at least one organic heterocyclic compound represented by general formula III, in combination.

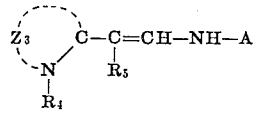
General Formula I



(I)

wherein Z_1 and Z_2 are atoms necessary to complete a benzimidazole ring, a benzothiazole ring, a naphthothiazole ring or a benzoselenazole ring; R_1 and R_2 are an alkyl group, a substituted alkyl group, a monovalent aliphatic unsaturated hydrocarbon group or an aralkly group; R_3 is a hydrogen atom or an alkyl group, said R_3 being a hydrogen atom when Z_1 and Z_2 are the atoms to complete a benzimidazole ring; and X_1^- is an anion group,

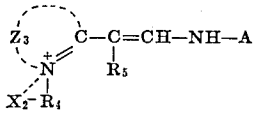
General Formula II



(II)

wherein Z_3 is the atoms necessary to complete a benzimidazole ring or a naphthoimidazole ring; R_4 is an alkyl group, a substituted alkyl group, a monovalent aliphatic unsaturated hydrocarbon group or an aralkyl group; R_5 represents hydrogen atoms or an alkylene group necessary t complete a ring when R_4 and R_5 are bonded to form the ring; and A is an unsubstituted or a substituted phenyl group.

General Formula III

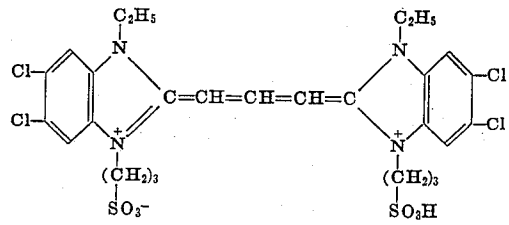


(III)

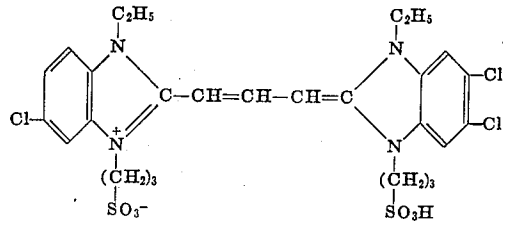
wherein X_2^- is an anion group and A, Z_3, R_4 and R_5 have the same meaning as in the general formula II.

In these formulas, for example, R_1, R_2, and R_4 are an alkyl group such as methyl, ethyl or propyl group, a substituted alkyl group such as 2-hydroxyethyl, 2-methoxyethyl, carboxymethyl, 2-carboxyethyl, 3-carboxypropyl, 4-carboxybutyl, 2-sulfoethyl, 3-sulfopropyl, 4-sulfobutyl, 3-sulfobutyl or a 2-carboethoxyethyl group, a monovalent aliphatic unsaturated hydrocarbon group such as an aryl group, and an aralkyl group. R_3 is a hydrogen atom or an alkyl group such as methyl or ethyl group. With respect to Z_1, Z_2 and Z_3, the ring may be substituted with a substituent, for example, a halogen atom, cyano, trifluoromethyl, phenyl, carboalkoxy, alkyl, hydroxyl or alkoxy group. X_1^- and X_2^- need not be present when the quaternary nitrogen atom and R_1 and R_2, or R_4 form a betaine structure. The details thereof will be understood by making reference to the following examples of suitable compounds, which are not intended to limit the invention.

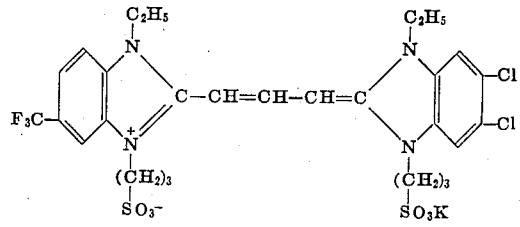
IA



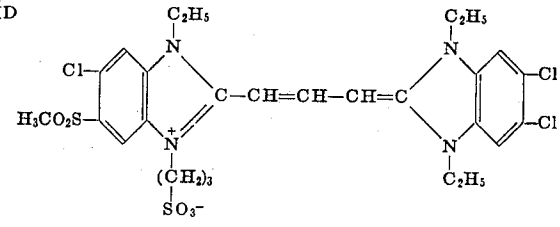
IB



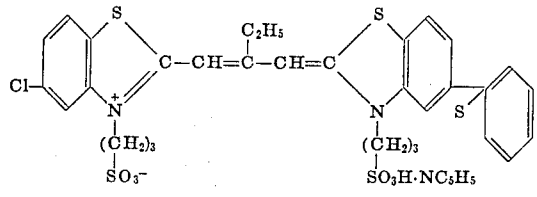
IC



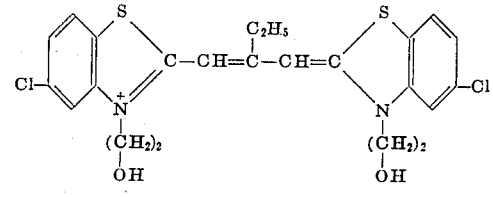
ID



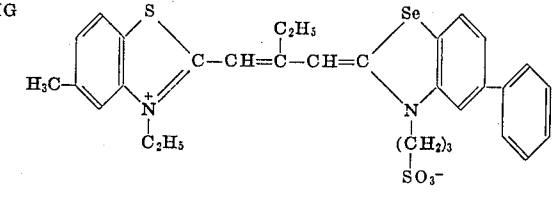
IE



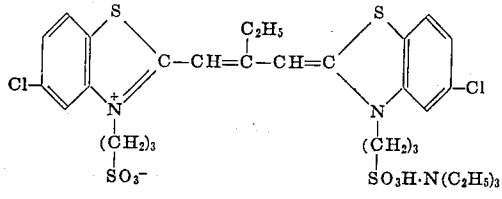
IF



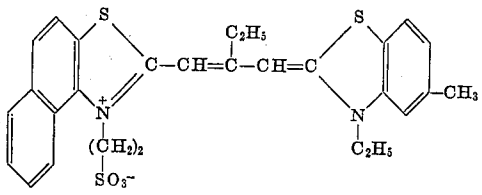
IG



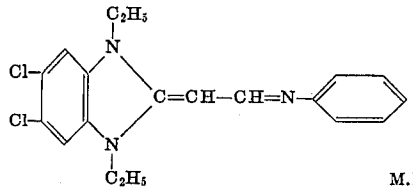
IH



IJ

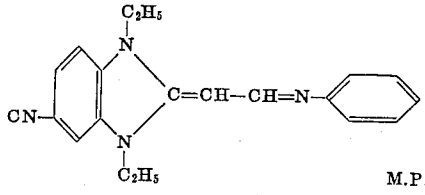


IIA



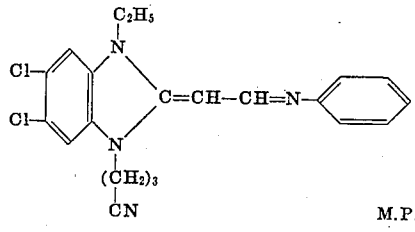
M.P. 151° C.

IIB



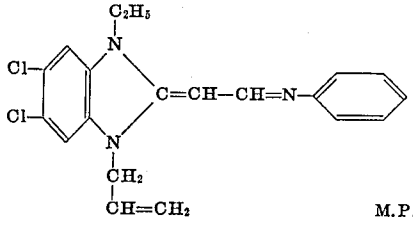
M.P. 135° C.

IIC



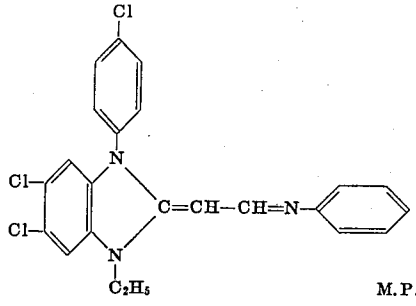
M.P. 162° C.

IID



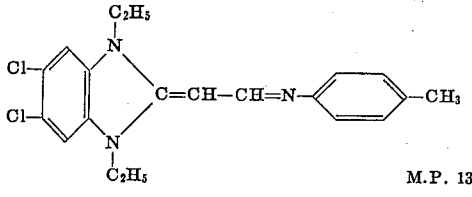
M.P. 102° C.

IIE



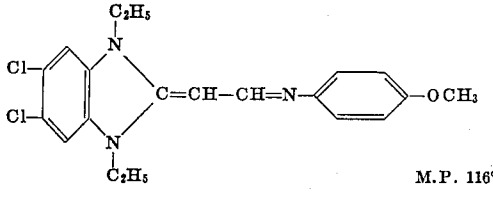
M.P. 234° C.

IIF



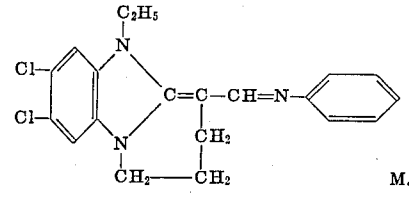
M.P. 134° C.

IIG



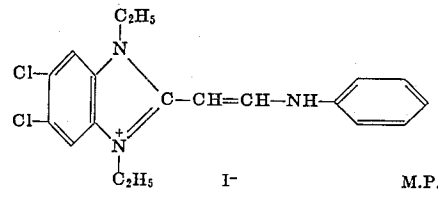
M.P. 116° C.

IIH



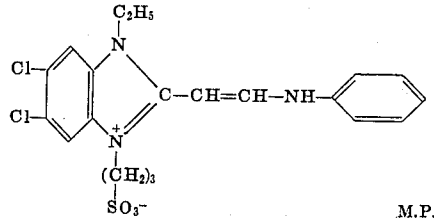
M.P. 178°C.

IIIA



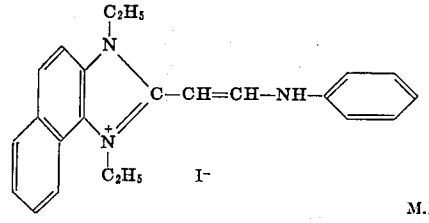
M.P. 251°C.

IIIB



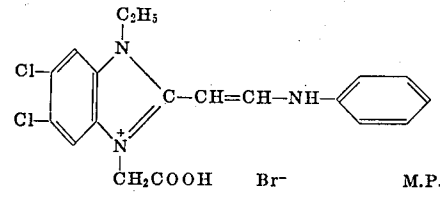
M.P. 283°C.

IIIC



M.P. 225°C.

IIID

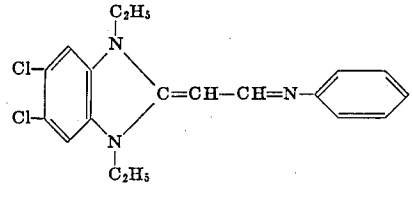


M.P. 220°C.

The organic heterocyclic compounds of the invention, represented by general formula II and III, can be synthesized by known methods. Compounds of general formula II can readily be obtained by treating compounds of the general formula III with an aqueous alkaline solution.

A typical synthesis of the compounds represented by general formulas II and III are shown by the following examples.

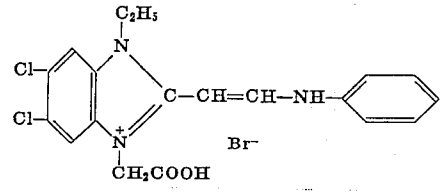
Synthesis Example 1:



IIA

4.7 g. of 2-(beta-anilinovinyl)-5,6-dichloro-1,3diethylbenzimidazolium iodide was suspended in 70 ml. of acetone and then a solution of 2 g. of caustic soda in 25 ml. of water was dropwise added thereto at room temperature while stirring. After 20 minutes, a large amount of water was added. A crystallized product was filtered, washed with water, dried and recrystallized in ligroine to give 1.2 g. of compound II melting at 151° C. The spectral absorption maximum wavelength thereof was 384 millimicrons (in methanol)

Synthesis Example 2:



IIID

3.5 g. of 1-carboxymethyl-5,6-dichloro-3-ethyl-2-methylhenzimidazolium bromide and 3.8 g. of diphenylformamidine were heated and fused at 160° C. and reacted for 2 hours, the reaction product being gradually solidified. After cooling, it was crystallized with acetone and washed with acetone to obtain 3.4 g. of compound IIID melting at 220° C. (decomposed). The spectral absorption maximum wavelength thereof was 384 millimicrons (in methanol).

Compounds IIB, IIC, IID, IIE, IIF, IIG, IIH, IIIA, IIIB, and IIIC can be obtained by similar methods to the ones above described.

The sensitizing dye or organic heterocyclic compound used in the invention is dissolved in a water-soluble organic solvent, for example, methanol, ethanol, butanol or pyridine, and added to a silver halide photographic emulsion. The addition may be carried out in solution form separately, or after being mixed. The type of silver halide used in this photographic emulsion may be silver bromide, silver iodobromide, silver chlorobromide and silver chloroiodobromide. Into the silver halide emulsion there may be incorporated, in addition to the gelatin, a silver halide, a sensitizing dye and an organic heterocyclic compound, a chemical sensitzer, a stabilizer an antifoggant, a coating agent, a photographic dye stuff such as an antiirradiation dye, a filter dye or an antihalation dye, a binder (besides gelatin) and, if necessary, a color former.

The invention will now be illustrated more specifically by the following examples.

EXAMPLE 1

A silver iodobromide gelatin emulsion prepared in the conventional manner was placed in a beaker and dissolved in a thermostatic heater at 40° C. A predetermined amount of a methanol solution of a dye represented by the general formula I having a predetermined concentration and a predetermined amount of a methanol solution of a dye represented by the general formula II or III, having a predetermined concentration, were added thereto and stirred.

Thereafter, the mixture was allowed to stand for 10 minutes in a thermostatic heater at 37° C. and stirred to obtain a complete emulsion. The obtained emulsion was uniformly applied onto a glass support in a proportion of 7.0 ml. per cabinet size, and then set and dried to obtain a sample of a light-sensitive material.

Optical wedge exposure of the sample was carried out by the use of two light sources, a light source having a color temperature of 5,400° K. obtained form a light source having a color temperature of 2,666° K. through a DG conversion filter and a yellow light obtained from the same but further filtered through No. 12 Filter (Trade Mark, made by Fuji Photo Film Co., Ltd.), permitting only light of a long wavelength (longer than 500 millimicrons).

The sample was then developed at 20° C. for 10 minutes with a developer as hereafter described, passed through a stop solution and a fixing solution and then washed with water to give a strip. The density thereof was measured by means of S-type Densitometer (Trade Mark, made by Fuji Photo Film Co., Ltd.) to determine the degree of spectral sensitization. The standard optical density for determining the sensitivity was the point of: [fog density + 0.10].

The degrees of spectral sensitization are shown (relatively) in table 1.

A sample of the same light-sensitive material obtained in the foregoing manner was subjected to spectral exposure using a reflection-type grating spectral sensitometer and then developed, as described above, to give a strip. Measurement of the density thereof yielded a spectral sensitivity curve as shown in the accompanying drawing.

Composition of the developer used

Water (50° C.)	750 ml.
Metol	2 g.
Anhydrous sodium sulfite	100 g.
Hydroquinone	5 g.
Borax	2 g.
Water to 1,000 ml.	
pH=8.70±0.10	

TABLE 1

No.	Amount of sensitizing dye used, ml. (molar conc.)	Amount of super sensitizer used, ml. (molar conc.)	Relative spectral speed	Fog	Sensitizing max. wavelength (mμ)
1	I A(4×10^{-4}) 4	----------	100	0.10	583
	I A(4×10^{-4}) 8	----------	100	0.10	583
	I A(4×10^{-4}) 4	II E(4×10^{-4}) 4	125	0.11	570
	I A(4×10^{-4}) 4	II E(4×10^{-4}) 8	125	0.14	564
2	I A(4×10^{-4}) 4	II F(4×10^{-4}) 4	141	0.14	568
	I A(4×10^{-4}) 4	II F(4×10^{-4}) 8	141	0.13	560
	I A(4×10^{-4}) 4	II F(4×10^{-4}) 16	178	0.20	558
3	I A(4×10^{-4}) 4	II H(4×10^{-4}) 4	129	0.19	570
	I A(4×10^{-4}) 4	II H(4×10^{-4}) 8	118	0.21	563
4	I A(4×10^{-4}) 4	III A(4×10^{-4}) 4	152	0.17	578
	I A(4×10^{-4}) 4	III A(4×10^{-4}) 8	141	0.18	578
	I A(4×10^{-4}) 4	III A(4×10^{-4}) 16	141	0.22	567
5	I A(4×10^{-4}) 4	III B(4×10^{-4}) 2	132	0.10	570
	I A(4×10^{-4}) 4	III B(4×10^{-4}) 2	132	0.10	570
	I A(4×10^{-4}) 4	III B(4×10^{-4}) 8	142	0.11	560
	I A(4×10^{-4}) 4	III B(4×10^{-4}) 16	142	0.08	560
6	I A(4×10^{-4}) 4	III C(4×10^{-4}) 2	118	0.10	572
	I A(4×10^{-4}) 4	III C(4×10^{-4}) 4	142	0.13	568
	I A(4×10^{-4}) 4	III C(4×10^{-4}) 8	152	0.14	560
7	I C(4×10^{-4}) 2	----------	100	0.13	572
	I C(4×10^{-4}) 4	----------	118	0.17	572
	I C(4×10^{-4}) 8	----------	100	0.20	572
	I C(4×10^{-4}) 4	II A(4×10^{-4}) 4	126	0.20	560
	I C(4×10^{-4}) 4	II A(4×10^{-4}) 8	126	0.20	550
	I C(4×10^{-4}) 4	II B(4×10^{-4}) 4	126	0.20	560
	I C(4×10^{-4}) 4	II B(4×10^{-4}) 4	141	0.14	540
	I C(4×10^{-4}) 4	II B(4×10^{-4}) 16	126	0.11	540
9	I D(4×10^{-4}) 2	----------	71	0.16	570
	I D(4×10^{-4}) 4	----------	100	0.17	575
	I D(4×10^{-4}) 8	----------	100	0.18	575
	I D(4×10^{-4}) 4	II A(4×10^{-4}) 4	141	0.20	570
	I D(4×10^{-4}) 4	II A(4×10^{-4}) 8	166	0.17	560

TABLE 1

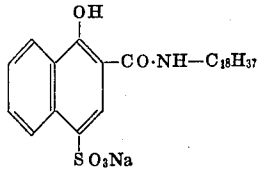
No.	Amount of sensitizing dye used, ml. (molar conc.)	Amount of super sensitizer used, ml. (molar conc.)	Relative spectral speed	Fog	Sensitizing max. wavelength (mμ)
10	I E(8×10⁻⁴) 2		60	0.09	642
	I E(8×10⁻⁴) 4		85	0.10	642
	I E(8×10⁻⁴) 8		100	0.14	642
	I E(8×10⁻⁴) 4	II A(4×10⁻⁴) 4	110	0.18	630
	I E(8×10⁻⁴) 4	II A(4×10⁻⁴) 8	118	0.18	625
	I E(8×10⁻⁴) 4	II A(4×10⁻⁴) 16	132	0.12	620
1	I E(8×10⁻⁴) 4	II C(4×10⁻⁴) 4	142	0.15	635
	I E(8×10⁻⁴) 4	II C(4×10⁻⁴) 8	142	0.15	635
	I E(8×10⁻⁴) 4	II C(4×10⁻⁴) 16	152	0.15	620
12	I F(8×10⁻⁴) 2		85	0.10	650
	I F(8×10⁻⁴) 4		100	0.14	650
	I F(8×10⁻⁴) 8		100	0.13	650
13	I F(8×10⁻⁴) 4	II C(4×10⁻⁴) 4	118	0.15	642
	I F(8×10⁻⁴)	II C(4×10⁻⁴) 8	141	0.16	630
	I F(8×10⁻⁴)	II C(4×10⁻⁴) 16	141	0.18	615
14	I G(8×10⁻⁴) 2		100	0.13	640
	I G(8×10⁻⁴) 4		115	0.15	640
	I G(8×10⁻⁴) 8		115	0.15	640
	I G(8×10⁻⁴) 4	II A(4×10⁻⁴) 4	159	0.16	630
	I G(8×10⁻⁴) 4	II A(4×10⁻⁴) 8	166	0.17	625
	I G(8×10⁻⁴) 4	II A(4×10⁻⁴) 16	200	0.12	625
15	I G(8×10⁻⁴) 4	II C(4×10⁻⁴) 4	166	0.15	635
	I G(8×10⁻⁴) 4	II C(4×10⁻⁴) 8	200	0.15	625
	I G(8×10⁻⁴) 4	II C(4×10⁻⁴) 16	200	0.13	622
16	I J(4×10⁻⁴) 2		90	0.10	660
	I J(4×10⁻⁴) 4		100	0.11	660
	I J(4×10⁻⁴) 8		111	0.13	660
	I J(4×10⁻⁴) 4	II A(4×10⁻⁴) 4	130	0.11	650
	I J(4×10⁻⁴) 4	II A(4×10⁻⁴) 8	135	0.11	645

EXAMPLE 2

100 g. of a silver iodobromide gelatin emulsion prepared in the conventional manner was placed in a beaker and dissolved in a thermostatic assembly at 37° C. A sensitizing dye and an organic heterocyclic compound were added thereto in a manner similar to that of example 1 while stirring. The resulting mixture was allowed to stand at 37° C. for 30 minutes.

20 ml. of a 5 percent alkaline solution of cyan coupler having a following structural formula was then added thereto and the mixture stirred. Thereafter, the mixture was neutralized with citric acid to a pH of 6.5. A hardener and surface active agent (for coating) were then added thereto, and the resultant solution coated onto a film support, and dried, to obtain a sample of a red-sensitive color sensitive material.

CYAN COUPLER



The sample was subjected to optical wedge exposure or spectral exposure in a manner similar to that of example 1, developed at 20° C. for 10 minutes by the use of a color developer containing a N,N'-diethyl-aminoparaaminoaniline derivative and then subjected to a first fixing, a bleaching, a second fixing and a washing with water to obtain a cyan negative image. The density thereof was secured with a red filter to estimate the relative spectral sensitizations thereof. The results are shown in table 2.

TABLE 2

No.	Amount of sensitizing dye used, ml. (molar conc.)	Amount of super sensitizer used, ml. (molar conc.)	Relative spectral speed	Fog	Sensitizing max. wavelength (mμ)
17	I H(8×10-4) 2		76	0.08	650
	I H(8×10-4) 4		91	0.10	655
	I H(8×10-4) 8		100	0.10	655
	I H(8×10-4) 4	II B(4×10-4) 4	142	0.10	642
	I H(8×10-4) 4	II B(4×10-4) 8	142	0.11	635
	I H(8×10-4) 4	II B(4×10-4) 16	142	0.11	625
18	I H(8×10-4) 4	II G(4×10-4) 4	118	0.10	640
	I H(8×10-4) 4	II G(4×10-4) 8	142	0.11	630
	I H(8×10-4) 4	II G(4×10-4) 16	142	0.11	620

NOTE.—Composition of the color forming developer used:

	G.
N,N'-diethylaminoparaaminoaniline sulfate	2.0
Sodium sulfite	2.0
Sodium carbonate (monohydrate)	50
Hydroxylamine hydrochloride	1.5
Potassium bromide	1.0
Water to 1,000 ml.	

FIG. 1 and FIG. 2 of the drawing show the spectral sensitivity curves in the cases of using a sensitizing dye alone and with an organic heterocyclic compound for comparison. In FIG. 1, Curve I is a spectral sensitivity curve resulting from using 4 ml. of IA (4×10^{14} molar concentration) alone per 100 g. of the photographic emulsion, Curve II is that for using 4 ml. of IIF (4×10^{1}molar concentration) alone, and Curve III and Curve IV are those resulting from using 4 ml. of the foregoing IA with 4 ml. and 8 ml., respectively, of the foregoing IIF in example 1. In FIG. 2, Curve V is a spectral sensitivity curve resulting upon using 4 ml. of IH (4×10^{14} molar concentration) alone per 100 g. of the photographic emulsion, and Curve VI and Curve VII are the curves resulting from using 4 ml. of the foregoing IH with 4 ml. and 8 ml., respectively, of 11B (4×10^{1} ^{4} molar concentration) in combination, as in example 2.

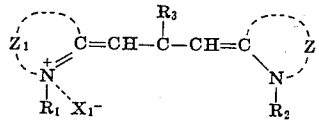
To further illustrate the preferred form of the present invention, the dye represented by general formula I is generally

present in amounts of from about 1×10^{16} mole to about 0.40 mole per kilogram of silver halide emulsion. Further, the amount of the materials represented by general formulas II or III will generally range from about 1/10 to about 5 times the amount of the dye represented by general formula I (molar basis).

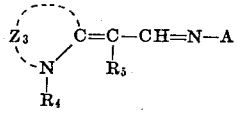
Further, in the compounds represented, the alkyl group per se, as for example represented by R_1, has from one to five carbon atoms.

What is claimed is:

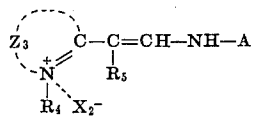
1. A silver halide photographic emulsion containing from 1×10^{-6} to 0.4 mole, per kg. of said emulsion, of at least one sensitizing dye represented by the following formula I:



wherein Z_1 and Z_2 are the atoms necessary to complete a heterocyclic ring selected from the group consisting of a benzimidazole ring, a benzothiazole ring, a naphthothiazole ring and a benzoselenazole ring; R_1 and R_2 are a member selected from the group consisting of an alkyl group of one to five carbon atoms, a substituted alkyl group wherein the alkyl group has from one to five carbon atoms and wherein the substituent is hydroxy, alkoxy having from one to five carbon atoms, carboxy, sulfo- or carboxy-alkoxy wherein the alkoxy group has from one to five carbon atoms, an aryl group and an aralkyl group wherein the alkyl moiety has from one to five carbon atoms; R_3 is a member selected from the group consisting of a hydrogen atom and an alkyl group having from one to five carbon atoms, said R_3 being a hydrogen atom when Z_1 and Z_2 are atoms forming a benzimidazole ring; and X_1^1 is an acid anion group; and at least one organic hetercyclic compound of formulas II or III, wherein formula II is:

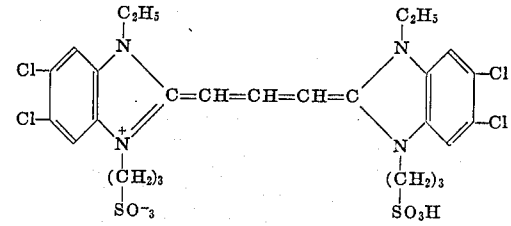


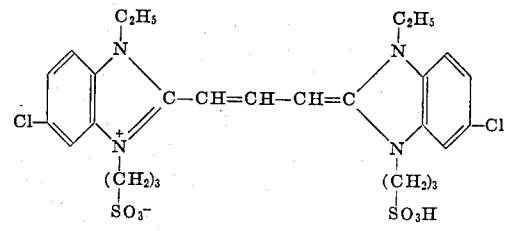
wherein Z_3 represents the atoms necessary to complete a heterocyclic ring selected from the group consisting of a benzimidazole ring and a naphthoimidazole ring; R_4 is a member selected from the group consisting of an alkyl group having from one to five carbon atoms, a substituted alkyl group wherein the alkyl group has from one to five carbon atoms and wherein the substituent is hydroxy, alkoxy of one to five carbon atoms, carboxy, sulfo- or carboxy-alkoxy wherein the alkoxy moiety has from one to five carbon atoms, an aryl group and an aralkyl group wherein the alkyl moiety has from one to five carbon atoms; R_5 is a member selected from the group consisting of a hydrogen atom and an alkylene group necessary to complete a ring when R_4 and R_5 are bonded to form the ring; and A is a member selected from the group consisting of phenyl and substituted phenyl; wherein formula III is:

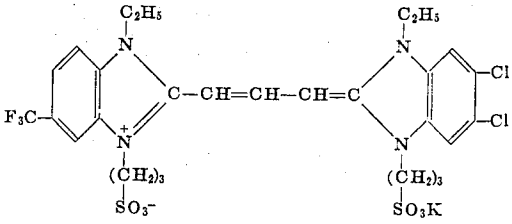


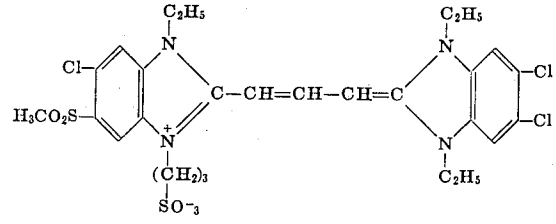
wherein X_2^1 is an acid anion group, and A, Z_3, R_4 and R_5 have the same meaning as in formula II, wherein said heterocyclic compound is present in an amount of from 1/10 to 5 times the amount of said sensitizing dye, on a molar basis.

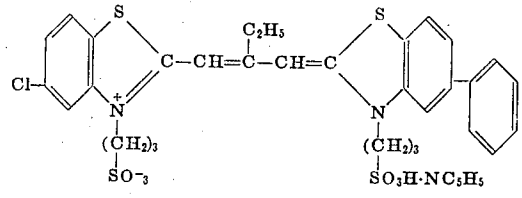
2. A silver halide photographic emulsion as claimed in claim 1, wherein said sensitizing dye represented by the general formula 1 is a member selected from the group consisting of:

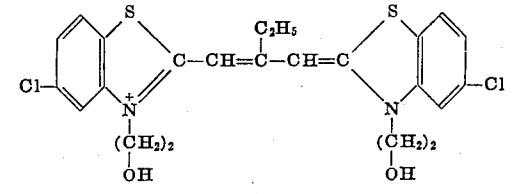


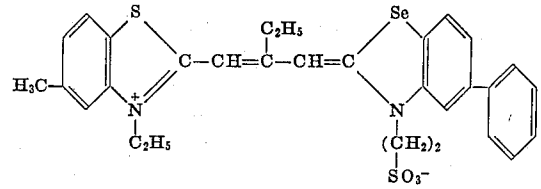


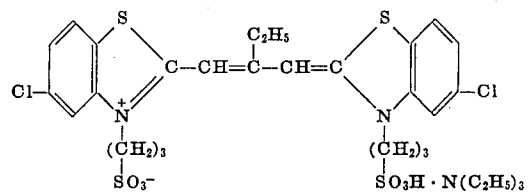




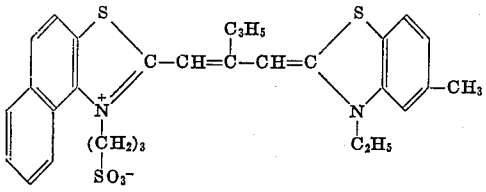




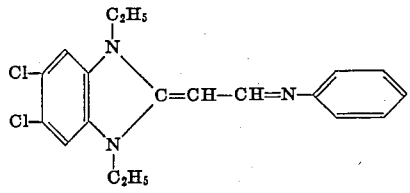


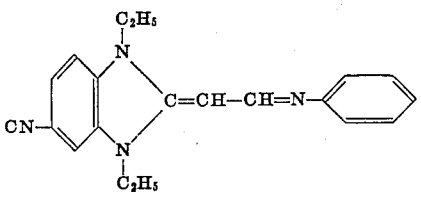


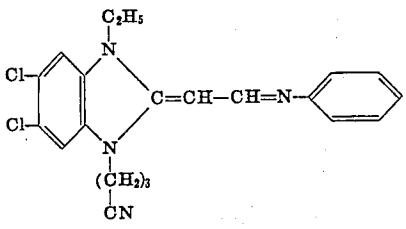
and

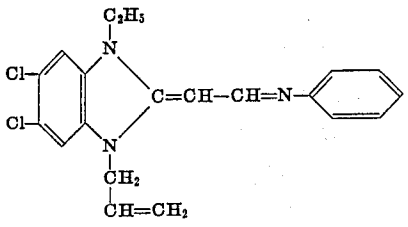


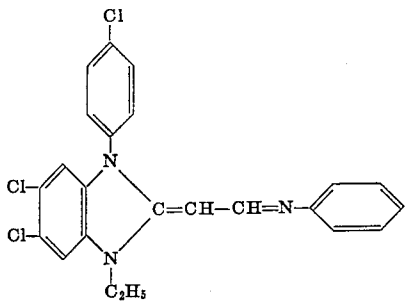
3. A silver halide photographic emulsion as claimed in claim 1, wherein said organic heterocyclic compound represented by general formula II is a member selected from the group consisting of:

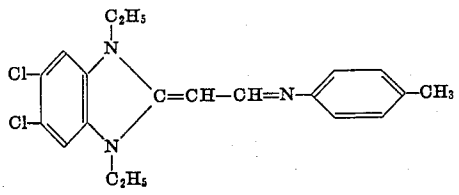


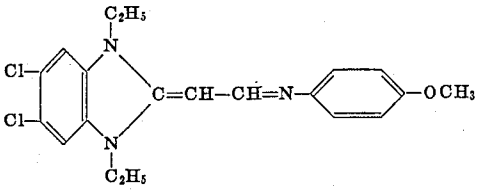




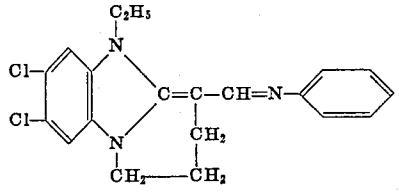




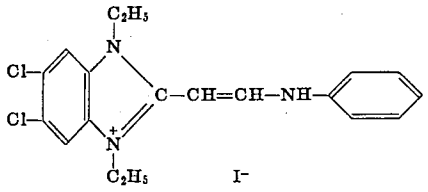


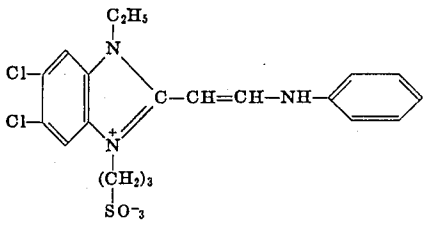


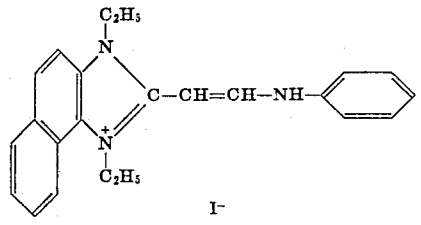
and



4. A silver halide photographic emulsion as claimed in claim 1, wherein said organic heterocyclic compound represented by the general formula III is a member selected from the group consisting of:







and