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Sakazume et al.

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[54] **SILVER HALIDE PHOTOSENSITIVE MATERIALS FOR COLOR PHOTOGRAPHY**

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[21] Appl. No.: **325,338**

[30] **Foreign Application Priority Data**

Jan. 24, 1972 Japan 47-8300

[52] **U.S. Cl.** **96/74,** 96/132, 96/143, 260/240.7, 260/240.65

[51] **Int. Cl.** **G03c 7/32,** G03c 1/16

[58] **Field of Search** 96/74, 140, 132, 143; 260/240.7, 240.65

[56] **References Cited**

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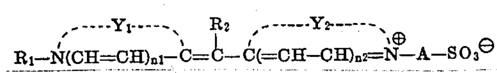
Primary Examiner—David Klein
Assistant Examiner—Alfonso T. Suvo Pico
Attorney, Agent, or Firm—Bierman & Bierman

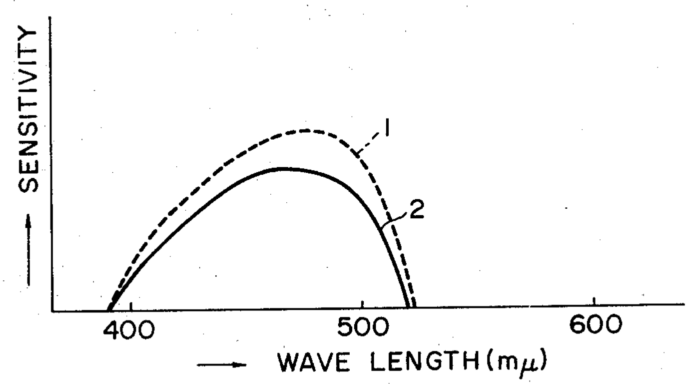
[57] **ABSTRACT**

A silver halide photosensitive material for color photography providing excellent color reproducibility is disclosed which comprises a support and at least three emulsion layers supported thereon; said layers being a red-sensitive emulsion layer, a green-sensitive emulsion layer, and a blue-sensitive emulsion layer; the blue-sensitive emulsion layer containing a sensitizing dye represented by the following formula:



Wherein Y_1 and Y_2 each stand for a non-metallic atomic group necessary for forming a nitrogen-containing heterocyclic ring nucleus selected from the group consisting of pyrroline, thiazoline, thiazole, benzothiazol, naphthothiazole, selenazole benzoselenazole, naphthoselenazole, oxazole, benzoxazole, naphthoxozole, imidazole, benzimidazole, pyridine, and quinoline, which heterocyclic ring nucleus may be substituted by a halogen atom, a lower alkyl group, a lower alkoxy group, or an aryl group, which group may be substituted by a halogen atom, a lower alkyl group or a lower alkoxy group; R_1 stands for a lower alkyl group, a hydroxyalkyl group, or a sulfoalkyl group; R_2 is a hydrogen atom or a lower alkyl group; A designates an alkylene group or a group $-(CH_2)_2-O-(CH_2)_2-$ or, $-(CH_2)_2-O-CH_2CH(OH)CH_2-$; and n_1 and n_2 are each 0 or 1.

5 Claims, 2 Drawing Figures



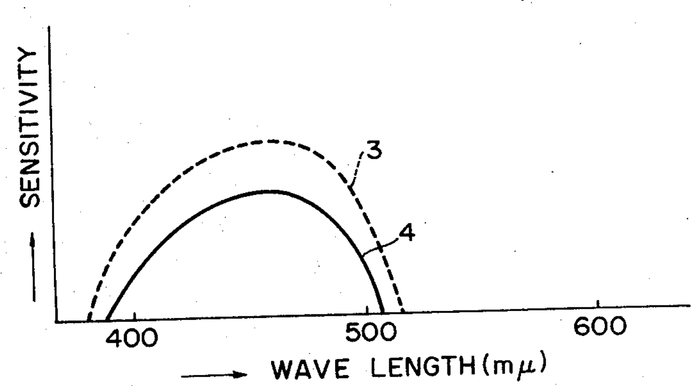


FIG. 1

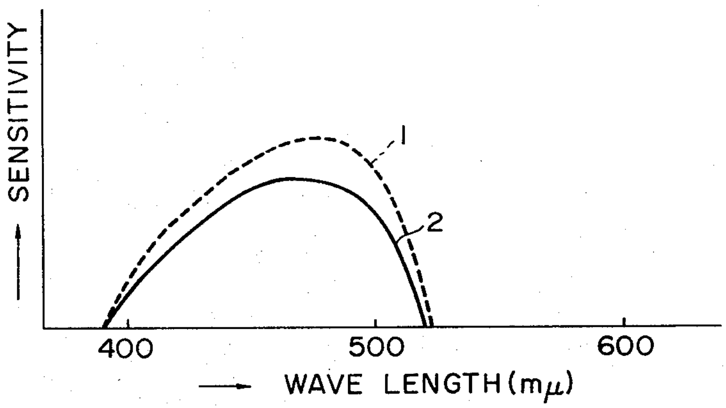
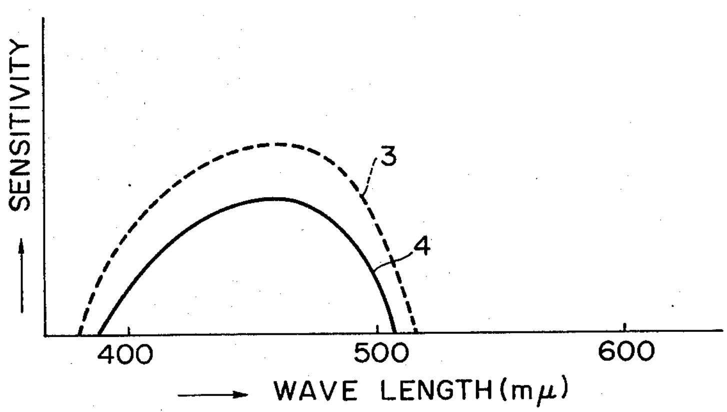

SENSITIVITY
1
2
400
500
600
WAVE LENGTH (mμ)

FIG. 2


SENSITIVITY
3
4
400
500
600
WAVE LENGTH (mμ)

SILVER HALIDE PHOTOSENSITIVE MATERIALS FOR COLOR PHOTOGRAPHY

This invention relates to a silver halide photosensitive material for color photography. More particularly, it relates to a coupler-containing, silver halide, photosensitive material for color photography which includes a blue sensitive emulsion layer sensitized by a spectral sensitizer.

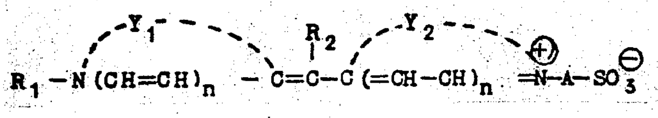
In silver halide photosensitive materials for color photography, chemical sensitization using sulfur or noble metals can increase the sensitivity of the blue sensitive emulsion layer. However, when the sensitivity inherent in the silver halide is increased without use of sensitizing dyes, the particle size becomes coarser, resulting in loss of clarity and sharpness in the reproduced images.

In some cases, the sensitivity region inherent to the silver halide is utilized as the spectral sensitivity region of the blue sensitive emulsion layer. Sometimes, these silver halide sensitive materials do not have the desired spectral sensitivity in the blue sensitive emulsion layer especially toward the longer wavelengths. Attempts have been made to increase the sensitivity of the blue-sensitive emulsion layer in the range of the longer wavelengths by the use of a spectral sensitizer.

However, most dyes heretofore used for this purpose are too effective and expand the photosensitive region of the blue sensitive emulsion layer excessively toward the longer wavelength region. This forms an image of an undesirable yellow color and degrades the color reproducibility in the green image. Also, it reduces the sensitivity inherent in the silver halide and leaves color stains on the photosensitive material after development. Because of these defects, such dyes are not completely satisfactory as spectral sensitizers for the blue sensitive emulsion layer. Moreover, when photosensitive materials prepared with such dyes are stored under high temperature and humidity conditions, the sensitivity of the blue sensitive emulsion layer is drastically lowered, resulting in formation of fog or color stain. With the recent demand for acceleration of the processing of photosensitive materials, high temperatures are necessary. When photosensitive materials comprising such sensitizing dyes are developed at such high temperatures, the developing rates in the red sensitive emulsion layer and, the green sensitive emulsion layer differ from that of the blue sensitive emulsion layer. As a result, good balance of the photographic characteristics of these three layers is not obtained and the color reproducibility is greatly impaired. Accordingly, sensitizing dyes suitable for the blue sensitive emulsion layer, without such defects, has been long sought by those skilled in the art.

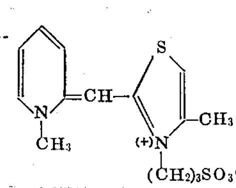
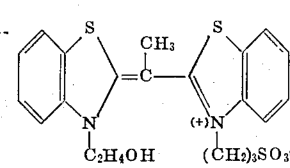
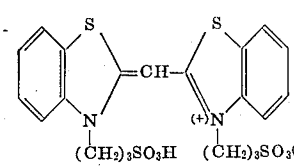
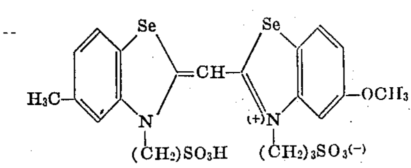
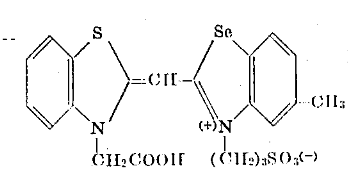
It is, therefore, a primary object of this invention to provide a coupler-containing, silver halide, photosensitive material for color photography having excellent color reporducibility, which comprises a blue sensitive emulsion layer sensitized by sensitizing dyes free of the afore mentioned defects.

This object can be attained by using a silver halide photosensitive material comprising a support and at least three emulsion layers thereon; namely a red sensitive emulsion layer, a green sensitive layer, and a blue sensitive layer, wherein a compound of the following general formula is incorporated in the blue sensitive emulsion layer:

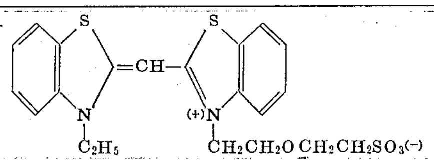
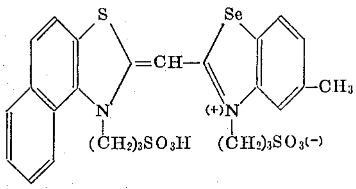
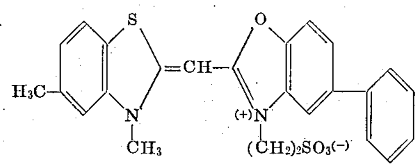
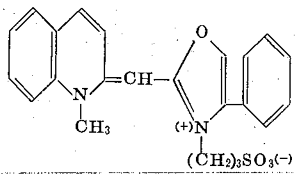
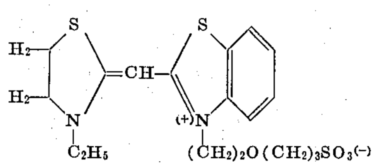
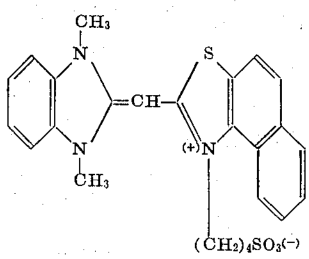
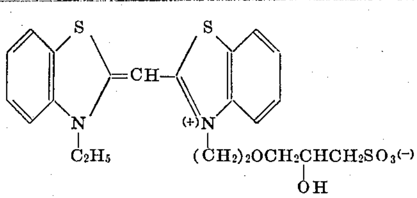
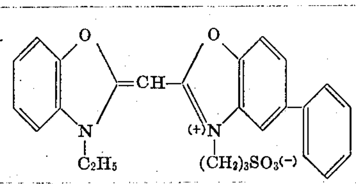
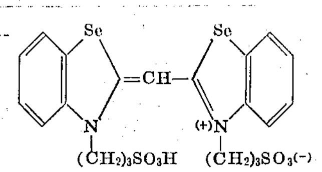


Wherein Y_1 and Y_2 each stand for a non-metallic atomic group necessary for forming a nitrogen containing heterocylic ring nucleus selected from the group consisting of pyrroline, thiazoline, thiazole, benzothiazole, naphthothiazole, selenazole, benzoselenazole, naphthoselenazole, oxazole, benzoxazole, naphthoxazole, imidazole, benzimidazole, pyridine and quinoline; which nucleus may be substituted by a halogen atom, a lower alkyl group, a lower alkoxy group or an aryl group; which group may in turn be substituted by halogen, lower alkyl or lower alkoxy; R_1 stands for lower alkyl, hydroxy alkyl, carboxyalkyl or sulfoalkyl; R_2 is hydrogen or lower alkyl; A designates alkylene,—$(CH_2)_2O(CH_2)_2$—, or — $(CH_2)_2OCH_2CH(OH)CH_2$—; and n_1 and n_2 are each 0 or 1.

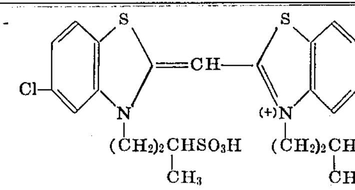
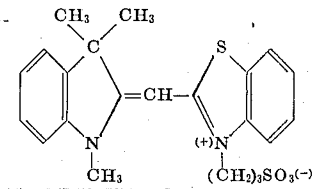
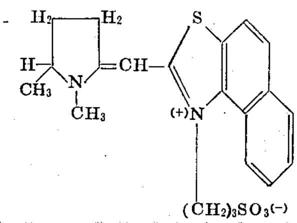
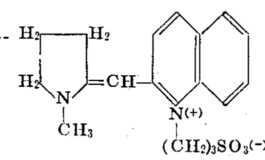
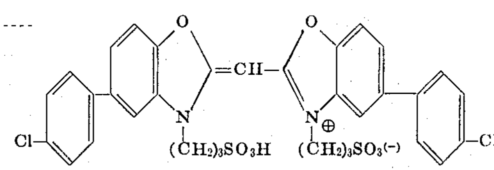
Typical examples of compounds expressed by the above general formula and useful in this invention are listed below. However, the list is exemplary only and is not intended to limit the invention.

		Maximum absorption in methanol (mμ)
(1)		443
(2)		480
(3)		425
(4)		442
(5)		431

Continued

		Maximum absorption in methanol (mμ)
(6)		426
(7)		448
(8)		421
(9)		434
(10)		384
(11)		410
(12)		427
(13)		382
(14)		430

Continued

		Maximum absorption in methanol (mμ)
(15)		427
(16)		430
(17)		400
(18)		422
(19)		390

The compounds of the above general formula useful in this invention can readily be synthesized by methods disclosed in, for instance, specification of British Pat. No. 660,408 and U.S. Pat. No. 3,149,105.

The compounds of the present invention are preferably added to the emulsions in the form of solutions in a watermiscible organic solvent such as methanol or ethanol. The addition of such compounds may be effected at any desired point during the preparation of the emulsions. In general, however, it is preferable that they be added just after the chemical ripening or chemical sensitization. The compounds are incorporated in an amount of 0.01 to 0.5 g per mole of silver halide, although the preferred amount can vary depending on the kind of additive and silver halide emulsion.

The couplers to be incorporated in the silver halide photosensitive materials for color photography are not particularly critical in this invention, and couplers customarily used in this field can be used effectively. For instance, the blue sensitive layer may contain a compound which can react with an oxide of a color developer containing a primary amino group to form a yellow dye. The amount of such coupler to be added in generally 1.0 to 200g per mole of the silver halide. The coupler is preferably incorporated into the emulsion as an aqueous alkali solution or as a solution in a high or low boiling point organic solvent.

It is also possible to incorporate other photographic additives such as stabilizers, film-hardening agents, pH—adjusting agents, viscosity—increasing agents, coating assistants and color stain preventive agents in the photosensitive material. Synthetic and natural high molecule compounds such as gelatin, casein and polyvinyl alcohol can be used singly or in combination as a binder.

The silver halide may, for example, be silver chloride, silver bromide, silver iodide-bromide and silver chloride-iodide-bromide. Various materials such as paper, cellulose acetate film, polyester film, polycarbonate and polyolefineoated paper may be used as the support.

The silver halide photosensitive material according to this invention can achieve a good balance in photographic characteristics between the red, green and blue sensitive layers even in high-temperature, high-speed development. It is also one of the advantages of this invention that the silver halide photographic material is freer from spot-like fog than the photographic material of the prior art. Spot-like fog often arises during development according to prior art and is believed to result from a small quantity of fine metal stuck to the surface of the photosensitive material during its preparation, processing or during actual photographing.

This discovery is further illustrated in more detail by the following Examples, which illustrate but do not limit the invention.

Example 1

A color negative emulsion of silver iodidebromide containing 5 mole percent of silver iodide was chemically ripened and 0.15g per mole of silver halide of anhydro-5,5'-dichloro-3,3'-disulfopropyl-9-ethyl-thiacarbocyanine hydroxide was added as a sensitizing dye to the emulsion in the form of a methanol solution. Then, 50g per mole of silver halide of 4-chloro-1-hydroxy-2-n-octyl naphthamide as a cyan coupler was further added in the form of the dispersion of the following composition:

Composition of Coupler Dispersion	
Coupler	100 g
Dibutyl phthalate	100 ml
Ethyl Acetate	300 ml
5% Aqueous solution of Alkanol B (manufactured by Du Pont)	150 ml
6% Aqueous solution of gelatin	500 ml

Then, a stabilizer, a film-hardening agent, a coating assistant and a pH-adjusting agent were added to the emulsion to form a red sensitive emulsion.

Similarly, a green sensitive emulsion was prepared by using a sensitizing dye, anhydro-5,5'-diphenyl-3,3'-disulfopropyl-9-ethyl-oxacarbocyanine hydroxide in an amount of 0.15g per mole of the silver halide and, as a coupler, 1-(2,4,6-trichloro-phenyl)-[3-(2,4-di-tertiary-amylphenoxyacetamide)benzamido]-5-pyrazolone in an amount of 60g per mole of the silver halide.

A color negative emulsion of silver bromideiodide containing 4.5 mole percent of silver iodide was chemically ripened and divided into seven portions. From these seven portions of the emulsion, seven kinds of blue sensitive emulsions were prepared by adding compounds (7), (9) or (14) of this invention individually in an amount of 0.00g, 0.10g or 0.15g per mole of the silver halide. After the resulting mixtures were sufficiantly agitated to stabilize the absorption of the sensitizing dyes, **70**g per mole of silver halide of 4-dodecylbenzoyl-2'-methoxyacetoanilide was incorporated as a yellow coupler into each mixture in the form of a coupler dispersion. The dispersion was prepared in the same manner as the above described red and green sensitizing emulsions. Then a stabilizer, a film-hardening agent, a coating assistant and a pH-adjusting agent were incorporated into each of the resulting compositions.

For each of the blue sensitive emulsions, a photographic film was prepared by coating on a cellulose triacetate film base. An anti halation layer, a red sensitive emulsion layer, a gelatin film layer, a green sensitive layer, a colloidal silver-containing yellow filter layer, a blue sensitive and a gelatin protective layer were successively coated on the base in that order.

These seven samples were exposed to artificial daylight of 160 luxes (5,400°K) by employing a sensitometer (model KS–1 manufactured by Konishiroku Photo Industry Co., Ltd.), and subjected to the color development treatment according to the following procedures:

Color Development Steps and Recipes

(1)	Color Development (24°C., 12 minutes)	
	Benzyl alcohol	3.8 ml
	Anhydrous sodium sulfite	2.0 g
	N-Ethyl-N-B-methanesulfonamide-ethyl-3-methyl-4-aminoaniline sulfate	5.0 g
	Sodium carbonate (monohydrate)	50.0 g
	Potassium bromide	1.0 g
	Water to make	1 liter

The p^H was adjusted to 10.8 by addition of sodium hydroxide.

(2)	First Fixation (24°C., 5 minutes) 150 g of sodium thiosulfate was added to enough water to make 1 liter of solution	
(3)	Water Washing (24°C., 5 minutes)	
(4)	Bleaching (24°C., 6 minutes)	
	Formula:	
	Potassium ferricyanide	100 g
	Potassium bromide	50 g
	Water to make	1 liter
(5)	Water Washing (24°C., 5 minutes)	
(6)	Second Fixation (24°C., 5 minutes),	the same recipe as that of the first fixation
(7)	Water Washing (24°C., 10 minutes)	
(8)	Drying	

With respect to each of the resulting color negative images, the relative blue light sensitivity of the blue sensitive emulsion layer and the degree of the residual coloration were measured and the results are shown in Table 1. The relative sensitivity is expressed as a relative value based on the blue light sensitivity (100) of the sample (1) containing no sensitizing dyes, and the degree of the residual coloration is expressed as a value of the complementary color concentration at the non-image area.

Table I

Sample No.	Sensitizing Compound: Compound No.	Amount (g per mole of silver halide)	Relative Sensitivity	Degree of Residual Coloration
1	—	—	100	0.10
2	(7)	0.10	125	0.10
3	(7)	0.15	130	0.11
4	(9)	0.10	110	0.10
5	(9)	0.15	125	0.10
6	(14)	0.10	120	0.10
7	(14)	0.15	135	0.11

As is seen from the results shown in Table 1, it will readily be understood that the samples containing the compounds of this invention exhibit not only a low degree of the residual coloration but also a high blue light sensitivity and are thus particularly suitable as sensitizing dyes for blue sensitive emulsion.

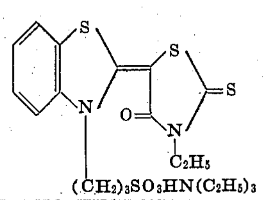
Example 2

A color reversable emulsion of silver iodidebromide containing **5** mole % of silver iodide was chemically ripened and 0.15g per mole of silver halide of anhydro 5,-5′-disulfopropyl-9-ethyl-thiacarbocyane hydroxide was added as a sensitizing dye to the emulsion in the form of a methanol solution. Then 50g per mole of 4-chloro-1-hydroxy-2-n-octylnaphthamide was added as a cyan coupler in the form of a dispersion prepared in the same manner as in Example 1, the resulting was well mixed and dispersed. A stabilizer, a film-hardening agent, a coating assistant and a pH-adjusting agent, were then added to form the red sensitive emulsion.

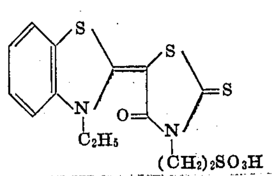
According to the same procedures as set forth above with respect to the preparation of the red sensitive emulsion, a green sensitive emulsion was prepared by employing, as a sensitizing dye, anhydro-5,5′-diphenyl-disulfopropyl-9-ethyl-oxacarbocyanine hydroxide in an amount of 0.15g per mole of the silver halide and, as a magenta coupler, 1-(3-carboxyphenyl)-3-(4-stearoylaminophenyl)-5-pyrazolone in an amount of 60g per mole of the silver halide.

According to the same procedures as set forth above for the preparation of the red sensitive emulsion, blue sensitive emulsions were prepared by employing as a sensitizing dye 0.10g or 0.20g per mole of the silver halide of compound (4) or (14) of this invention or dye (A) or (B) below. As a yellow coupler, 4-dodecylbenzoyl-2′-methoxyacetoanilide (yellow coupler) in an amount of 70g per mole of the silver halide is used. Similarly, a blue sensitive emulsion without sensitizing dye was also prepared.

Comparative dye A (disclosed in the specification of Belgian Pat. No. 738,921):



Comparative dye B (disclosed in the specification of U.S. Pat. No. 3,480,434):



With use of the so prepared red, green, and 9 blue sensitive emulsions, layer structures were formed on cellulose triacetate film bases having an antihalation layer, in the same manner as in Example 1, thereby obtain 9 silver halide color reversal photosensitive materials differing only in the blue sensitive layer. These photosensitive materials were used as test samples.

In the same manner as in Example 1, these samples exposed to light, and the high-temperature, high-speed reversal color development was carried out according to the following steps to obtain color positive images:

Reversal Color Development Steps and Recipes

(1) Film-Prehardening (38°C., 2 minutes and 30 seconds)		
50% Aqueous solution of sulfuric acid	5	ml
Sodium sulfate	154	g
Sodium acetate	20	g
37% Aqueous solution of formalin	27	ml
Water to make	1	liter
(2) Neutralization (38°C., 30 seconds)		
(3) First Development (38°C., 2 minutes and 30 minutes)		
Sodium polyphosphate	2	g
Sodium bisulfite	8	g
Phenidone	0.4	g
Hydroquinone	5	g
Sodium Carbonate (monohydrate)	30	g
10% Aqueous solution of potassium thiocyanide	15	ml
Potassium bromide	1.5	g
0,1 % Aqueous solution of potassium iodide	10	ml
Anhydrous sodium sulfite	40	g
Water to make	1	liter
(4) First Stopping		
(5) Water Washing (38°C., 1 minute)		
(6) Reversal Light Explosure		
(7) Color Development (38°C., 3 minutes and 40 seconds)		
Sodium polyphosphate	5	g
Benzyl alcohol	5	g
Anhydrous sodium sulfite	7	g
Sodium phoshate	35	g
Potassium bromide	1	g
0.1% Aqueous solution of potassium iodide	90	ml
Sodium hydroxide	3	g
4-Amino-N-methyl-N-(B-methane-sulfoamide-ethyl)-m-toluyl-B-phenyl-ethylamine hydrochloride	10	g
Water to make	1	liter
(8) Second Stopping (38°C., 30 seconds)		
(9) Water Washing (38°C., 1 minute)		
(10) Bleaching (38°C., 1 minute and 30 seconds)		
Potassium ferricyanide	100	g
Potassium bromide	50	g
Water to make	1	liter
(11) Water Washing (38°C., 20 seconds)		
(12) Fixation (38°C., 1 minute and 30 seconds)		
Sodium thiosulfate	150	g
Water to make	1	liter
(13) Water Washing (38°C., 1 minute)		
(14) Drying		

With respect to each of the color positive images obtained, the relative sensitivities of the blue sensitive layers and the blue densities (D min) of the high light portions were determined. The results are shown in table 2. In the Table, the "Immediate Test" data were obtained when the freshly prepared samples were tested. The "Test after Preservation" data were obtained when the samples were tested after they had been maintained at high temperature (**50**°c) and high humidity relative humidity **80** percent for 2 days. The relative sensitivity is expressed as a relative value based on the sensitivity (100) in the "Immediate Test" of the sample containing no sensitizing dye in the blue sensitive layer.

Table 2

Sample No.	dye Added and Its Amount (g per mole of silver halide) Kind	Amount	Immediate Test Relative Sensitivity	Immediate Test Dmin	Test after Preservation Relative Sensitivity	Test after Preservation Dmin
8	—	—100	0.06	93	0.07	
9	comparative colorant (A)	0.10	115	0.07	94	0.08
10	comparative colorant (A)	0.20	110	0.08	100	0.09
11	comparative colorant (B)	0.10	120	0.08	93	0.09
12	comparative colorant (B)	0.20	115	0.08	96	0.09
13	illustrated compound (4)	0.10	125	0.06	120	0.06
14	illustrated compound (A)	0.20	140	0.07	135	0.07
15	illustrated compound (12)	0.10	115	0.06	110	0.06
16	illustrated compound (12)	0.12	125	0.07	120	0.07

With respect to each of samples subjected to the immediate test, the values of the maximum density (D max), the minimum density (D min) and gamma (r) of each of the sensitive layers were determined to evaluate their photographic characteristics. The results shown in Table 3 were obtained.

Table 3

Sample No.	Added dye and Its Amount (g per mole of halide) Kind	Amount	Blue Sensitive Emulsion layer Dmax	Blue Dmin	Blue r	Green Sensitive Emulsion Layer Dmax	Green Dmin	Green r	Red Sensitive Emulsion Layer Dmax	Red Dmin	Red r
8	—	—	3.1	0.06	1.90	3.3	0.05	2.10	3.4	0.03	2.12
9	comparative colorant (A)	0.10	3.2	0.07	1.85	3.3	0.05	2.10	3.4	0.03	2.12
10	comparative colorant (A)	0.20	3.1	0.08	1.91	3.3	0.05	2.10	3.4	0.03	2.12
11	comparative colorant (B)	0.10	3.2	0.08	1.94	3.3	0.05	2.10	3.4	0.03	2.12
12	comparative colorant (B)	0.20	3.1	0.08	1.98	3.3	0.05	2.10	3.4	0.03	2.12
13	illustrated compound (4)	0.10	3.3	0.06	2.11	3.3	0.05	2.10	3.4	0.03	2.12
14	illustrated compound (4)	0.20	3.4	0.07	2.10	3.3	0.05	2.10	3.4	0.03	2.12
15	illustrated compound (12)	0.10	3.3	0.06	2.12	3.3	0.05	2.10	3.4	0.03	2.12
16	illustrated compound (12)	0.20	3.3	0.07	2.10	3.3	0.05	2.10	3.4	0.03	2.12

From the results shown in Tables 2 and 3, it will readily be understood that silver halide photosensitive materials prepared with use of sensitizing dyes of this invention are far superior to the silver halide photosensitive materials with no sensitizing dye as well as those using "comparable" prior art dyes. The blue light sensitivity is much higher and the sensitivity reduction after storage under high temperature and high humidity conditions is very low. Further, the Dmin value is lower and a clear image of no residual coloration can be obtained. Moreover, even when high-temperature, high-speed development is used a good balance is attained among the three emulsion layers and thereby excellent color reproducibility is obtained.

In order to test formation of spot-like fog, "immediate test" samples (8) to (16) were subjected to the following test:

200mg of metallic zinc powder was added to 5l of water under a agitation and the resultant mixture was filtered to remove the larger zinc particles, thereby forming an aqueous suspension of zinc. The sample was dipped for 30 seconds in this suspension and dried. Without exposure to light, the treated sample was subjected to high-temperature, high-speed reversal color development under the same conditions as described above.

In the samples containing no sensitizing dye in the blue sensitive layer (8) and containing the prior art "comparable" dyes in the blue (9–12), 90 to 120 fog spots were formed per 100 cm^2. However, according to the present invention (13–16), only 20 to 40 of fog spots were formed per 100cm^2. As is apparent from the foregoing results, the dyes of this invention control the formation of fog spots resulting from the presence of fine metallic powder.

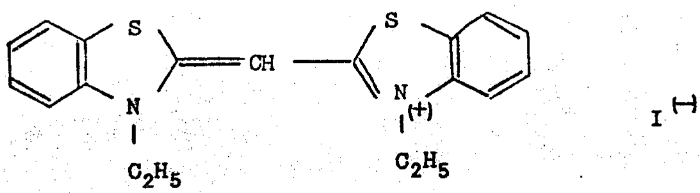
Example 3

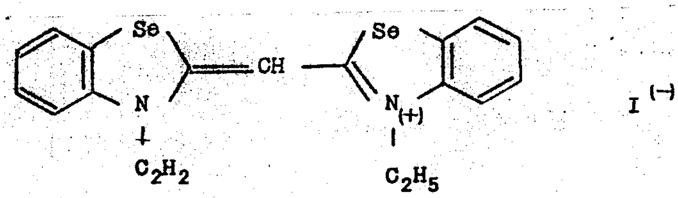
According to the procedures of Example 1, various silver halide color negative photosensitive materials were prepared as follows:

One silver halide color negative photosensitive material containing no sensitizing dye in the blue sensitive layer;

four silver halide color negative photosensitive materials containing 0.10 or 0.15g per mole of silver halide of compounds (3) or (4) of this invention in the blue sensitive layer, and;

four silver halide color positive photosensitive materials containing comparative dyes (C) or (D) in an amount of 0.10 or 0.15g per mole of silver halide in the blue sensitive layer.





These samples were exposed to light under the same conditions as in Example 1, and color negative images were obtained by color development treatment according to the same procedures as in Example 1 except that the treatment temperature
and treatment time were changed as indicated below.

Color Development Treatment

1. Color Development (31°C., 5 minutes)
2. First Fixation (31°C., 2 minutes and 30 seconds)
3. Water Washing (31°C., 2 minutes and 30 seconds)
4. Bleaching (31°C., 3 minutes)
5. Water Washing (31°C., 2 minutes and 30 seconds)
6. Second Fixation (31°C., 2 minutes and 30 seconds)
7. Water Washing (31°C., 5 minutes)
8. Drying

In order to determine the stability of the foregoing samples they were maintained at a temperature of 50°C., and a relative humidity of 80 percent for 2 days. They were then exposed to light and subjected to the color development in the same manner as described above to obtain the color negative image.

With respect to each of the resulting color negative images, the blue light sensitivity of the blue sensitive layer and the residual coloration were determined and the results are shown in Table 4. In the Table, the "Immediate Test" data were obtained from the fresh samples and the "Test after Preservation" data were obtained from samples which had been stored under the high temperature and high humidity conditions as described above. The relative sensitivity is a relative value based on the value (100) of the sensitivity in the "Immediate Test" of the sample containing no sensitizing dye in the blue sensitive layer, and the residual coloration is expressed in terms of the value of the complementary color concentration of the non-image area.

From the results shown in Table 4, it will easily be understood that silver halide photosensitive material prepared in accordance with this invention is far superior to silver halide photosensitive materials without any sensitizing dye as well as those materials using prior art "comparable" dyes. When the high-temperature development treatment is applied, a higher blue light sensitivity is attained, and, even after storage under high temperature and high humidity conditions, the reduction in sensitivity is extremely slight and a sufficient sensitivity is retained. Moreover, the degree of the residual coloration is low, resulting in a very clear image.

The spectrophotography was conducted on the same samples as described above to examine the spectral sensitivity curves of blue sensitive emulsion layers. The results are shown in FIGS. **1** and **2.**

In FIG. **1,** broken line (**1**) is the spectral sensitivity curve of the blue sensitive emulsion layer of sample (23) having compound (3) of this invention therein in an amount of 0.15g per mole of silver halide. Solid line (**2**) is the spectral sensitivity curve of the blue sensitive emulsion layer of sample (17) containing no sensitizing dye.

In FIG. **2,** broken line (3) is the spectral sensitivity curve of sample (25) having compound (14) of this in-

Table 4

Sample No.	dye Added and Its Amount (g per mole of silver halide)		Immediate Test		Test after Preservation	
	Kind	Amount	Relative Sensitivity	Residual Sensitivity	Relative Sensitivity	Residual Coloration
17	—	—	100	0.11	93	0.13
18	comparative colorant (C)	0.10	94	0.12	88	0.14
19	comparative colorant (C)	0.15	90	0.12	86	0.14
20	comparative colorant (D)	0.10	92	0.12	89	0.14
21	comparative colorant (D)	0.15	95	0.12	90	0.14
22	illustrated compound (3)	0.10	125	0.11	125	0.11
23	illustrated compound (3)	0.15	140	0.11	135	0.11
24	illustrated cp,°pimd (14)	0.10	130	0.11	120	0.11
25	illustrated compound (14)	0.15	135	0.12	130	0.12

vention therein in an amount of 0.15g per mole of the silver halide. Solid line (4) is the spectral sensitivity curve of the blue sensitive layer of sample (19) having comparative dye (C) therein in an amount of 0.15g per mole of silver halide. As is apparent from these Figures, the blue sensitive emulsion layer having the compounds of this invention therein has a desirable spectral sensitivity distribution with low residual coloration.

We claim:

1. A silver halide photosensitive material for color photography comprising a support and at least three emulsion layers supported thereon; said layers being a red-sensitive emulsion layer, a green-sensitive emulsion layer, and a blue-sensitive emulsion layer: the blue-sensitive emulsion layer containing a sensitizing dye represented by the following formula:

$$\overbrace{R_1-N(CH=CH)_{n_1}-C}^{Y_1}=\overset{R_2}{\overset{|}{C}}-\overbrace{C(=CH-CH)_{n_2}=\overset{\oplus}{N}}^{Y_2}-A-SO_3^{\ominus}$$

Wherein Y_1 and Y_2 each stand for a non-metallic atomic group necessary to form a nitrogen-containing heterocyclic ring nucleus selected from the group consisting of pyrroline, thiazoline, thiazole, benzothiazol, naphthothiazole, selenazole, benzoselenazole, naphthoselenazole, oxazole, benzoxazole, naphthoxozole, imidazole, benzimidazole, pyridine, and quinoline, which nucleus may be substituted by a halogen atom, a lower alkyl group, a lower alkoxy group, or an aryl group, which group may in turn be substituted by halogen, lower alkyl or lower alkoxy; R_1 stands for lower alkyl, hydroxyalkyl, or sulfoalkyl; R_2 is hydrogen or lower alkyl, A designates alkylene,

$-(CH_2)_2-0-(CH_2)_2-$or$-(CH_2)_2-0$
$CH_2CH(OH)CH_2-$; and n_1 and n_2 are each 0 or 1.

2. A silver halide photosensitive material for color photography according to claim **1**, wherein each of said layers contains a coupler.

3. A silver halide photosensitive material for color photography according to claim **1**, wherein said heterocyclic ring nucleus in said general formula is selected from thiazole, benzothiazole, selenazole, and benzoselenazole.

4. A silver halide photographic material for color photography according to claim **1**, wherein said blue-sensitive emulsion layer contains a yellow coupler, said green-sensitive emulsion layer contains a magenta coupler, and said red-sensitive emulsion layer contains a cyan coupler.

5. A silver halide photosensitive material for color photography according to claim **4**, wherein said heterocyclic nuclei in said sensitizing dye are each selected from thiazole, benzothiazole, selenazole, and benzoselenazole.

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