May 25, 1971 SHUI SATO ET AL 3,580,723

LIGHT-SENSITIVE SILVER HALIDE PHOTOGRAPHIC EMULSION

Filed Dec. 12, 1968

FIG. 1

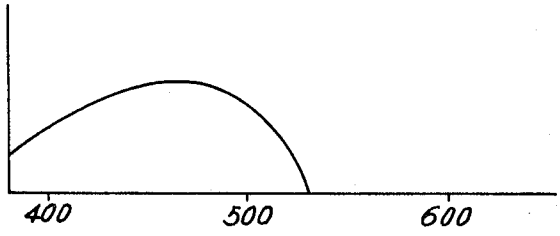


FIG. 2

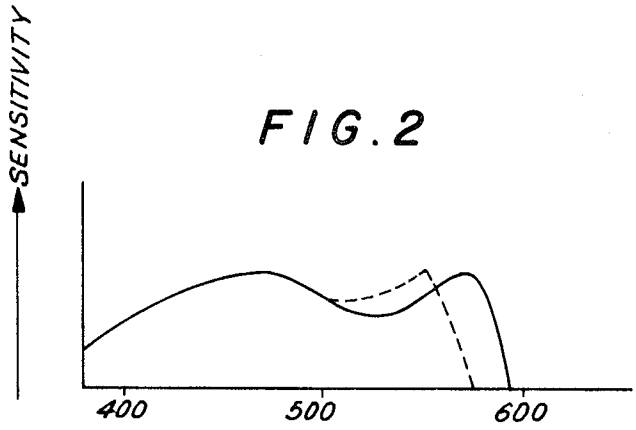
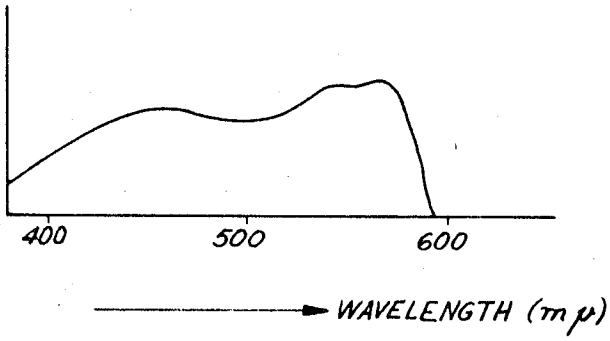


FIG. 3



United States Patent Office

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LIGHT-SENSITIVE SILVER HALIDE PHOTOGRAPHIC EMULSION

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Int. Cl. G03c 1/28

U.S. Cl. 96—122 12 Claims

ABSTRACT OF THE DISCLOSURE

Light sensitive silver halide photographic emulsions are supersensitized by coating with a supersensitizer constituted by a combination of two different oxacarbocyanine dyes.

This invention relates to a light-sensitive silver halide photographic emulsion supersensitized with a combination of two kinds of oxacarbocyanine dyes. Particularly, this invention relates to the supersensitization of a light-sensitive color-photographic silver halide emulsion having a magenta color coupler.

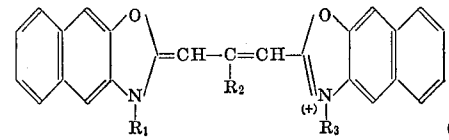
As the method for increasing spectral sensitivity of a photographic emulsion layer, there has been known the so-called supersensitization wherein a sensitizing dye, together with another organic compound different in chemical structure from the sensitizing dye, is incorporated into a photographic emulsion.

In the supersensitization of a silver halide photographic emulsion, it is required to obtain an increased sensitizing effect without fogging (residual color property) and without adverse interaction with any other photographic additives. In the prior art, however the known combinations of sensitizing dyes which are appropriate for optical sensitization are very few.

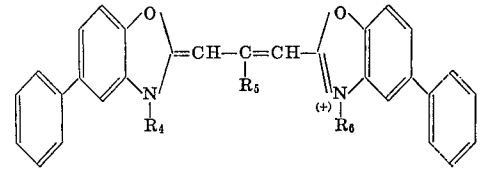
It is one object of the invention to provide a light-sensitive silver halide photographic emulsion having high sensitivity without any undesired fogging. Another object of the invention is to provide a green light-sensitive silver halide color-photographic emulsion having adequate spectral sensibility to afford the best image reproduction. Still

another object of the invention is to provide a high speed, green light-sensitive photographic emulsion which does not suffer from a decrease of spectral sensitivity due to the diffusion of super-sensitizers and the incorporation of a gelatine coagulant or a magenta color coupler.

In accordance with the invention, all of the above objects are satisfactorily accomplished by using, as supersensitizer, a combination of at least one sensitizing dye of Formula I with at least one sensitizing dye of Formula II,



$(X^-)_{n-1}$ (I)

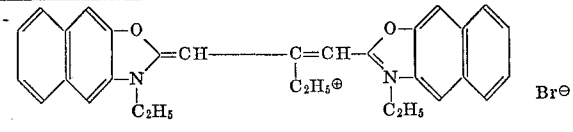
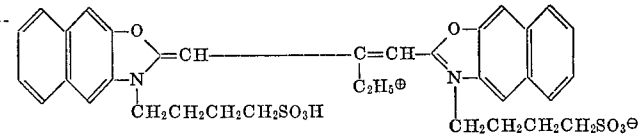
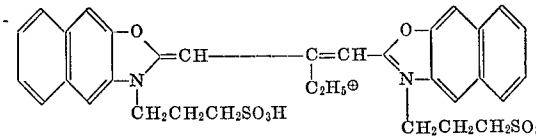
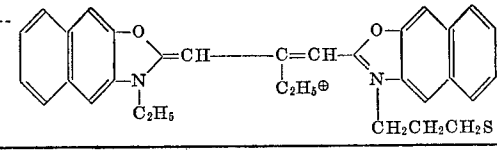


$(X^-)_{n-1}$ (II)

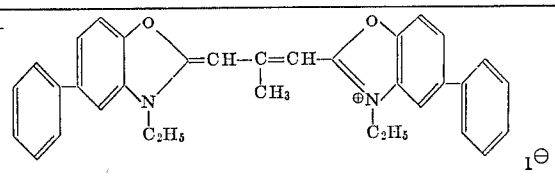
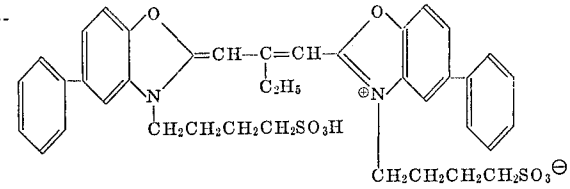
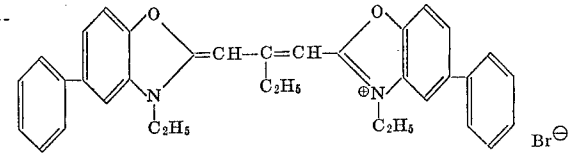
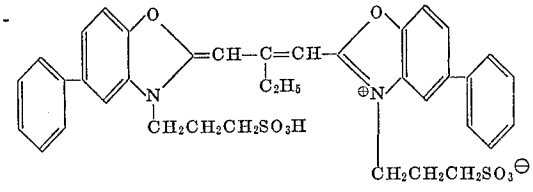
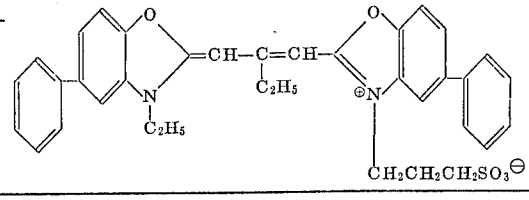
wherein R_1, R_3, R_4 and R_6 are independently selected from the group consisting of a lower alkyl group, a sulfoalkyl group of a carboxyalkyl group; R_2 and R_5 are a lower alkyl group; X is an anionic group; and n is 1 or 2, provided that at least one of said R_1, R_3, R_4 and R_6 is a sulfoalkyl group. Suitable lower alkyl groups include methyl, ethyl, etc. As sulfoalkyl groups are included 3-sulfopropyl, 4-sulfobutyl, etc. The usability of the above-indicated combination of two different sensitizing dyes as a supersensitizer has not been known previously in the photographic art. One of the characteristics of the invention is that remarkable effects are obtained when either one of the sensitizing dyes used has at least one sulfoalkyl group as either one of R_1, R_3, R_4 and R_6.

Typical oxacarbocyanine sensitizing dyes having the above-indicated formulas are the following.

For the Formula I

Compound Number	Structural formula
(1)	
(2)	
(3)	
(4)	

For the general Formula II

Compound Number	Structural formula
(5)	
(6)	
(7)	
(8)	
(9)	

The essential requirement to accomplish the present invention is to use at least one sensitizing dye of the Formula I and at least one sensitizing dye of the Formula II in combination. All of the sensitizing dyes of the Formula I and II are known as ortho-type sensitizing dyes. Among these, the sensitizing dye of the Formula I is a green light-sensitive sensitizing dye having spectral sensitivity maximum at a long wavelength region of 550–580 mμ, whereas the sensitizing dye of the Formula II is a green light-sensitive sensitizing dye having spectral sensitivity maximum at a short wavelength region of 530–550 mμ. Because of this, if the sensitizing dye of the Formula I or II is used alone, it is not possible to obtain a green light-sensitive photographic emulsion sensitized over a sufficiently wide wavelength region. According to the present invention, it is possible to impart high green light sensitivity to a photographic emulsion.

When using the combination of the sensitizing oxacarbocyanine dyes of the Formulas I and II according to the present invention, new distinct sensitivity maxima which are not found by the sole use of the individual sensitizing dyes appear, due to the synergistic action of the sensitizing dyes, whereby a high speed green light-sensitive photographic emulsion is obtained.

The distribution of spectral sensitivity maxima of the supersensitized photographic emulsion will be easily controlled by the choice of the types and amounts of individual sensitizing dyes of the Formulas I and II. These sensitizing dyes are dissolved first into a water-miscible organic solvent such as methanol, ethanol, etc. to give a solution which is then added to a photographic emulsion. Alternatively, two organic solvent solutions may be prepared by individually dissolving the sensitizing dyes which are then added to the photographic emulsion. The addition of the sensitizing dyes to the photographic emulsion may be made at any stage during the preparation of said photographic emulsion. In general, it is preferable to make such addition at a stage after the completion of second ripening. The photographic emulsion to which the sensitizing dyes are to be added may be any type of light-sensitive silver halide photographic emulsions including silver iodobromide, chlorobromide, bromide and chloride emulsions. The amounts of the sensitizing dyes may vary depending on the type of photographic emulsion to which said dyes are added, but they are usually within the range of 1 to 100 mg. as the total of the sensitizing dyes I and II per kilogram of the emulsion, the suitable ratio between I and II being 4:1 to 1:4. However, the above-indicated amounts and ratio are not always critical. Further, the photographic emulsions of the present invention may contain a gold sensitizer, a sulfur sensitizer, a reductive sensitizer or a polyalkyleneoxide sensitizer. Further, it may contain the usual photographic additives such as antifoggant, storage stabilizer, hardener, coating aid, etc. In addition to the sensitizing dyes I and II as defined above, other sensitizing dyes including pseudocyanine, carbocyanine and mercocyanine dyes can be used.

The photographic emulsion of the present invention can be coated on a support in a manner known per se, to thereby give a light-sensitive photographic element. Suitable supports include glass plate, cellulose triacetate or polyester film base, and baryta paper.

The present invention will be explained in detail by way of the following examples.

EXAMPLE 1

A high speed photographic negative emulsion is prepared by subjecting a silver iodobromide emulsion containing 5 mol percent of silver iodide to second ripening using the gold- and sulfur-sensitization process. Separately, the sensitizing dyes of the Formulas I and II are prepared as 0.1% methanolic solutions. These two methanolic solutions are added singly or in combination in the below-indicated amounts per kg. of the above-said emulsion. Each of the emulsions is stirred at 40° C. for about 10 minutes to obtain sufficiently stable spectral sensitization and thereafter mixed with the indicated amount of 1-(4-phenoxy-3-sulfophenyl)-3-pentadecyl - 5 - pyrazolone (color coupler). The resulting dispersions are adjusted to pH 6.8. Each of the resultant green light-sensitive emulsions is coated on a film base to have light-sensitive photographic films.

These films are exposed to light according to the JIS method K–7610 and then treated at 20° C. for 10 minutes with a color developer of the following formulation:

	G.
N,N-diethyl-p-phenylenediamine sulfate	2.5
Sodium sulfite (anhydrous)	2.0
Sodium carbonate (monohydrate)	82.0
Potassium bromide	2.0
Water to make up one liter.	

The thus treated film samples are treated by stopping, fixing, bleaching, water washing and then drying. Fog and yellow light sensitivity of the film samples are measured. The results are set forth in Table 1, wherein the sensitivity values are expressed as relative speed to the yellow-light sensitivity, defined as 100, of the emulsion added with the sensitizing dye No. (6) alone.

TABLE 1

Sensitizing dyes	Amount of 0.1% methanolic solution (ml./kg. emulsion)	Fog	Relative speed	Spectral sensitivity maximum (mμ)
No. (2)	40	0.03	50	580
No. (2)	60	0.03	60	
No. (6)	40	0.03	100	550
No. (6)	60	0.03	90	
No. (2) + No. (6)	[1] 20 + [1] 40	0.03	140	570
No. (2) + No. (6)	[1] 30 + [1] 30	0.03	130	570

[1] In combination.

As for the respective sample emulsion, spectral sensitivity is measured by means of a grating spectrograph (light source 2848° K.).

FIG. 1 shows the spectral sensitivity curve of the silver iodobromide emulsion used in this Example 1. In FIG. 2, the solid line and the dotted line show the spectral sensitivity curves of the emulsions added with the sensitizing dyes No. (2) and No. (6), respectively. FIG. 3 shows the spectral sensitivity curve of the emulsion according to this invention to which the sensitizing dyes No. (2) and No. (6) are added in combination.

As is obvious from the above Table 1 and the figures, the light-sensitive photographic emulsion according to this invention is more highly supersensitized and much more improved in spectral sensitivity in comparison with the emulsion added with any one of the sensitizing dyes alone.

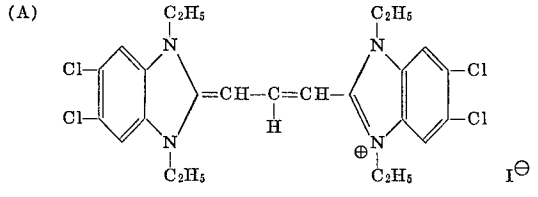
EXAMPLE 2

A high speed photographic negative emulsion the same as that used in the Example 1 is prepared. The sensitizing dyes according to the present invention are added in combination to the emulsion in the below-indicated amounts per kg. of the emulsion.

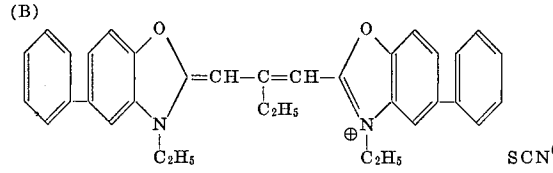
The resulting emulsion is further added with the indicated amount of a coupler prepared by dissolving 1-(2,4,6 - trichlorophenyl)-3-[3-(2,4-di-tert. amylphenoxyacetamide) benzamide[-5-pyrazolone in di-n-butyl phthalate and ethyl acetate by heating and dispersing the resulting solution in gelatine solution with sodium alkylbenzenesulfonate. The pH value of the resulting dispersion is adjusted to 6.8. Immediately or after incubation at 40° C. for 3 hours, the green light-sensitive emulsion thus obtained is coated and dried on a film base.

A control sample is prepared by using the combination of the sensitizing dyes disclosed in U.S. Patent 2,688,545 which is coated and dried under the same condition as above. The sensitizing dyes used have the following formulas:

(A)



(B)



These films are exposed to light in a similar manner to that in Example 1 and then treated at 21° C. for 10 minutes with a color developer of the following formulation:

N-ethyl-N-β-methanesulfonamido-ethyl-3-methyl-amino aniline sulfate—2.5 g.
Sodium sulfite (anhydrous)—2.0 g.
Benzyl alcohol—3.8 ml.
Sodium hexametaphosphate—2.0 g.
Sodium carbonate (monohydrate)—50.0 g.
Potassium bromide—1.0 g.
Sodium hydroxide—0.6 g.
Water to make up one liter.

The thus treated film samples are subsequently subjected to the same treatments effected in Example 1 after development. The results of measurement on fog and sensitivity are set forth in Table 2, wherein the sensitivity values are expressed as relative speed to the yellow light sensitivity, defined as 100, of the emulsion added with the combination of the control dyes (A) and (B).

TABLE 2

Sensitizing dyes	Amount of 0.1% methanolic solution (ml./kg. emulsion)	Immediately after the preparation of emulsion: Relative speed	Immediately after the preparation of emulsion: Fog	Incubated at 40° C. for 3 hrs. after the preparation of emulsion: Relative speed	Incubated at 40° C. for 3 hrs. after the preparation of emulsion: Fog
No. (3) + No. (7)	[1] 20 + [1] 40	110	0.03	100	0.03
No. (3) + No. (8)	[1] 20 + [1] 40	130	0.03	130	0.04
No. (2) + No. (5)	[1] 30 + [1] 30	120	0.03	120	0.04
Control: (A) + (B)	[1] 30 + [1] 30	100	0.04	90	0.06

[1] In combination.

EXAMPLE 3

A reversal color photographic silver iodobromide emulsion containing 3 mol percent of silver iodide is treated

with a gelatine coagulant and then subjected to a second ripening using gold- and sulfur-sensitization process. Immediately after the second ripening, the resulting emulsion is divided into three portions. To each of the emulsions, are added the sensitizing dyes of the Formulas I and II in combination as 0.1% methanolic solution in the below-indicated amount per kg. of the emulsion.

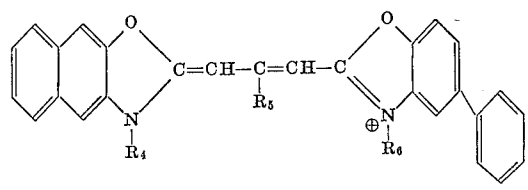
After completion of the ripening, each of the resulting emulsion is further added with an optimum amount of a stabilizer and the indicated amount of a magenta color coupler prepared by dissolving 1-(4-phenoxyphenyl)-3-heptadecyl-5-pyrazolone in di-n-butyl phthalate and ethyl acetate by heating and dispersing the resulting solution in gelatine solution with sodium alkylbenzenesulfonate. The pH value of the resulting dispersions is adjusted to 6.8. Each of the green light-sensitive reversal color-photographic emulsion thus obtained is coated and dried on a film base.

Immediately thereafter, or after incubation at 55° C. for 3 days or at 50° C. for 3 days under 80% of relative humidity, these films are exposed to light in a similar manner to that as in the Example 1 and then treated at 20° C. for 10 minutes with a first developer of the following formulation:

	g.
Metol	3
Hydroquinone	6
Sodium carbonate (anhydrous)	50
Potassium bromide	1

Water to make up one liter.

The resulting film samples are then treated by stopping, hardening and water washing in the usual manner and subjected to re-exposure with white light. Treatment with the color developer as used in Example 1 is carried out at 20° C. for 12 minutes. The thus treated films are subjected to stopping, bleaching, fixing and water washing and then dried. Results of measurement of speed and fog (color stain) are set forth in Table 3, wherein the sensitivity values are expressed as relative speed to the yellow light sensitivity, defined as 100, of the emulsion added with control dyes immediately after the preparation of the emulsion.



$(X^-)_{n-1}$ (II)

wherein R_1, R_3, R_4 and R_6 are independently selected from the group consisting of lower alkyl groups, and sulfoalkyl groups having up to four carbon atoms; R_2 and R_5 are lower alkyl groups; X is an anion and n is 1 or 2, provided that at least one of R_1, R_3, R_4, and R_6 is a sulfoalkyl group.

2. A light-sensitive silver halide photographic emulsion as claimed in claim **1**, wherein said supersensitizer is constituted by a combination of 3,3'-disulfobutyl-9-ethyl-5,6,5',6'-dibenzo-oxacarbocyanine and 3,3'-disulfobutyl-9-ethyl-5,5'-diphenyl-oxacarbocyanine.

3. A light-sensitive silver halide photographic emulsion as claimed in claim **1**, wherein said supersensitizer is constituted by a combination of 3,3'-disulfobutyl-9-ethyl-5,6,5',6'-dibenzo-oxacarbocyanine and 3,3'-diethyl-9-ethyl-5,5'-diphenyl-oxacarbocyanine bromide.

4. A light-sensitive silver halide photographic emulsion as claimed in claim **1**, wherein said sensitizer is constituted by a combination of 3,3'-disulfopropyl-9-ethyl-5,6,5',6'-dibenzo - oxacarbocyanine and 3,3' - diethyl-9-ethyl-5,5',-diphenyl-oxacarbocyanine bromide.

5. A light-sensitive silver halide photographic emulsion as claimed in claim **1**, wherein said supersensitizer is constituted by a combination of 3,3'-disulfopropyl-9-ethyl-5,6,5',6'-dibenzo-oxacarbocyanine and 3,3'-disulfopropyl-9-ethyl-5,5'-diphenyl-oxacarbocyanine.

TABLE 4

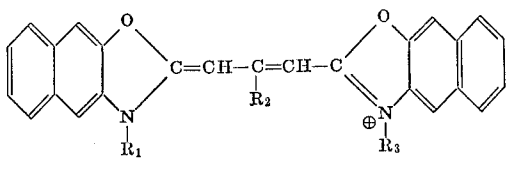
Sensitizing Dyes	Amount of 0.1% methanolic solution (ml./kg.emulsion)	Fresh		Incubated at 55° C. for 3 days after the preparation		Incubated at 50° C., 80% relative humidity for 3 days after the preparation	
		Relative speed	Fog	Relative speed	Fog	Relative speed	Fog
No. (4)	130 } 160 }	130	0.03	120	0.03	120	0.03
No. (8)							
No. (2)	130 } 160 }	120	0.03	130	0.04	120	0.03
No. (7)							
Control:							
(A)	130 } 160 }	100	0.04	80	0.05	90	0.04
(B)							

[1] In combination.

It is evident from the above Tables 2 and 3, that the light-sensitive silver halide photographic emulsion according to the present invention is free from fog and highly sensitive in the presence of a coupler and even under severe conditions.

What is claimed is:

1. A light-sensitive silver halide photographic emulsion which comprises, as a supersensitizer, a combination of at least one sensitizing dye of the Formula I with at least one sensitizing dye of the Formula II,



(I)

$(X^-)_{n-1}$

6. A light-sensitive silver halide photographic emulsion as claimed in claim **1**, wherein said supersensitizer is constituted by a combination of 3-ethyl-3'-sulfopropyl-9-ethyl-5,6,5',6'-dibenzo-oxacarbocyanine and 3,3'-disulfopropyl-9-ethyl-5,5'-diphenyl-oxacarbocyanine.

7. A light-sensitive silver halide photographic emulsion as claimed in claim **1**, further comprising at least one member of the group consisting of a gold sensitizer, a sulfur sensitizer, a reductive sensitizer and polyalkylene oxide sensitizer.

8. A light-sensitive silver halide photographic emulsion as claimed in claim **1**, further comprising a magenta color coupler.

9. A light-sensitive silver halide photographic material which comprises a support and, coated thereon a layer of

the light-sensitive silver halide photographic emulsion as claimed in claim **1**.

10. A light-sensitive silver halide photographic emulsion as claimed in claim **1** wherein the sulfoalkyl group is 3-sulfopropyl or 4-sulfobutyl.

11. A light-sensitive silver halide photographic emulsion as claimed in claim **1** wherein the lower alkyl group is methyl or ethyl.

12. A light-sensitive silver halide photographic emulsion as claimed in claim **1** wherein the anion is bromide or iodide.

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WILLIAM D. MARTIN, Primary Examiner

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U.S. Cl. X.R.

96—124, 125, 126