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YOSHIKATA SAKAGUCHI ET AL

3,694,217

SILVER HALIDE PHOTOGRAPHIC EMULSION

Filed Sept. 12, 1969

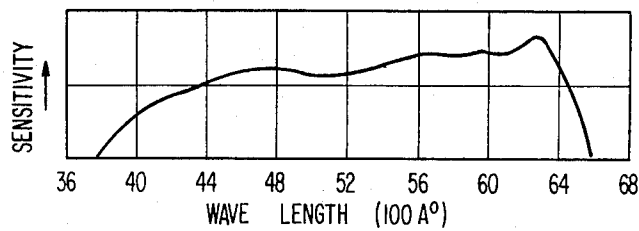


FIG. 1

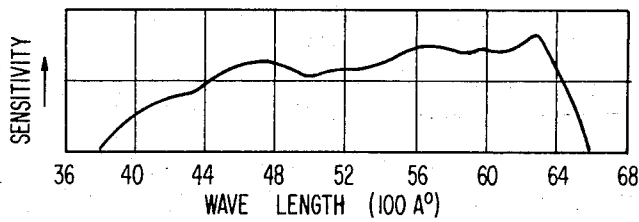


FIG. 2

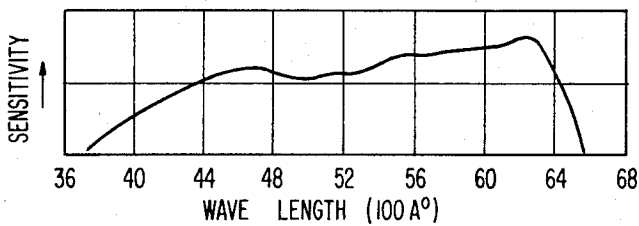


FIG. 3

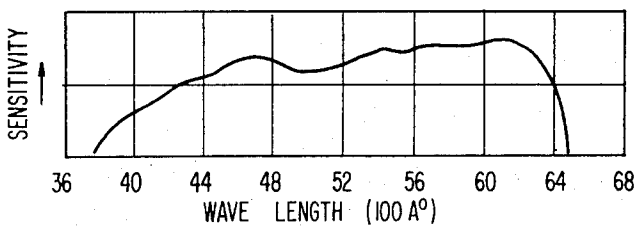


FIG. 4

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1

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SILVER HALIDE PHOTOGRAPHIC EMULSION
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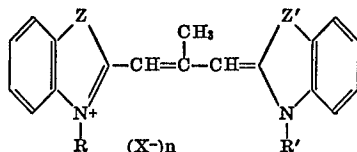
Claims priority, application Japan, Sept. 12, 1968,
43/65,704

Int. Cl. C09b 23/06; G03c 1/18
U.S. Cl. 96—130

9 Claims

ABSTRACT OF THE DISCLOSURE

A silver halide photographic emulsion having therein at least one sensitizing dye represented by the following formula:



wherein Z and Z' are individually selected from the group consisting of a sulfur and a selenium atom, R is selected from the group consisting of an ethyl group, an n-propyl group, an n-butyl group and an allyl group, R' is selected from the group consisting of a γ -sulfopropyl group, a γ -sulfobutyl group, a δ -sulfobutyl group, a δ -carboxybutyl group and an ω -carboxypentyl group, X represents an anion, and n is 0 or 1, n being 0 when the dye is an intramolecular salt.

BACKGROUND OF THE INVENTION

Field of the invention

This invention relates to a spectrally sensitized silver halide photographic emulsion and, more particularly, to a silver halide photographic emulsion having a maximum spectral sensitization within the range of from about 620 m μ to 645 m μ and a high sensitivity to red light.

Description of the prior art

It is well known in the manufacture of silver halide photographic emulsions that by the addition of a sensitizing dye to a silver halide photographic emulsion, the sensitive wave length region of the photographic emulsion is expanded and the emulsion is spectrally sensitized. In many cases, light sensitive photographic materials are incorporated with a single sensitizing dye so as to sensitize in a desired wave length region, while, in most cases, combinations of two or more sensitizing dyes are used. However, the total sensitivity obtained by the use of a combination of two or more sensitizing dyes is usually lower than the sum of the spectral sensitivities obtained by separate uses of the sensitizing dyes. For instance, in the case where a combination of two or more sensitizing dyes differing in spectral sensitizing wave length regions are used with each other for the purpose of sensitizing in a desired wave length region, the sensitizing effect in a longer wave length region of a sensitizing dye having its maximum spectral sensitization in a longer wave length region is greatly affected by the other sensitizing dye having its spectral sensitivity in a shorter wave length region and, in general, the sensitization effect (attributable to the aggregation of sensitizing dyes on particles of silver halide) in a longer wave length region is lowered.

Thus, a significant problem exists among various spectral sensitization techniques with respect to combinations

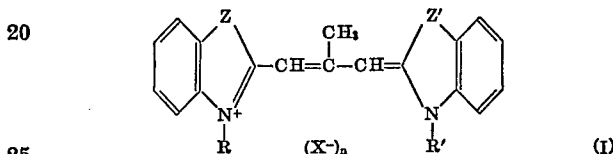
2

of sensitizing dyes in which each sensitizer has no adverse effect on the other and, preferably, there is obtained an increased spectral sensitivity.

The principal object of the present invention is to provide a silver halide photographic emulsion containing a novel sensitizing dye which will afford a high spectral sensitivity in a spectral sensitization wave length region of about 620 to 645 m μ without any decrease in either the total sensitivity and in the red sensitivity, even when used in combination with an ortho sensitizer, and further, which will not retain any stain in the sensitive material after development.

SUMMARY OF THE INVENTION

The object of the present invention is attained by incorporating in a silver halide photographic emulsion a mesomethylcarbocyanine dye represented by the Formula I.



wherein Z and Z' represent sulfur or selenium atoms, R represents an ethyl, n-propyl, allyl or n-butyl group, R' represents a γ -sulfopropyl, γ -sulfobutyl, δ -sulfobutyl, δ -carboxybutyl or ω -carboxypentyl group, and n represents 0 or 1 (in the case of an intramolecular salt, n=0).

BRIEF DESCRIPTION OF THE DRAWINGS

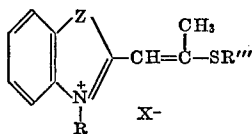
FIGS. 1-4 show spectral sensitization spectra obtained by employing a dye of the present invention alone, in combination with known dyes, and by employing a conventional dye alone and in combination with other known dyes, respectively.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The special feature of the chemical structure of the sensitizing coloring matter used in the present invention consists of the substituents R and R'. It has been found that the spectral sensitizing property of, especially, mesomethylthiacarbocyanines, mesomethylselenathiacarbocyanines and mesomethylselenacarbocyanines is affected to a great extent by the substituents R and R'. Namely, we have found that only when a mesomethylcarbocyanine dye is incorporated in a silver halide photographic emulsion, in which R' is a sulfoalkyl or carboxyalkyl group, and R and R' are as designated in the above general Formula I, it is possible to obtain an excellent spectral sensitization with the result that the object of the present invention is attainable. In cases where there is incorporated in a silver halide emulsion a mesomethylthiacarbocyanine, mesomethylselenathiacarbocyanine, or mesomethylselenacarbocyanine containing substituent R and R' other than those as mentioned above, similarly, there is obtained a sensitized emulsion having a maximum spectral sensitization within the range of about 620 m μ to 645 m μ , and a high red sensitivity. However, if such mesomethylcarbocyanine dyes are used in combination with a known ortho sensitizing dye, such as thia-2'-cyanine or 2,2'-cyanine, its sensitizing property in a red region corresponding to the maximum spectral sensitization (approximately 620 to 645 m μ) due to the aggregation of the mesomethylcarbocyanine dye on the silver halide particles is adversely affected, and, consequently, the red sensitivity of the emulsion is lowered to a great extent, so that the use of such mesomethylcarbocyanines is disadvantageous for the object of the present invention.

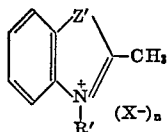
3

The mesomethylcarbocyanines of Formula I for use in the present invention may be synthesized by known processes. Namely, a sensitizing dye as in Formula I may be synthesized by reacting, in reflux, a compound of the general Formula II



(II)

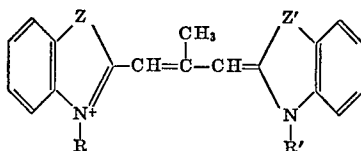
wherein Z, R and X have the same meanings as designated above and R'' represents an alkyl group, such as methyl or ethyl, with a compound of the general Formula III



(III)

wherein Z', R', X and n have the same meanings as designated above in the presence of a basic condensing agent, such as trimethylamine or triethylamine and in a suitable solvent, such as methanol, ethanol or propanol.

Representative examples of the sensitizing dyes which may be used in the present invention will be listed in the following table.

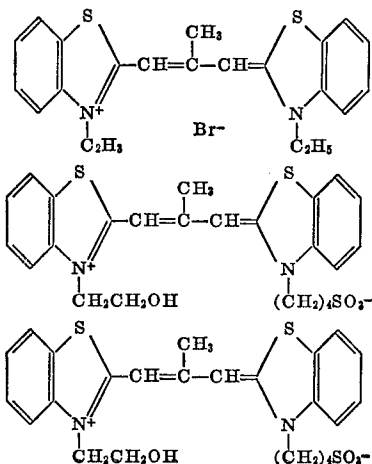


(I)

TABLE 1

Sensitizing dye No.	Z	Z'	R	R'	X-	M.P. (° C.)
1.....	S	S	-C ₂ H ₅	-(CH ₂) ₃ SO ₃ ⁻	-----	282
2.....	S	S	-C ₂ H ₅	-CH ₂ CH ₂ CH-CH ₃ SO ₃ ⁻	-----	283
3.....	S	S	-C ₂ H ₅	-(CH ₂) ₄ SO ₃ ⁻	-----	280
4.....	S	S	-C ₂ H ₅	-(CH ₂) ₄ COOH	Br ⁻	248
5.....	S	S	-C ₂ H ₅	-(CH ₂) ₅ COO ⁻	-----	155
6.....	S	S	-C ₂ H ₅	-(CH ₂) ₄ SO ₃ ⁻	-----	276
7.....	S	S	-C ₂ H ₅	-(CH ₂) ₄ COOH	Br ⁻	238
8.....	S	S	-C ₂ H ₅	-(CH ₂) ₄ SO ₃ ⁻	-----	245
9.....	S	S	-C ₂ H ₅	-(CH ₂) ₄ SO ₃ ⁻	-----	253
10.....	S	S	n-C ₃ H ₇	-(CH ₂) ₃ SO ₃ ⁻	-----	268
11.....	S	S	n-C ₃ H ₇	-CH ₂ CH ₂ -CHCH ₃ SO ₃ ⁻	-----	294
12.....	S	S	n-C ₃ H ₇	-(CH ₂) ₄ SO ₃ ⁻	-----	259
13.....	S	S	n-C ₃ H ₇	-(CH ₂) ₄ COOH	Br ⁻	258
14.....	S	S	n-C ₃ H ₇	-(CH ₂) ₅ COOH	Br ⁻	238
15.....	S	S	n-C ₃ H ₇	-(CH ₂) ₃ SO ₃ ⁻	-----	258
16.....	S	S	n-C ₄ H ₉	-(CH ₂) ₃ SO ₃ ⁻	-----	165
17.....	S	S	n-C ₄ H ₉	-CH ₂ CH ₂ -CHCH ₃ SO ₃ ⁻	-----	291
18.....	S	S	n-C ₄ H ₉	-(CH ₂) ₄ SO ₃ ⁻	-----	258
19.....	S	S	n-C ₄ H ₉	-(CH ₂) ₄ COOH	Br ⁻	196
20.....	S	S	n-C ₄ H ₉	-(CH ₂) ₄ SO ₃ ⁻	-----	274
21.....	S	S	-CH ₂ CH=CH ₂	-(CH ₂) ₃ SO ₃ ⁻	-----	213
22.....	S	S	-CH ₂ CH=CH ₂	-(CH ₂) ₄ SO ₃ ⁻	-----	269

The following are sensitizing dyes which are used for comparison in the examples described hereinafter:



55

The sensitizing dye of the present invention is able to spectrally sensitize silver halide photographic emulsions.

In particular, it is useful for expanding the spectral sensitive region of gelatino silver halide emulsions. In addition, it can sufficiently sensitize emulsions of the type containing a hydrophilic colloid other than gelatin, such as, e.g., agar collodion, water soluble cellulose derivatives, polyvinyl alcohol or like natural or synthetic resinous materials. The emulsion used in the present invention may be an emulsion which contains a mixed silver halide, such as silver iodobromide or silver chlorobromide. The photoemulsion which is sensitized in accordance with the present invention may be prepared by incorporating one or more sensitizing dyes in a photographic emulsion in an ordinary manner. In practice, the dye is usually added to the emulsion while in solution in a suitable solvent, such as methanol or ethanol. The amount of the sensitizing dye to be incorporated in the emulsion may vary in a wide range of from 5 to 200 mg. per kg. of emulsion, depending on the required effect.

60

A

65

B

70

C 75

5

The photographic emulsion used in accordance with the present invention may be, in addition, super-sensitized and hyper-sensitized according to conventional methods. In the manufacture of the photographic emulsions which may be used in accordance with the present invention, there may be incorporated therein by conventional methods one or more ordinarily used additives, such as sensitizers, stabilizers, anti-bronzing agents, hardeners, surface active agents, anti-foggants, plasticizers, developing promoters, color developers, or fluorescent whitening agents.

The photographic emulsion in accordance with the present invention may be applied in the usual manner to a suitable support, such as, e.g., sheet glass, a film of cellulose derivative, a film of synthetic resin or baryta paper.

The present invention will be further illustrated by the following examples.

Example 1.—A silver halide photographic emulsion was prepared by incorporating one of the sensitizing dyes as indicated above in a silver iodobromide emulsion (AgI: AgBr=7 moles; 93 moles). Separately, another silver halide photographic emulsion was prepared by incorporating a sensitizing dye of the present invention in combination with a known green-sensitive sensitizing dye. These emulsions were separately applied to a triacetylcellulose film base and, after drying, exposed through a Fuji #7 filter (made by Fuji Photo Film Co., Ltd., transmitting light having a wave length longer than 580 m μ) to a daylight of 64 luxes (corresponding to 5,400° K.) and developed.

The developing solution used was of the formulation as indicated in Table 2.

TABLE 2

N-methyl-p-aminophenol sulfate	20	G.
Hydroquinone	5.0	
Sodium sulfite	100	
Borax	2.0	
Diluted with water to make 1 liter.		

In Table 3 is shown the degrees of color sensitization and maxima of sensitization obtained by separate addition of the sensitizing dyes as indicated in Table 1. In Table 4 is shown the degrees of spectral sensitization and maxima of sensitization obtained by the separate addition of the sensitizing dyes indicated above as sensitizing dyes for comparison. In Table 5 is shown the degrees of spectral sensitization and maxima of sensitization obtained by various combinations of sensitizing dyes selected from those listed in Table 1 and those as indicated above for comparison with a known green-sensitive sensitizing dye.

TABLE 3

Sensitizing Dye No.	Amount of sensitizing dye added (millimole/kg. emulsion)	Emulsion	Maxima of sensitization	Red sensitivities
1	0.06	AgBr/I	625-628	120
2	0.06	AgBr/I	625	160
3	0.06	AgBr/I	628	160
4	0.06	AgBr/I	628	160
5	0.06	AgBr/I	628-630	125
6	0.06	AgBr/I	640	130
7	0.06	AgBr/I	638	160
8	0.06	AgBr/I	640	160
9	0.06	AgBr/I	645	140
10	0.06	AgBr/I	625-628	140
11	0.06	AgBr/I	628	150
12	0.06	AgBr/I	625-628	130
13	0.06	AgBr/I	625	130
14	0.06	AgBr/I	625	130
15	0.06	AgBr/I	640	120
16	0.06	AgBr/I	625	120
17	0.06	AgBr/I	622	140
18	0.06	AgBr/I	625	140
19	0.06	AgBr/I	625	120
20	0.06	AgBr/I	638	130
21	0.06	AgBr/I	628	120
22	0.06	AgBr/I	624	130

The red sensitivities were indicated in terms of relative

6

sensitivity, assuming that the red sensitivity of sensitizing dye A was 100.

TABLE 4

Sensitizing Dye No.	Amount of sensitizing coloring matter added (millimole/kg. emulsion)	Emulsion	Maxima of sensitization	Red sensitivities
A	0.06	AgBr/I	625-628	100
B	0.06	AgBr/I	600	50
C	0.06	AgBr/I	620	53
D	0.06	AgBr/I	625	62
E	0.06	AgBr/I	628	150
F	0.06	AgBr/I	630	150
G	0.06	AgBr/I	628	150

The red sensitivities were indicated by terms of relative sensitivity, assuming that the red sensitivity of sensitizing coloring matter A was 100.

TABLE 5

Sensitizing Dye No.	Amount of sensitizing dye added (millimole/kg. emulsion)	Emulsion	Maxima of sensitization	Red sensitivities
3	0.06	AgBr/I	628	100
3	0.053			
H	0.015	AgBr/I	628	100
I	0.015	AgBr/I	628	100
I	0.06			
4	0.053	AgBr/I	628	100
4	0.053			
H	0.015	AgBr/I	628	100
I	0.015	AgBr/I	625	100
I	0.06			
E	0.053	AgBr/I	620	75
E	0.053			
H	0.015	AgBr/I	620	75
I	0.015	AgBr/I	630	100
I	0.06			
F	0.053	AgBr/I	625	80
F	0.053			
H	0.015	AgBr/I	625	80
I	0.015	AgBr/I	628	100
I	0.06			
G	0.053	AgBr/I	625	80
G	0.053			
H	0.015	AgBr/I	625	80
I	0.015			

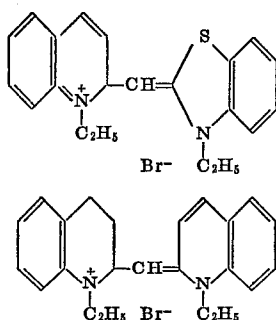
The red sensitivities were indicated in terms of relative sensitivity, assuming that the red sensitivity of an emulsion having incorporated therein, by itself, sensitizing dye F was 100.

In the accompanying drawings, FIG. 1 indicates a spectral sensitization spectrum obtained by using great extent when used in combination with green-sensitization spectrum obtained by using sensitizing dye 3 in combination with known green-sensitive coloring matter H and I; FIG. 3 indicates a spectral sensitization spectrum obtained by using sensitizing dye E alone; and FIG. 4 indicates a spectral sensitization spectrum obtained by using sensitizing dye F in combination with the known green-sensitive sensitizing dyes H and I.

As is evident from FIGS. 3 and 4, where sensitizing dye E was used for comparison purposes, its maximum sensitization in the red region (J-band) falls off to a great extent when used in combination with green-sensitive sensitizing dye H and this causes a remarkable depression of the red sensitivity, while, when employing sensitizing dye 3 of the present invention, the phenomenon that will cause such a depression of red sensitivity does not occur even if it is used in combination with the green-sensitive sensitizing dyes H and I.

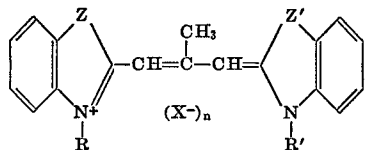
The known green-sensitive sensitizing dyes used in combination with the sensitizing dye of the present invention are those having the following structures.

7



What is claimed is:

1. A silver halide photographic emulsion having incorporated therein at least one sensitizing dye represented by the following formula:



wherein Z and Z' are individually selected from the group consisting of a sulfur and a selenium atom, R is selected from the group consisting of an ethyl group, an n-propyl group, an n-butyl group and an allyl group, R' is selected from the group consisting of an γ -sulfopropyl group, a γ -sulfobutyl group, a δ -sulfobutyl group, a δ -carboxybutyl group and a ω -carboxypentyl group, X represents an anion, and n is 0 or 1, n being 0 when the dye is an intramolecular salt.

2. The silver halide photographic emulsion as in claim 1, wherein said emulsion further contains a green sensitive sensitizing dye.

3. The silver halide photographic emulsion as in claim 1, wherein the maximum spectral sensitivity of said emulsion is from 620 to 645 m μ .

4. The silver halide photographic emulsion as in claim 1, wherein the amount of said sensitizing dye varies from 5 to 200 milligrams per kilogram of emulsion.

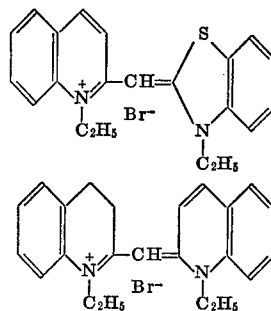
5. The silver halide photographic emulsion as in claim

8

1, wherein said emulsion further contains at least one conventional additive selected from the group consisting of sensitizers, stabilizers, anti-bronzing agents, hardeners, surface active agents, anti-foggants, plasticizers, developing promoters, color developers and fluorescent whitening agents.

6. A silver halide photographic material comprising a hydrophobic support having thereon a photographic emulsion layer consisting of the silver halide emulsion of claim 1.

7. The silver halide photographic emulsion as in claim 2 wherein said green sensitizing dye is selected from the group consisting of



8. The silver halide photographic emulsion as in claim 1, wherein said emulsion further contains an ortho-sensitizer.

9. The silver halide photographic emulsion as in claim 8, wherein said orthosensitizer comprises thia-2'-cyanine or 2,2'-cyanine.

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