

[54] **SILVER HALIDE SUPERSENSITIZED PHOTOGRAPHIC EMULSION**

[75] Inventors: **Keisuke Shiba; Akira Sato**, both of Ashigara-Kamigun, Kanagawa, Japan

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

[22] Filed: **June 25, 1970**

[21] Appl. No.: **49,981**

[30] **Foreign Application Priority Data**

June 25, 1969 Japan44/50117

[52] U.S. Cl.96/124, 96/139

[51] Int. Cl.G03c 1/14

[58] Field of Search.....96/124

[56] **References Cited**

UNITED STATES PATENTS

2,533,427	12/1950	Carroll	96/124
2,541,400	2/1951	Brooker et al.....	96/120
2,701,198	2/1955	Carroll et al.	96/124
3,038,800	6/1962	Luckey et al.....	96/139

Primary Examiner—J. Travis Brown

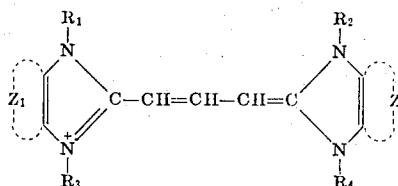
Attorney—Sughrue, Rothwell, Mion, Zinn and Macpeak

[57]

ABSTRACT

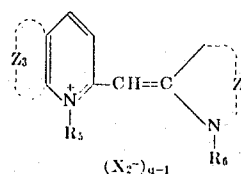
A silver halide photographic emulsion is super-sensitized in the green wave length region by adding thereto at least one sensitizing dye of the following formula I and at least one sensitizing dye of the following formula II; and, optionally a compound of the following formula III:

FORMULA I



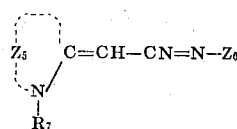
(X1⁻)_{p-1}

FORMULA II



(X2⁻)_{q-1}

FORMULA III



The substituents are described in detail hereinbelow.

22 Claims, No Drawings

SILVER HALIDE SUPERSENSITIZED PHOTOGRAPHIC EMULSION

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a super-sensitized silver halide photographic emulsion and more particularly it relates to a supersensitized silver halide photographic emulsion for increasing particularly the spectral sensitivity in the green region. Furthermore, the invention relates to a super-sensitized silver halide photographic emulsion containing couplers for making color photographic light-sensitive materials.

2. Description of the Prior Art

It is well known that a spectral sensitizing method is one of the techniques employed in the manufacture of silver halide photographic emulsions, and that the sensitizing method is an indispensable technique for the production of color photographic light-sensitive materials. The spectral sensitivity obtained by the method is influenced not only by the chemical structure of the sensitizing dye to be used and the properties of the silver halide emulsion to be used, such as the composition of the halogen and the crystal system of the silver halide contained in the emulsion, the manner of chemical ripening, the silver ion concentration and the hydrogen ion concentration of the emulsion, but also by the various kinds of additives added to the silver halide emulsion.

In many cases, the spectral sensitivity is reduced. However, when a certain kind of sensitizing dye is used together with a dye or a colorless aromatic compound having a specific chemical structure according to the chemical structure and the properties of the sensitizing dye, a higher spectral sensitivity is obtained than when using each of the sensitizing dyes alone. This is known as a super-sensitizing action.

In particular, silver halide emulsions used for producing color photographic light-sensitive materials contain a large amount of couplers, and when a coupler is incorporated in a silver halide photographic emulsion containing a sensitizing dye, the spectral sensitivity becomes lower than the spectral sensitivity obtained by using the sensitizing dye alone. In addition, the presence of the coupler reduces the super-sensitizing action.

Also, the spectral sensitivity distribution in the green region, in which man's visual sensitivity is high, is one of the most important factors for the color reproduction of color photographic light-sensitive materials and for the quality of the image obtained.

Therefore, various studies have been made concerning the sensitization of silver halide emulsions in the green region. For example, a method of using a combination of a benzimidazolocarbo-cyanine dye and a pseudocyanine dye is described in the specification of U. S. Pat. No. 2,701,198. However, when the method described in the aforementioned U. S. patent is applied to a silver halide emulsion containing a coupler, only a low sensitivity is obtained due to the presence of the coupler in the emulsion.

Also, a method of using a combination of a benzimidazolocarbo-cyanine dye and a benzoxazolocarbo-cyanine dye is described in the specification of Japanese Pat. Publication No. 4936/68. However, this method has the disadvantages that the sensitivity in the

shorter wave length side of the green region, e.g., in a wave length region of 500—530 m μ is large, and also the contamination effect by the dyes after development is large.

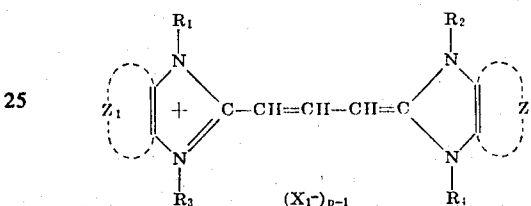
Therefore, a primary object of the present invention is to provide a silver halide photographic emulsion having both a high spectral sensitivity in a wave length region of 500—530 m μ and less of a contamination by the dyes after development.

Another object of the present invention is to provide a silver halide photographic emulsion used for producing a color photographic light-sensitive material having a high green sensitivity in the presence of a coupler.

SUMMARY OF THE INVENTION

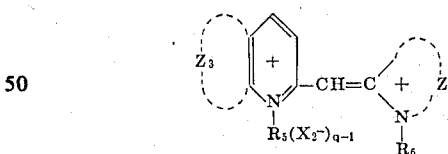
The above objects of the present invention can be attained by super-sensitizing a silver halide photographic emulsion with at least one sensitizing dye represented by the following formula I:

FORMULA I



wherein R_1 and R_2 (which may be same or different) each represent an alkyl group, an aryl group or a substituted alkyl group; R_3 and R_4 (which may be same or different) each represent an alkyl group, an aryl group or a substituted alkyl group (including a substituted alkyl group having a sulfo group); at least one of said R_3 and R_4 being a substituted alkyl group having a sulfo group; Z_1 and Z_2 (which may be same or different) each represents a non-metallic atomic group necessary to complete a heterocyclic nucleus of the benzimidazole series; X_1^- represents an acid anion group usually employed in cyanine dyes; and p is an integer of 1 or 2, p being 1 when the cyanine dye of formula I forms an intermolecular salt; and at least one of the sensitizing dyes represented by the following formula II:

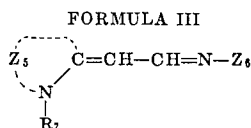
FORMULA II



wherein Z_3 represents a non-metallic atomic group necessary to complete a heterocyclic nucleus of the 2-quinoline series; Z_4 represents a non-metallic atomic group necessary to complete a benzoxazole nucleus, a naphthoxazole nucleus, a benzthiazole nucleus, a benz-selenazole nucleus, a naphthothiazole nucleus, or a naphthoselenazole nucleus, each being unsubstituted or substituted by an alkyl group, a phenyl group, a halogen atom, an alkoxy group or an alkoxy group having a sulfo group; R_5 and R_6 (which may be same or different) each represents an alkyl group or a substituted alkyl group (including a substituted alkyl group having a sulfo group); at least one of said R_5 and R_6 being a substituted alkyl group having a sulfo group ex-

cept where the heterocyclic nucleus containing Z_4 has been substituted by a substituted alkoxy group having a sulfo group; X_2^- represents an acid anion group usually employed in cyanine dyes; and q is an integer of 1 or 2, q being 1 when the cyanine dye of formula II forms an intermolecular salt.

Furthermore, it has been discovered according to the present invention that a particularly better result is obtained by incorporating a compound represented by the following formula III in the above-mentioned silver halide photographic emulsion:



wherein R_7 represents an alkyl group or a substituted alkyl group; Z_5 represents a non-metallic atomic group necessary to complete a heterocyclic nucleus of the benzimidazole series; and Z_6 represents a phenyl group or a substituted phenyl group, such as a phenyl group substituted by alkyl groups, alkoxy groups, and the like.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

In the above-mentioned formulas I and II, the alkyl groups of R_1 to R_6 include: methyl, ethyl, n-propyl, isopropyl, n-butyl and iso-butyl groups; and as the substituted alkyl groups of R_1 to R_6 there may be illustrated: an allyl group, an aralkyl group, a β -acetoxylethyl group, a γ -acetoxypropyl group, a γ -carboxypropyl group, a β -carboxyethyl group, a γ -sulfatopropyl group, a δ -sulfatobutyl group, a δ -N-acetylsulfamyl butyl group and a β -hydroxyethyl group. In particular, as the substituted alkyl group having a sulfo group, there may be illustrated a β -sulfopropyl group, a β -sulfobutyl group, a δ -sulfobutyl group, a 2-(3-sulfopropoxy)ethyl group, a 2-[2-(3-sulfopropoxy)ethoxy]ethyl group, and a 2-hydroxy-1-sulfopropyl group.

As the benzimidazole series nucleus completed by Z_1 , Z_2 or Z_5 , there may be illustrated: benzimidazole and benzimidazole containing, as a component of the skeletal-structure thereof, a benzene ring substituted by at least one of the following: a halogen atom, an N-unsubstituted or alkyl substituted sulfamyl or carbamyl group, an N-disubstituted sulfamyl group such as a morpholino sulfonyl group, an alkyl sulfonyl group, a trifluoromethyl group, an unsubstituted or substituted alkyl group, a cyano group, a phenyl group, a carboalkoxyl group, a hydroxyl group, and an alkoxy group.

Also, the 2-quinoline series nucleus completed by Z_3

in the above-mentioned formula II may be, for example, 2-quinoline and 2-quinoline containing, as a component of the skeletal-structure thereof, a benzene ring substituted by at least one of the following: an alkyl group and a halogen atom.

The substituted alkyl group of R_7 in the above-mentioned formula III is, for example, a sulfoalkyl group neutralized by a cation, such as alkali metal ions, organic ammonium ions, a pyridinium ion, a benzylthiuronium ion, and the like, usually employed in cyanine dyes, a cyanoalkyl group and an allyl group.

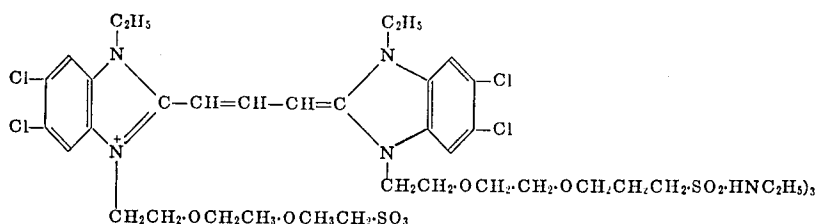
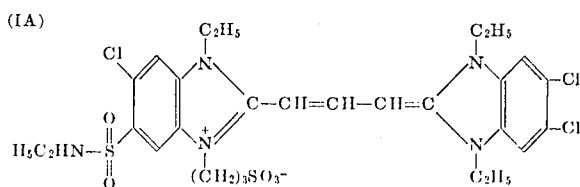
As X_1 and X_2 in the formulas I and II, there may be illustrated, e.g., a halogen, perchlorate, thiocyanate, p-toluene sulfonate, benzene sulfonate, methyl sulfate and ethyl sulfate ions.

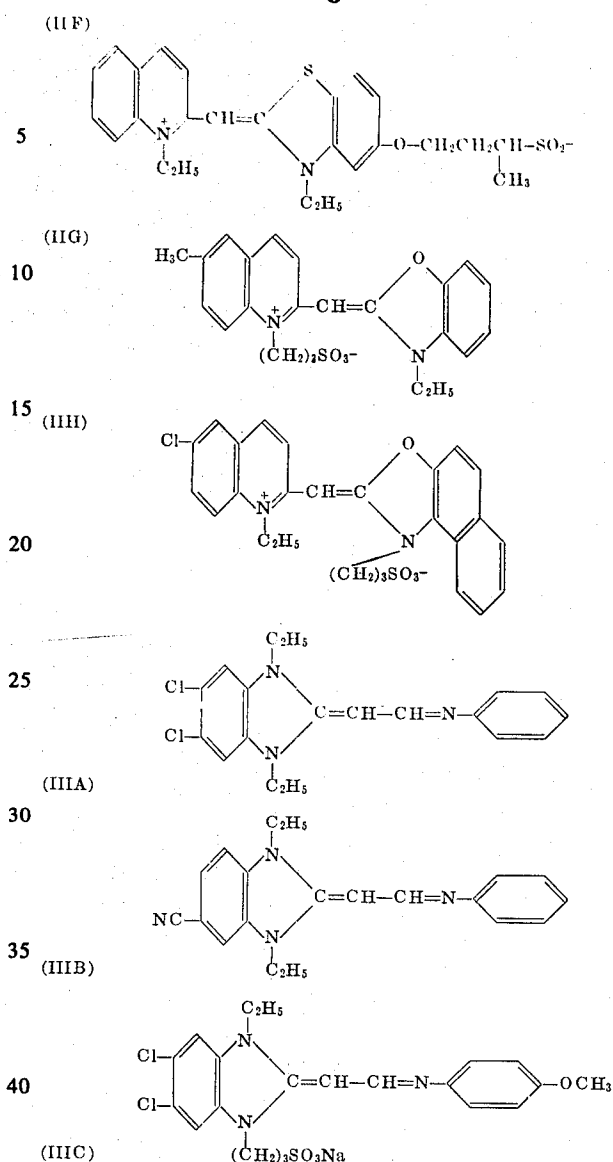
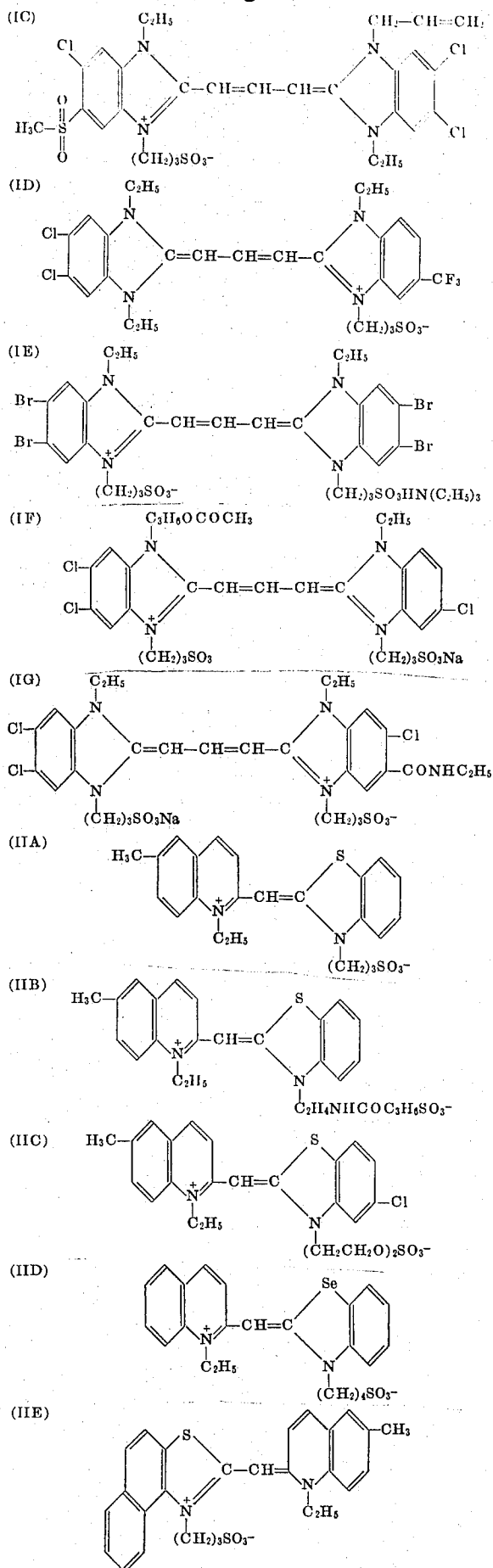
The sensitizing dye represented by formula II has at least one sulfo group in the heterocyclic nucleus containing Z_4 or at R_5 or R_6 . The spectral sensitization obtained by using the sensitizing dye represented by the formula II is ordinarily reduced by the introduction of a sulfo group, but when the sensitizing dye represented by the formula I is used together therewith, the spectral sensitization is increased.

The sensitizing dye represented by the formula II may be substituted therein by an alkyl group, a phenyl group, a halogen atom, an alkoxy group, or an alkoxy group substituted by at least a sulfo group; in other words, the substituent is so selected that the maximum sensitivity obtained by using at least one sensitizing dye of formula II and at least one compound of formula I in combination does not shift to a longer wave length side than that of the sensitizing dye of formula II.

The compound represented by formula III shows a super-sensitizing action to the sensitizing dye represented by formula I and to the sensitizing dye represented by formula II, and by using the compound represented by formula III together with the combination of the other two sensitizing dyes, the green sensitivity is further increased and at the same time the sensitivity in the wave length region of 500-530 m μ , which is present at a shorter wave length side of the green region, is further increased.

The compounds which may be used in the present invention will be further illustrated by reference to the following illustrative formulas, which are merely illustrative, and not limiting, in nature.





45 The above-mentioned sensitizing dyes or the other compounds which may be used in this invention may be synthesized by known methods.

For instance, they can be synthesized by the methods described in the specifications of U. S. Pat. Nos. 2,503,776 and 2,778,823; Belgian Pat. Nos. 590,607; 704,296; 668,014; 669,133; 669,934; 673,554; and 697,006; British Pat. Nos. 742,112; 955,964; 975,504; and 980,234; Japanese Pat. Publication Nos. 14112/65; 23467/65; and 13823/68; and Japanese Pat. Application Nos. 55439/67 and 76071/67.

Also, other sensitizing dyes and the compounds used in this invention, which were not described above, may also be easily synthesized by referring to the specifications of the above patents.

60 The compounds used in this invention are incorporated in a silver halide emulsion as solutions in water or a water-soluble organic solvent such as methanol, ethanol, and pyridine. The sensitizing dyes represented by formula I and formula II, respectively, may be added to a silver halide emulsion as a mixture of the solutions thereof or as separate solutions. The amounts of these dyes are greatly influenced by the nature of the silver halide emulsion to be used. Usually, the total amount of

the above-mentioned sensitizing dyes (I and II) and compound III are preferably from 1×10^{-6} mol to 1×10^{-3} mol, per mol of silver halide. The weight ratio of the amount of the sensitizing dye represented by formula II to the amount of the sensitizing dye represented by formula I is preferably from 10:1 to 1:2, but this ratio is varied by the amount of the compound represented by formula III to be added.

As the silver halide emulsion which may be used in this invention, there may be illustrated: a silver iodobromide emulsion, a silver bromide emulsion, a silver chlorobromide emulsion, etc. The silver halide emulsion used in this invention is mainly a gelatino silver halide emulsion but the emulsion may contain, besides gelatin, polyvinyl alcohol, an alginic acid polymer, polyvinyl imidazole, polyvinyl pyrrolidone, or copolymers thereof, or may be an emulsion thereof.

The silver halide emulsion of this invention is applied to a suitable support according to the desired use, such as a paper, a glass plate, a cellulose triacetate film, a polyethylene terephthalate film, other plastic films than above, a baryta-coated paper, a resin-coated paper, or a synthetic paper.

The present invention will be illustrated further by the following examples which are merely illustrative and not limited in nature.

EXAMPLE 1

50 g of 1-phenyl-3-[3-(2,4-di-tertiaryamylphenox-yactamido)-benzamido]5-pyrazolone was dissolved in 100 ml of dibutyl phthalate by heating and the resultant solution was added to 1 liter of a 10 percent aqueous gelatin solution. Then, 50 ml of a 5 percent aqueous solution of sodium alkylbenzene sulfonate was added thereto and they were dispersed by emulsification by means of a high speed rotary mixer (the product is called the dispersion of the magenta coupler).

1 kg. of a silver iodobromide emulsion (containing 0.25 mol of silver and 4.0 mol percent of iodine) prepared by a conventional method was placed in a beaker and melted at 40°C. After adding to the emulsion the sensitizing dye in the amounts shown in Table 1, the emulsion was stirred for 15 minutes. Further, 400 g. of the dispersion of the magenta coupler as prepared above was added to the emulsion with stirring and after adding further suitable amounts of a hardening agent and an ampholite surface active agent as a wetting agent to the mixture with stirring, the resultant mixture was applied to a cellulose triacetate film in a thickness of 7 microns to obtain a sample of a green-sensitive light-sensitive material.

The sample was cut into strips and subjected to an optical wedge exposure through Yellow Filter No. K-12 made by Fuji Photo Film Co. by using a sensitometer of 5400°K in color temperature of the light source. The strip thus exposed was developed for 12 minutes at 20°C in a color developer having the following composition:

N,N-diethyl-p-aminoaniline sulfate	2.0 g
Sodium sulfite	2.0 g
Sodium carbonate monohydrate	50.0 g
Hydroxylamine hydrochloride	1.5 g
Potassium bromide	1.0 g
Water to make	1000 ml
(pH, 10.8 $\pm$ 0.1)	

Thereafter, the strip was further processed in a first fixing solution, a bleaching solution and a second fixing solution and washed with water to obtain a magenta image. After drying the sample strips thus processed, the green filter density was measured by using an S-type Densitometer made by Fuji Photo Film Co., from which characteristic curves were obtained. From these results, the densities at the point of fog plus 0.20 were calculated and the results are shown in Table 1.

The compositions of the bleaching solution and the fixing solution used in the above processing were as follows:

Composition of the Bleaching Solution

Ferricyanide	100 g
Potassium bromide	20 g
Water to make	1000 ml
(pH, 6.9 $\pm$ 0.3)	

Composition of the Fixing Solution

Hypo	200 g
Sodium sulfite	20 g
Acetic acid (28%)	45 ml
Boric acid	7.5 g
Potassium alum	20 g
Water to make	1000 ml
(pH, 4.5 $\pm$ 0.2)	

TABLE 1

Dye	Amount (ml) (mol concentration)	Dye	Amount (ml) (mol concentration)	(A)	(B)
(IA)	40(5×10^{-4})	—	—	115	0.17
	80	—	—	120	0.23
	40	(IIC) 20(1×10^{-3})	—	142	0.18
	"	40	—	165	0.20
	"	120	—	158	0.23
	—	40	—	43	0.11
	—	120	—	50	0.12
(IB)	40(5×10^{-4})	—	—	100	0.13
	80	—	—	100	0.15
	40	(IIA) 40(1×10^{-3})	—	200	0.25
	"	80	—	186	0.25
	—	40	—	35	0.13
	—	80	—	35	0.13
	40	(IIB) 40(1×10^{-3})	—	220	0.21
	"	80	—	282	0.25
	—	40	—	43	0.13
	—	80	—	46	0.13
	40	(IID) 40(1×10^{-3})	—	190	0.23
	"	80	—	220	0.25
	—	40	—	33	0.11
	—	80	—	35	0.12
(IC)	40(5×10^{-4})	—	—	105	0.13
	80	—	—	105	0.15
	40	(IIE) 40(5×10^{-4})	—	200	0.19
	"	80	—	220	0.20
	—	160	—	220	0.22
	—	40	—	45	0.18
	—	80	—	50	0.17
	—	160	—	58	0.15
	40	(IIF) 20(1×10^{-3})	—	252	0.24
	"	40	—	282	0.27
	—	80	—	218	0.26
	—	20	—	50	0.22
	—	40	—	60	0.22
	—	80	—	60	0.22
(IE)	40(5×10^{-4})	—	—	110	0.18
	80	—	—	115	0.24
	40	40(1×10^{-3})	—	200	0.20
	"	80	—	234	0.21
	—	40	—	25	0.17
	—	80	—	25	0.19
(ID)	40(1×10^{-4})	—	—	118	0.18
	80	—	—	118	0.14
	40	(IIH) 40(5×10^{-4})	—	250	0.17
	"	80	—	316	0.20
	—	40	—	33	0.15
	—	80	—	40	0.15
(IG)	40(5×10^{-4})	—	—	100	0.15

	80	—	115	0.22
	40	(IIB) 40(1×10 ⁻³)	200	0.20
	"	80	220	0.25
(IF)	40	—	79	0.25
	80	—	85	0.27
	40	(IIC) 20(1×10 ⁻³)	118	0.27
	"	40	150	0.30

(A): Relative yellow filter sensitivity (SY)

(B): Fog.

EXAMPLE 2

As in Example 1, 1 kg of a silver iodobromide emulsion (containing 0.30 mol of silver and 6.0 mol% of iodine) was melted in a beaker at 40°C and the amounts of the sensitizing dyes I and II and the compound of formula III shown in Table 2 were added to the emulsion with stirring. 7 ml of the silver halide emulsion thus obtained was applied to a glass plate of cabinet size followed by drying to obtain a sample.

The sample was cut into strips and the strips were subjected to an optical wedge exposure by yellow light as in Example 1 and then developed in a developer having the following composition for 10 minutes at 20°C.

Composition of the Developer

Water	500 ml
Metol	0.3 g
Sodium pyrosulfite	38 g
Hydroquinone	6 g
Sodium carbonate monohydrate	22.5 g
Citric acid	0.7 g
Potassium bromide	0.9 g
Water to make	1000 ml

The strips were then fixed and the optical densities thereof were measured, the results of which are shown in Table 2.

TABLE 2

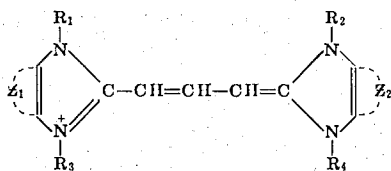
Dye	Amount(ml)	Dye	Amount(ml)	Compd	Amt (ml)	A	B
	(mol concentration)		(mol concentration)		(mol concentration)		
IB	40(5×10 ⁻⁴)	—	—	—	—	100	0.15
"	80 "	—	—	—	—	97	0.16
"	40 "	IIB40(1×10 ⁻³)	—	—	—	142	0.15
"	"	" 80 "	—	—	—	178	0.16
"	"	" 60 "	—	—	—	166	0.15
"	"	" " "	—	IIA	20(1×10 ⁻³)	200	0.15
"	"	" " "	—	"	40 "	200	0.16
"	"	" " "	—	"	80 "	190	0.16
"	"	" " "	—	IIIB	40(1×10 ⁻³)	178	0.16
"	"	" " "	—	"	80 "	190	0.16
"	"	" " "	—	IIIC	40(1×10 ⁻³)	190	0.16
"	"	" " "	—	"	80 "	200	0.17

(A): Relative yellow filter sensitivity (Sy)

(B): Fog

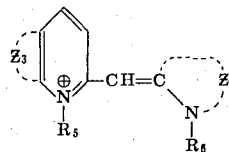
What is claimed is:

1. A super-sensitized silver halide photographic emulsion containing at least one sensitizing dye represented by the following first formula:



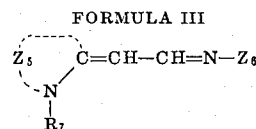
wherein R₁ and R₂ each represents alkyl, acetoxyalkyl or vinylalkyl; R₃ and R₄ are each alkyl, sulfoalkyl, sulfoalkoxyalkoxyalkyl or sulfoalkoxy-alkyl with at least one of R₃ and R₄ being sulfoalkyl, sulfoalkoxyalkoxyalkyl or sulfoalkoxyalkyl, Z₁ and Z₂, which may be the same or different, each represents a non-metallic atomic group necessary to complete a substituted heterocyclic nucleus of the benzimidazole series, said

substituent being alkyl, halogen, trifluoroalkyl, cyano, alkyl-sulfonyl, alkylsulfonyl or alkylcarbonyl; and at least one sensitizing dye represented by the following second formula:



wherein R₅ is alkyl or sulfoalkyl; R₆ is alkyl, sulfoalkyl, sulfoalkoxyalkoxy or sulfoalkylcarbonylalkyl; Z₃ represents a non-metallic atomic group necessary to complete a 2-quinoline substituted or unsubstituted heterocyclic nucleus, the substituent being alkyl or halogen; and Z₄ represents a non-metallic group necessary to complete a substituted or unsubstituted heterocyclic nucleus selected from the group consisting of benzoxazole, naphthoxazole, benzthiazole, benz-selenazole, naphthothiazole or naphthoselenazole, the substituent being halogen or sulfoalkoxy; with the proviso that when Z₄ contains a sulfoalkoxy group, R₅ and R₆ is alkyl.

2. A super-sensitized silver halide emulsion according to claim 1 wherein said silver halide emulsion further contains a compound represented by the following formula III:



wherein R₇ represents an alkyl group or a substituted alkyl group wherein the substituent is a sulfo group neutralized by a cation, a cyano group or a vinyl group; Z₅ represents an atomic group necessary to complete a heterocyclic nucleus of the benzimidazole series; and Z₆ represents a phenyl group or a substituted phenyl group wherein the substituent is alkyl or alkoxy.

3. A silver halide emulsion according to claim 1 wherein the alkyl group of R₁ to R₆ is methyl, ethyl, n-propyl, iso-propyl, n-butyl or iso-butyl.

4. A silver halide emulsion according to claim 2 wherein the alkyl group of R₁ to R₇ is methyl, ethyl, n-propyl, iso-propyl, n-butyl or iso-butyl.

5. A silver halide emulsion according to claim 1 wherein said substituted alkyl group is a vinylmethyl group, a benzyl group, a β-acetoxyethyl group, a γ-acetoxypropyl group, a γ-carboxypropyl group, a β-carboxyethyl group, a γ-sulfatopropyl group, a δ-sulfatobutyl group, a δ-N-acetylsulfamylbutyl group, a β-hydroxyethyl group, a γ-sulfopropyl group, a γ-sulfobutyl group, a δ-sulfobutyl group, a 2-(3-sulfopropoxy)ethyl group, a 2[2-(3-sulfopropoxy)ethoxy]ethyl group, or a 2-hydroxy-1-sulfopropyl group.

6. A silver halide emulsion according to claim 1 wherein the heterocyclic nucleus of the benzimidazole series completed by Z₁, Z₂ or Z₃ is a benzimidazole nucleus, or a benzimidazole nucleus containing, as a component of the skeletal-structure thereof, a benzene ring substituted by at least one of the groups consisting of a halogen atom, an N-unsubstituted or alkyl substituted sulfamyl or carbamyl group, an N-disubstituted sulfamyl group, an alkyl sulfonyl group, a trifluoromethyl group, an alkyl group, a cyano group, a

phenyl group, a carboalkoxyl group, a hydroxyl group and an alkoxyl group.

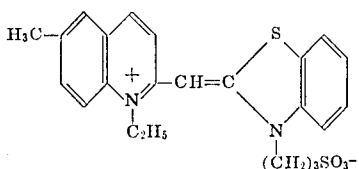
7. A silver halide emulsion according to claim 1 wherein the heterocyclic nucleus of the 2-quinoline series is a 2-quinoline nucleus or a 2-quinoline nucleus containing, as a component of the skeletal-structure thereof, a benzene ring substituted by at least one of the groups consisting of an alkyl group and a halogen atom.

8. A silver halide emulsion as in claim 1 wherein the light-sensitivity in the wave length region of 500-530 m μ is increased.

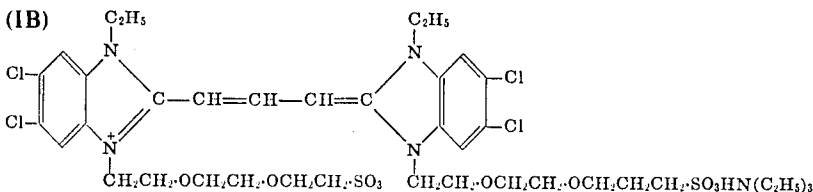
9. A silver halide emulsion as in claim 2 wherein the total amount of said sensitizing dyes I and II and said compound of formula III is within the range of from 1×10^{-6} mol to 1×10^{-3} mol per mol of silver halide.

10. A silver halide emulsion as in claim 1 wherein said emulsion contains the following sensitizing dyes:

(IIA)

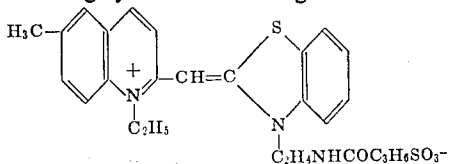


(IB)

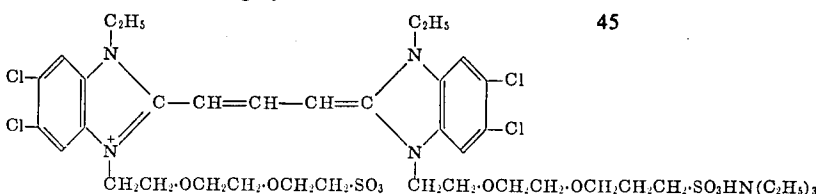


11. A silver halide emulsion as in claim 1 wherein said emulsion contains one sensitizing dye of formula I and a sensitizing dye of the following formula:

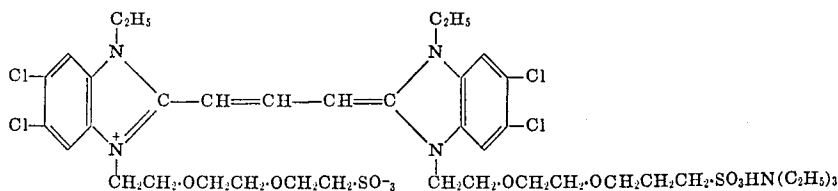
(IIB)



12. A silver halide emulsion according to claim 11 wherein said sensitizing dye of formula I is:

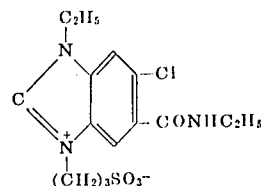
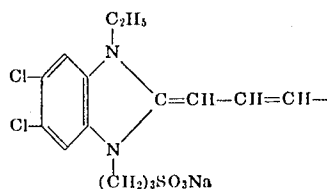


(IB)



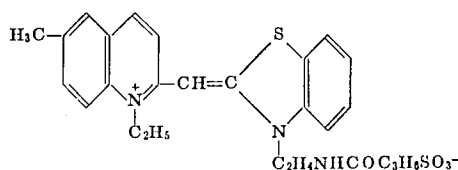
13. A silver halide emulsion according to claim 11 wherein said sensitizing dye of formula I is

(IG)



14. A silver halide emulsion as in claim 1 which contains the sensitizing dye of the following formula:

20 (IIB)

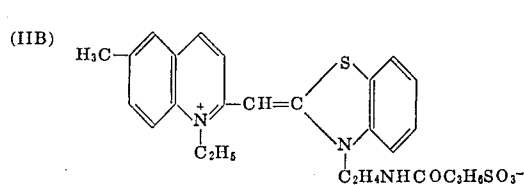


25

at least one sensitizing dye of formula II and at least one compound of formula III.

15. A silver halide emulsion according to claim 14 wherein said emulsion contains the following sensitizing dyes:

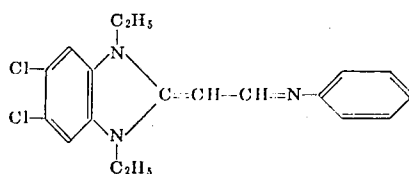
40



45

and a compound of the following formula:

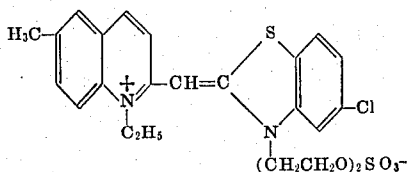
IIIA)



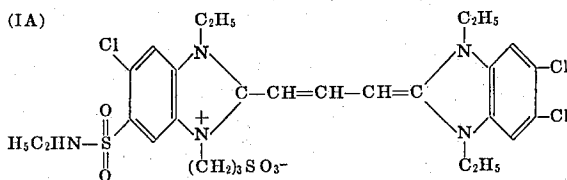
65

16. A silver halide emulsion as in claim 1 wherein said emulsion contains the following sensitizing dyes:

(IIC)

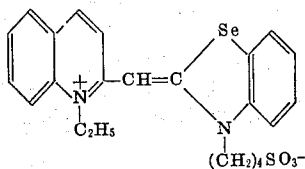


(IA)

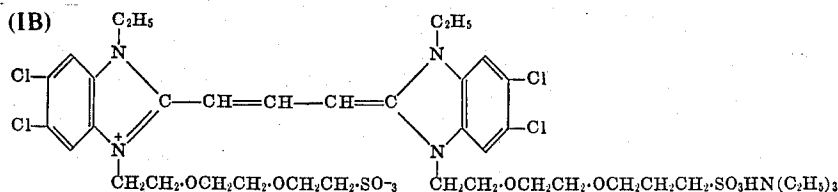


17. A silver halide emulsion as in claim 1 wherein said emulsion contains the following sensitizing dyes:

(IID)

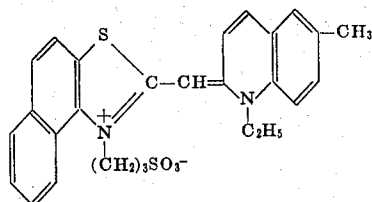


(IB)

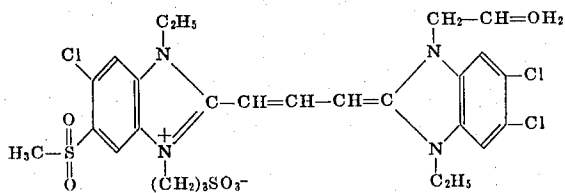


18. A silver halide emulsion as in claim 1 wherein said emulsion contains the following sensitizing dyes:

(IIE)

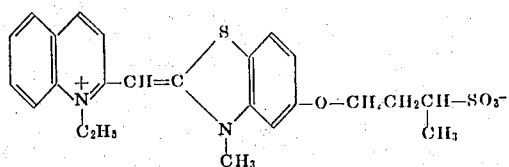


(IC)

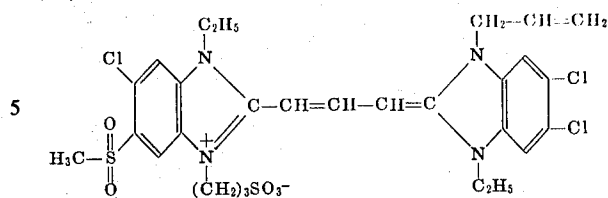


19. A silver halide emulsion as in claim 1 wherein said emulsion contains the following sensitizing dyes:

(IF)



(IG)

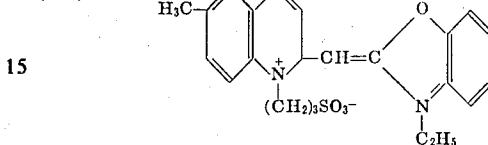


5

10

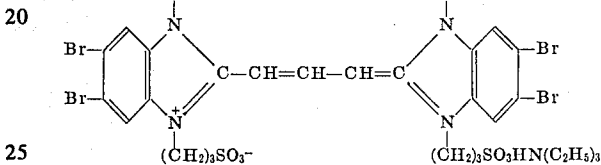
20. A silver halide emulsion as in claim 1 wherein said emulsion contains the following sensitizing dyes:

(IIG)



15

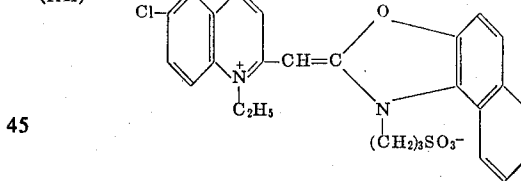
(IE)



25

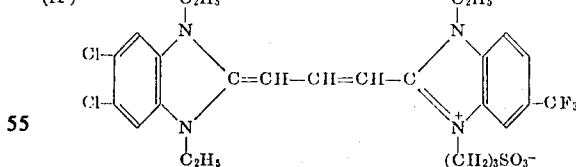
21. A silver halide emulsion as in claim 1 wherein said emulsion contains the following sensitizing dyes:

(IIH)



45

(IP)



55

22. A photographic light-sensitive element comprising a support having thereon at least one layer containing the photographic silver halide emulsion as in claim 1.

* * * * *