SILVER HALIDE SUPERSENSITIZED PHOTOGRAPHIC EMULSIONS

Filed April 25, 1973 3 Sheets-Sheet 1

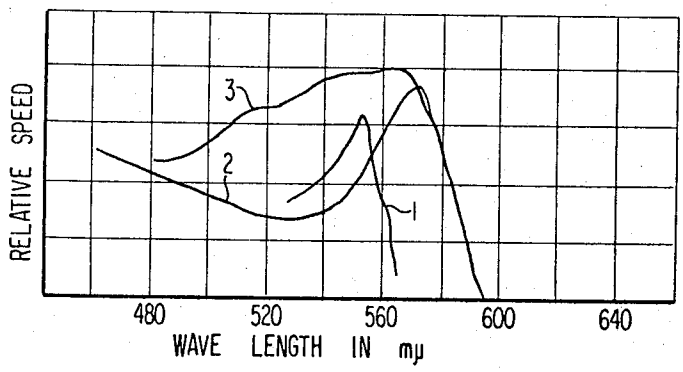


FIG. 1

FIG. 2

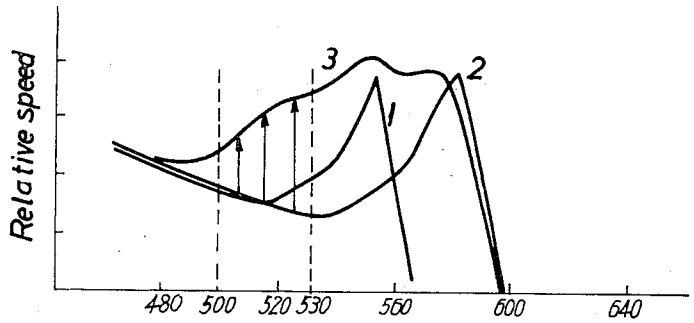


FIG. 3

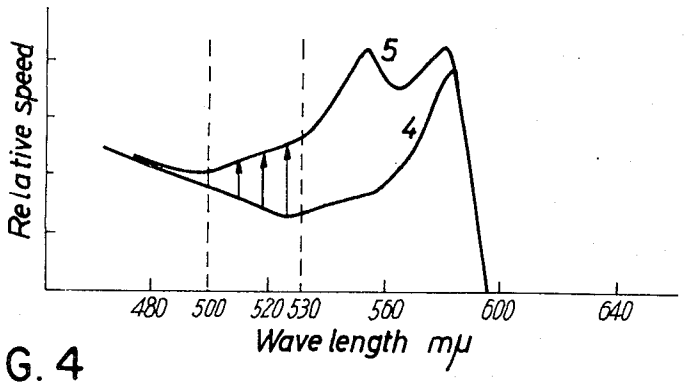


FIG. 4

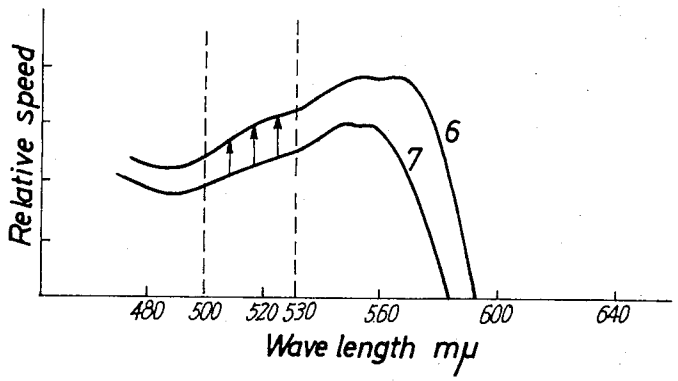
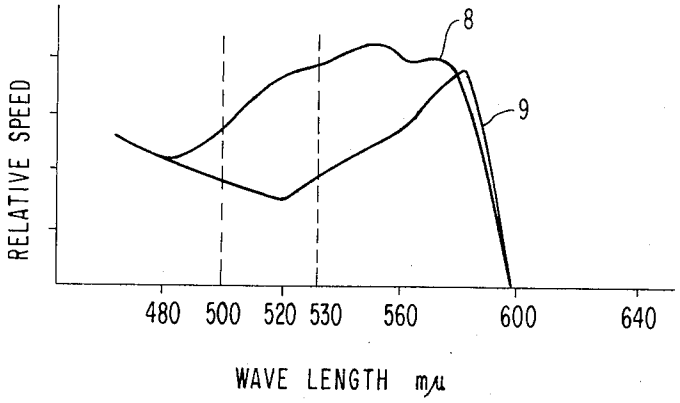


FIG. 5



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3,814,609

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SILVER HALIDE SUPERSENSITIZED PHOTOGRAPHIC EMULSIONS

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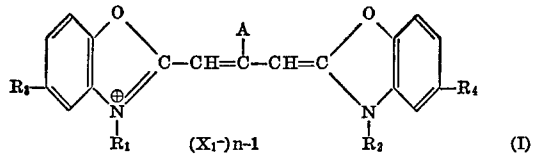
Continuation-in-part of application Ser. No. 276,999, Aug. 1, 1972, which is a continuation-in-part of application Ser. No. 47,702, June 19, 1970, both now abandoned. This application Apr. 25, 1973, Ser. No. 354,421
Claims priority, application Japan, June 19, 1969, 44/48,606
Int. Cl. G03c 1/14
U.S. Cl. 96—124 20 Claims

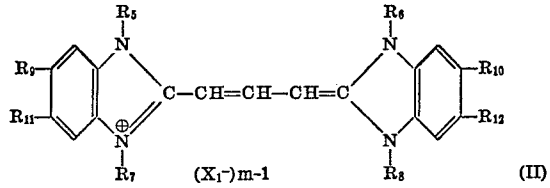
ABSTRACT OF THE DISCLOSURE

A silver halide light-sensitive photographic emulsion containing at least one sensitizing dye represented by the following formula I:



(I)

wherein A represents an alkyl group having from 1 to 4 carbon atoms; R_3 represents a halogen atom, a hydroxy group or a phenyl group; R_4 represents a hydrogen atom, a halogen atom, a phenyl group, a hydroxyl group, an alkyl group, or an alkoxy group; R_1 and R_2 each represents an alkyl group or an optionally neutralized sulfoalkyl group; X_1^- represents an acid anion; and n is 1 or 2; said n being 1 when at least one of said R_1 and R_2 is a sulfoalkyl group; and at least one sensitizing dye represented by the following formula II:



(II)

wherein R_5 and R_6 each represents an alkyl group or a substituted alkyl group; R_7 and R_8 each represents an alkyl group, a substituted alkyl group, an optionally neutralized sulfoalkyl group or a substituted alkyl group having an optionally neutralized sulfo group wherein the alkyl moiety thereof is attached to the sulfo group thereof through at least one alkoxyl group or directly connected with a hydroxy group and the sulfo group; at least one of said R_7 and R_8 representing a carbamylalkyl group or said sulfoalkyl group or said substituted alkyl group having a sulfo group; R_9, R_{10}, R_{11} and R_{12} each represents a hydrogen atom, an alkylsulfonyl group; an alkylsulfamoyl group, a N-di-substituted aminosulfonyl group, an alkylcarbamoyl group, a N-di-substituted carbamoyl group, a cyano group, a trifluoromethyl group or a halogen atom; X_1^- represents an acid anion; and m is 1 or 2; m being 1 when at least one of said R_7 and R_8 is the substituent having a sulfo group; at least one of said R_5 and R_6 being said substituted alkyl group or at least one of said R_7 or R_8 being said substituted alkyl group having an optionally neutralized sulfo group when all of said R_9, R_{10}, R_{11} and R_{12} are a hydrogen atom, a halogen atom or mixtures thereof; with the proviso that when said R_3 and R_4 are simultaneously phenyl, said R_9, R_{10}, R_{11} and R_{12} may not simultaneously be hydrogen or chlorine.

CROSS-REFERENCE TO RELATED APPLICATIONS

The present application is a continuation-in-part application of our co-pending application Ser. No. 276,999, filed Aug. 1, 1972, now abandoned, which is, in turn, a continuation-in-part of our earlier co-pending application Ser. No. 47,702, filed June 19, 1970, and now abandoned.

BACKGROUND OF THE INVENTION

Field of the invention

The present invention relates to a super-sensitized gelatino silver halide photographic emulsion. More particularly, it relates to a silver halide photographic emulsion for color photographic light-sensitive materials, the green sensitive range of the photographic emulsion having been spectrally sensitized.

DESCRIPTION OF THE PRIOR ART

It is well known that spectral sensitization is an important technique for the production of light-sensitive materials and in particular, the technique is an indispensable one for the production of color photographic light-sensitive materials. The color reproduction or the quality of the color image of a color photographic light sensitive material is particularly influenced by the spectral sensitivity or the distribution of spectral sensitivity of a green-sensitive region having a high visual sensitivity. Since even a slight difference in the spectral sensitivity of the green-sensitive region has a large influence on the quality of light sensitive materials, those engaged in the production of light sensitive materials have carefully studied the slight differences in the spectral sensitivity in the green-sensitive region of a photographic emulsion.

It is known that the spectral sensitivity of light sensitive materials is influenced by the properties of the silver halide emulsion used, such as its composition, crystal habit, grain size, manner of chemical ripening, the pH and the silver ion concentration of the silver halide; the kind of binder to be used; and the nature of additives such as an antifoggant, a stabilizer, a wetting agent, a coupler for color photographic light-sensitive material, a dispersing agent for the coupler, a plasticizer, and a hardening agent. In many cases, they act to reduce or instabilize the spectral sensitivity.

The spectral sensitivity of light sensitive materials is also largely influenced by the chemical structure of the sensitizing dye used for spectrally sensitizing silver halide photographic emulsions, and, in addition, is largely influenced by the manner of adding the sensitizing dye to the photographic emulsion, such as the addition amount thereof, the time of adding the dye, and the period when the photographic emulsion is allowed to stand after the addition of the sensitizing dye. A sensitizing dye may be used alone, but in many cases two or more sensitizing dyes are used for obtaining a desired spectral sensitivity distribution. In the latter case, it is rare that the use of the combination of two or more sensitizing dyes gives an additive spectral sensitivity. That is to say, in many cases, the spectral sensitivity obtained by using a combination of two or more sensitizing dyes is lower than the spectral sensitivity obtained by using each of the sensitizing dyes alone, and this is called "anti-sensitization."

On the contrary, it sometimes happens that the use of a combination of two or more sensitizing dyes gives a super-additive higher sensitivity, which is called "super-sensitization." In order to obtain a combination of two or more sensitizing dyes providing such a super-sensitization, each dye must be carefully selected, and it is known that the

selection of a combination of sensitizing dyes from the difference in their chemical structures is quite difficult. In other words, it is important to find a combination of two or more sensitizing dyes giving the super-sensitization action, i.e., giving a desired spectral sensitivity distribution and a high spectral sensitivity.

The green sensitizing technique for color photographic light-sensitive materials has been investigated by many persons but conventional techniques have various defects.

For example, U.S. Pat. No. 3,397,060 to Schwan et al. discloses the super-sensitization of green-sensitive silver halide emulsions by adding thereto a combination of:

(a) An oxacarbocyanine dye which does not contain more than one phenyl substituent, and

(b) A benzimidazolocarbocyanine dye.

A primary object of this invention is to provide a high-sensitive silver halide photographic emulsion having less of a color stain caused by the sensitizing dyes remaining therein after development, and wherein the sensitivity in the wave length region of from 500 mμ to 530 mμ has been increased.

More specifically, it is an object of the present invention to provide an improvement over the Schwan et al. reference mentioned above.

The formation of the above-mentioned color stain depends not only on the chemical structure of the sensitizing dye but also on the physical state of the sensitizing dye in the silver halide emulsion, e.g., its aggregation state, the interaction of the sensitizing dye with a coupler contained in the emulsion, and in particular, the interaction thereof with other sensitizing dyes to be incorporated in combination with it.

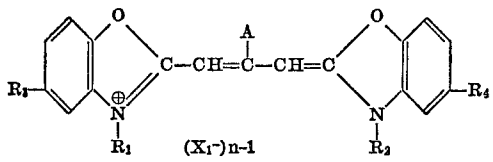
The present inventors have further discovered that by selecting a combination of specific sensitizing dyes, the formation or color stain can be reduced by the coaction thereof. It is difficult to selectively increase the sensitivity in the green-sensitive region, and particularly in a wave length region of from 500 mμ to 530 mμ. This is due to the fact that there are only a small number of sensitizing dyes capable of absorbing light of this wave length region on silver halide crystals while giving high sensitivity.

The present inventors have found that the above-mentioned object of the present invention can be attained by using a combination of sensitizing dyes capable of super-sensitizing by finely dividing the J-aggregate of each other.

SUMMARY OF THE INVENTION

The silver halide photographic emulsions of this invention contain at least one sensitizing dye represented by the following formula I and at least one dye represented by the following formula II:

Formula I



wherein:

A represents a lower alkyl group (i.e., having 1 to 4 carbon atoms;

R_3 represents a halogen atom (e.g., chlorine, bromine, etc.), a hydroxy group, or a phenyl group (e.g., phenyl, tolyl, etc.);

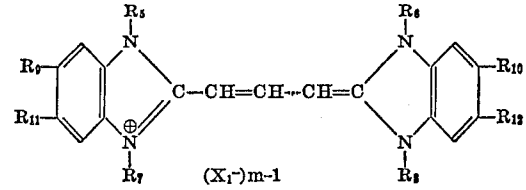
R_4 represents a hydrogen atom, a halogen atom (e.g., chlorine etc.), a phenyl group, a hydroxyl group, an aralkyl group, an alkyl group or an alkoxyl group;

R_1 and R_2 each represents an alkyl group or an optionally neutralized sulfoalkyl group (e.g., β-sulfoethyl, γ-sulfobutyl, etc.);

X_1^- represents an acid anion group of the type usually employed in the field of carbocyanine dyes (e.g., halogen, thiocyanate, perchlorate, benzylsulfonate, benzenesulfonate, methylsulfate, ethylsulfate, p-toluenesulfonate, etc.); and

n is 1 or 2; n being 1 when one of R_1 and R_2 is a sulfoalkyl group;

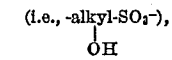
Formula II



wherein:

R_5 and R_6 each represents an alkyl group (e.g., methyl, ethyl, propyl, etc.) or a substituted alkyl group where the substituent is vinyl, acetoxy, hydroxy, etc. (e.g., vinylmethyl, acetoxypropyl, hydroxyethyl, etc.);

R_7 and R_8 each represents an alkyl group, a substituted alkyl group (the substituent being vinyl, acetoxy, hydroxy, carbamyl, etc.), an optionally neutralized sulfoalkyl group (e.g., α-alkyl group having an optionally neutralized sulfo group wherein (in the case of the alkoxy-substituted alkyl group) the alkyl moiety thereof is attached to the sulfo group thereof through 1 or 2 alkoxyl groups (i.e., -alkyl $(alkoxyl)_pSO_3^-$ where $p=1$ or 2), or (in the case of the hydroxy-substituted alkyl group) directly connected with a hydroxy group and the sulfo group



such as 2-(3-sulfopropoxy)ethyl, 2-[3-(3-sulfopropoxy) ethoxy]ethyl or 2-hydroxy-3-sulfopropyl; at least one of said R_7 and R_8 being a carbamylalkyl group, said sulfoalkyl group or said substituted alkyl group having a sulfo group;

R_9, R_{10}, R_{11} and R_{12} each represents a hydrogen atom, an alkylsulfonyl group (e.g., methylsulfonyl, ethyl sulfonyl, etc.), an alkylsulfamoyl group (e.g., methylsulfamoyl, ethylsulfamoyl, etc.), an N-di-substituted aminosulfonyl group (e.g., morpholinosulfonyl, etc.), an alkylcarbamoyl group (e.g., ethylcarbamoyl, etc.), an N-dissubstituted carbamoyl group (e.g., morpholino carbamoyl, etc.), a cyano group, a trifluoromethyl group, or a halogen atom (e.g., chlorine, bromine, fluorine, etc.);

X_2^- represents an acid anion group as defined for X_1^- above; and m is 1 or 2; m being 1 when at least one of R_7 and R_8 is a substituent having a sulfo group;

With the proviso that when R_9, R_{10}, R_{11} and R_{12} are simultaneously hydrogen or halogen or mixtures thereof, at least one of R_5 and R_6 is said substituted alkyl group or at least one of said R_7 and R_8 is said carbamylalkyl group or said alkoxy or hydroxy-substituted alkyl group having an optionally neutralized sulfo group; and

With the further proviso that when said R_3 and R_4 are simultaneously phenyl, said R_9, R_{10}, R_{11} and R_{12} may not simultaneously be hydrogen or chlorine.

BRIEF DESCRIPTION OF THE DRAWINGS

The figures are spectrograms showing the relative sensitivity (i.e., speed) of various photographic films employing super-sensitizing dye combinations according to the present invention as well as prior art combinations and individual dyes alone.

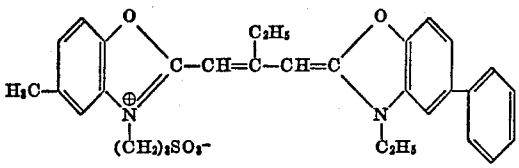
DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Among the sensitizing dyes represented by formula I according to the present invention, the sensitizing dye in which R_3 and R_4 are simultaneously a phenyl group has the disadvantage that a J-aggregate is liable to form and the formation of color stain is increased, but this drawback of the dye of formula I is overcome by using the

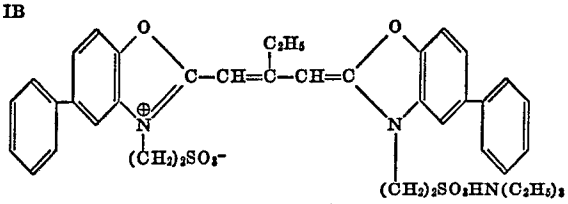
dye in combination with the sensitizing dye represented by the formula II (see the second proviso in the Summary of the Invention).

Typical examples of the sensitizing dyes which may be used in the practice of the present invention are shown below:

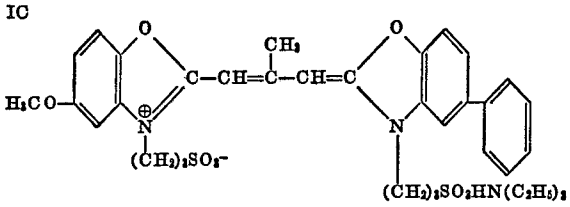
IA



IB



IC



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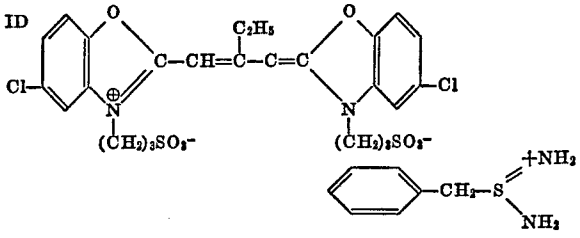
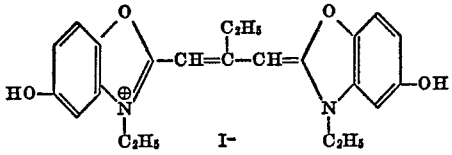
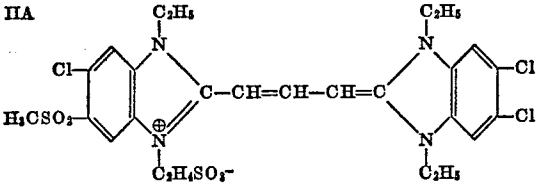


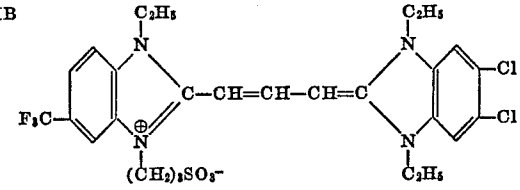
IE



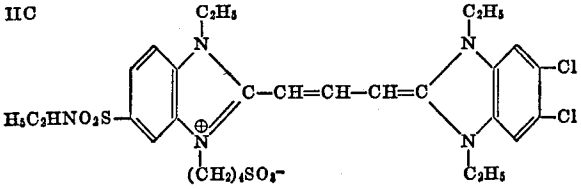
IIA



IIB



IIC



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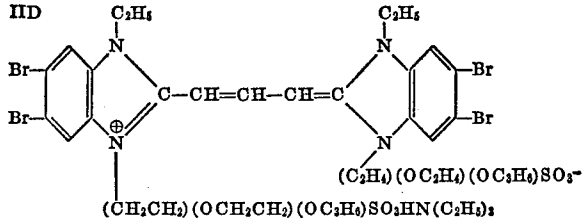

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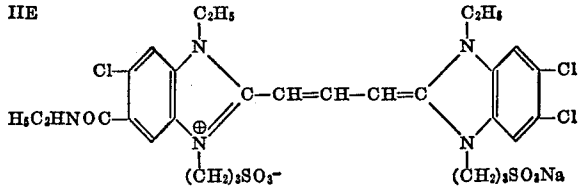
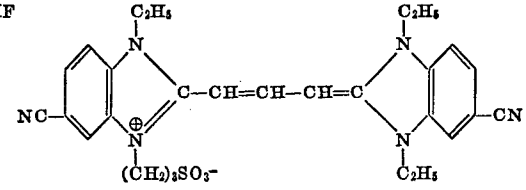


IIF



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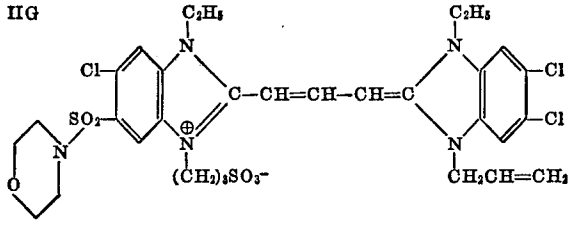
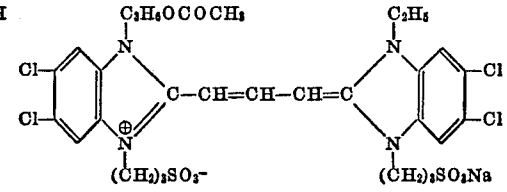
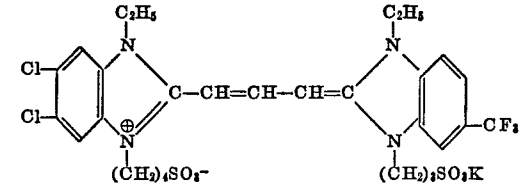


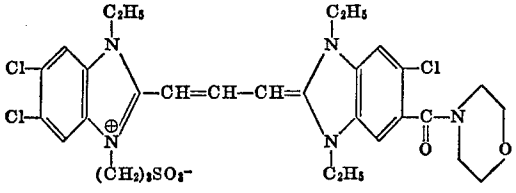
IIH



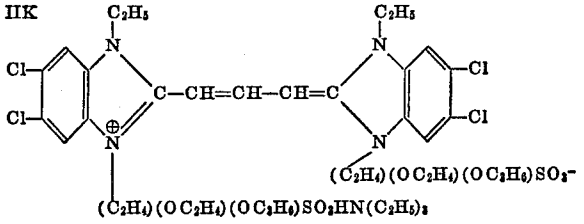
I-I



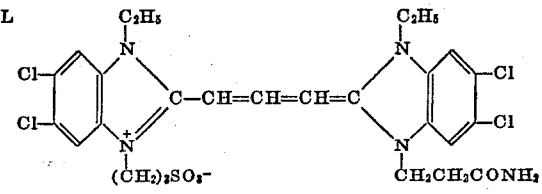
IIJ



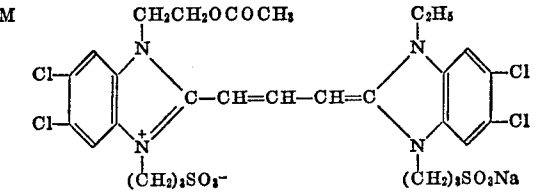
IIK



IIL



IIM



The above-mentioned sensitizing dyes used in this invention are known and they are described in the specifications of U.S. Pat. No. 3,268,334, British Pats. Nos. 840,223 and 742,112; Japanese Patent Publication No. 4931/68; Belgian Pats. Nos. 697,009, 704.296, 648,981 and 660,650; German Pat. No. 1,180,241; British Pats. Nos. 975,504, 980,234, 1,077,984 and 1,084,435; Belgian Pats. Nos. 673,554, 668,014 and 669,133; and Japanese Patent Publications Nos. 14,112/65 and 23,467/65. Furthermore, other sensitizing dyes which may be used in this invention may also be synthesized from the descriptions in the above-mentioned patents.

The sensitizing dyes of the present invention may be incorporated into the silver halide emulsions as solutions in water or a water-soluble organic solvent such as methanol or ethanol.

The sensitizing dye represented by formula I and the sensitizing dye represented by formula II may be dissolved in the solvents separately and these solutions may then be added to the silver halide emulsion separately or as a mixture thereof. The amounts of the sensitizing dyes are extremely influenced by the nature of the silver halide emulsion to be used, but ordinarily the amount thereof is preferably from 1×10^{-6} mole to 1×10^{-3} mole per 1 mole of silver halide. Also, the preferable molar concentration ratio of the amount of the sensitizing dye represented by formula I to the amount of the sensitizing dye represented by formula II is from 1:10 to 10:1.

The silver halide emulsion which may be used in this invention may contain, as the silver halide, silver iodobromide, silver bromide, silver chlorobromide, or silver iodochlorobromide. The silver halide emulsion used in this invention is generally a gelatino silver halide emulsion but silver halide emulsions other than those employing gelatin may be employed; e.g., those employing polyvinyl alcohol, alginic acid polymer, polyvinyl imidazole, polyvinyl pyrrolidine, or copolymers thereof. The gelatino silver halide emulsion of this invention may further contain any of the above-mentioned polymers.

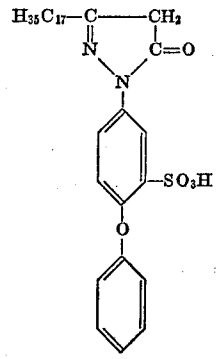
The present invention can also be applied to a silver halide emulsion containing, e.g., a photographic dye, an antifoggant, a stabilizer, a sensitizer, a coupler, a plasticizer, a wetting agent, etc. The silver halide emulsion of this invention may be applied to a proper support such as a paper, a glass plate, a cellulose triacetate film, a polyethylene terephthalate film, other plastic films, a resin-laminated paper, a resin-coated paper, or a synthetic paper.

The invention may be illustrated further by reference to the following examples, which are only illustrative, and not limiting, in nature:

EXAMPLE 1

1 kg. of a silver iodobromide (silver iodide: silver bromide 4 mol: 96 mol) prepared by a conventional manner was melted and after adding thereto definite amounts of solutions of sensitizing dyes having concentrations shown in Table 1, the mixture was stirred. After allowing the mixture to stand for 15 minutes at 40° C., in order to show clearly the effect of the reduction of sensitivity by the presence of a coupler, 200 ml. of a 5% alkaline aqueous solution of the magenta coupler having the structure shown below was added to the mixture and thereafter the pH of the mixture was immediately adjusted to 6.5 using citric acid while stirring. Thereafter, a hardening agent and saponin were added to the emulsion and the finished emulsion was uniformly applied to a film to a thickness of 7.0 microns.

Chemical structure of the magenta coupler:



By this procedure, various green-sensitive, light-sensitive materials were produced employing the combinations of the sensitizing dyes shown in Table 1.

The sample thus produced was cut and subjected to an optical wedge exposure using a yellow light of 5400° K. in color temperature through a K–12 filter made by Fuji Photo Film Co., Ltd.

The thus-exposed sample was developed for 10 minutes at 20° C.±0.2° C. in a developer having the following composition:

Water	ml	500
Metol	g	0.1
Potassium pyrosulfite	g	1.4
Anhydrous sodium sulfite	g	38
Hydroquinone	g	6
Sodium carbonate monohydrate	g	22.5
Citric acid	g	0.7
Potassium bromide	g	0.9

Water added to make 1000 ml.

The thus-developed photographic film was then fixed. The densities of the strips thus processed were measured using an S-type densitometer made by Fuji Photo Film Co., Ltd., whereby the relative spectral sensitivity (green sensitivity) was obtained. The results are shown in Table 1.

On the other hand, the spectrogram obtained by using a spectrograph containing a reflection-type diffraction grating, made by Narumi Shokai as Spectrograph GR–2 type (trademark), is shown in FIG. 1. Curve 1 represents the film having only sensitizing dye I–D therein, curve 2, only sensitizing dye II–B, and curve 3, a combination thereof, respectively. The sensitizing dyes and the correspondence thereof to the samples are shown in the remarks column in Table 1.

TABLE 1

Test No.	Dye	Amount of dye added (molar conc.), ml.	Dye	Amount of dye added (molar conc.), ml.	Relative green sensitivity	Fog	Remarks
1	(IA)	40 (5×10^{-4}) 80 80 80 --- 0	(IIA)	--- --- 20 (5×10^{-5}) 40 20 40	60 91 126 159 76 91	0.07 0.07 0.09 0.10 0.08 0.09	
2	(IA)	80 (5×10^{-4}) 80 --- ---	(IID)	20 (5×10^{-4}) 40 20 40	118 142 60 76	0.09 0.09 0.08 0.08	
3	(IB)	20 (1×10^{-3}) 40 40 40	(IIA)	--- 0 20 (5×10^{-4}) 40	89 100 142 142	0.07 0.08 0.08 0.09	
4	(IB)	40 (1×10^{-3}) 40 --- ---	(IIB)	20 (5×10^{-4}) 40 20 40	157 165 70 83	0.07 0.07 0.06 0.07	Samples of Curve 2.
5	(IB)	40 (1×10^{-3}) 40 --- ---	(IIC)	20 (5×10^{-4}) 40 20 40	141 141 71 83	0.08 0.08 0.07 0.09	
6	(IB)	40 40 --- ---	(IID)	20 (5×10^{-4}) 40 20 40	141 141 70 85	0.10 0.10 0.09 0.10	
7	(IC)	20 (1×10^{-3}) 40 80 40 40	(IID)	--- 0 --- 20 (5×10^{-4}) 40	31 43 60 115 132	0.06 0.08 0.08 0.08 0.09	
8	(ID)	20 (1×10^{-3}) 40 80 40 40 40	(IIB)	--- 0 0 20 (5×10^{-4}) 40 80	50 87 100 141 141 200	0.05 0.06 0.06 0.07 0.07 0.07	Samples of Curve 1. Samples of Curve 3.
9	(ID)	40 (1×10^{-3}) 40 --- ---	(IIE)	20 (5×10^{-4}) 40 20 40	141 150 71 92	0.08 0.09 0.08 0.09	
10	(ID)	40 (1×10^{-3}) 40 --- ---	(IIF)	20 (5×10^{-4}) 40 20 40	132 160 63 78	0.09 0.10 0.09 0.10	
11	(ID)	40 (1×10^{-3}) 40 --- ---	(IIG)	20 (5×10^{-4}) 40 20 40	140 150 63 75	0.10 0.15 0.10 0.12	
12	(ID)	40 (1×10^{-3}) 40 --- ---	(II-1)	20 (5×10^{-4}) 40 20 40	161 175 75 86	0.06 0.07 0.06 0.06	

EXAMPLE 2

The samples produced as in Example 1 were subjected to the wedge exposure as in Example 1 and then developed in a color developer having the composition shown below for 12 minutes at 20° C.±0.5° C. Thereafter the samples thus developed were subjected to a first fixing, a first water washing, bleaching, a second fixing, and a second water washing. The densities of the strips thus processed were measured through a green filter to obtain the relative green sensitivities shown in Table 2.

The composition of color developer:

	G.
N,n-diethylamino paraaminoaniline sulfate	2.0
Sodium sulfite	2.0
Sodium carbonate monohydrate	50.0
Hydroxylamine hydrochloride	1.5
Potassium bromide	1.0
Water added to make 1000 ml.	

TABLE 2

Test No.	Dye	Amount of dye added (molar conc. of dye solution), ml.	Dye	Amount of dye added (molar conc. of dye solution), ml.	Relative green sensitivity	Fog
13	I-D	20 (5×10^{-3}) 40 40 40 --- --- ---	II-H	--- --- 2 (5×10^{-4}) 4 1 2 4	100 130 166 200 32 63 70	0.14 0.19 0.20 0.24 0.12 0.17 0.20

EXAMPLE 3

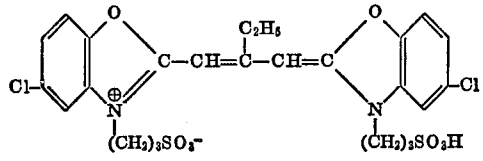
Samples were prepared as in Example 1 employing the dyes in the amounts shown in Table 3 below. The relative spectral sensitivity (green sensitivity) was measured in the same manner as in Example 1 and the results are shown in Table 3. FIGS. 2, 3 and 4 are spectrograms for the dye combinations shown in the "Remarks" column in Table 3.

TABLE 3

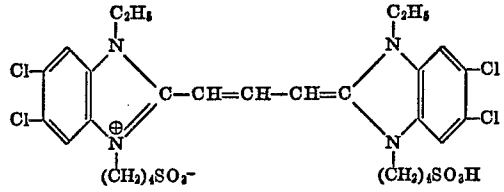
Test No.	Dye	Amount of dye added (molar conc.), ml.	Dye	Amount of dye added (molar conc.), ml.	Relative green sensitivity	Fog	Remarks
14	(ID)	80 (1×10^{-3})	(IIK)	----------	100	0.06	Fig. 2 (curve 1).
		80		20 (5×10^{-4})	151	0.10	
		80		40	200	0.11	Fig. 2 (curve 3).
		----------		20 (5×10^{-4})	85	0.11	
		----------		40	100	0.11	Fig. 2 (curve 2).
15	Dye 1	80	(Dye B)	20 (5×10^{-4})	141	0.09	
		80		40	158	0.09	Fig. 3 (curve 5).
		----------		20 (5×10^{-4})	76	0.09	
		----------		40	80	0.09	Fig. 3 (curve 4).
16	Dye 1	80	(IIE)	20 (5×10^{-4})	158	0.10	
		80		40	166	0.10	Fig. 4 (curve 6).
		----------		20 (5×10^{-4})	71	0.08	
		----------		40	92	0.09	
17	Dye 1	80	(Dye H)	20 (5×10^{-4})	75	0.12	
		80		40	80	0.15	Fig. 4 (curve 7).
		----------		20 (5×10^{-4})	31	0.14	
		----------		40	43	0.18	
18	(ID)	80	(IIL)	20 (5×10^{-4})	158	0.11	
		80		40	224	0.11	Fig. 5 (curve 8).
		----------		20 (5×10^{-4})	94	0.11	
		----------		40	117	0.11	Fig. 5 (curve 9).

In Table 3, the dyes designated "1," "H" and "B" are disclosed in U.S. Pat. No. 3,397,060 Schwan et al., and have the following structures:

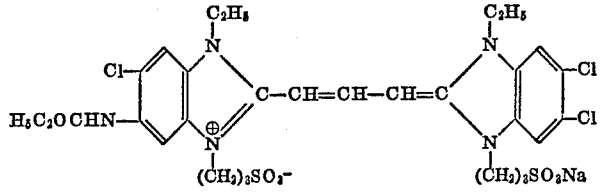
Dye 1



Dye B



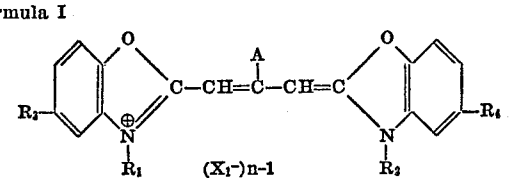
Dye H



What is claimed is:

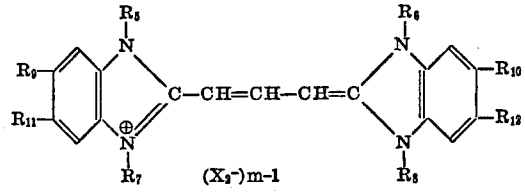
1. A silver halide light-sensitive photographic emulsion containing at least one sensitizing dye represented by the following formula I:

Formula I

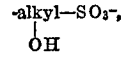


wherein A represents an alkyl group having from 1 to 4 carbon atoms; R_3 represents a halogen atom, a hydroxy group or a phenyl group; R_4 represents a hydrogen atom, a halogen atom, a phenyl group, a hydroxyl group, an alkyl group, or an alkoxyl group; R_1 and R_2 each represents an alkyl group or an optionally neutralized sulfoalkyl group; X_1^- represents an acid anion; and n is 1 or 2; said n being 1 when at least one of said R_1 and R_2 is a sulfoalkyl group; and at least one sensitizing dye represented by the following formula II;

Formula II



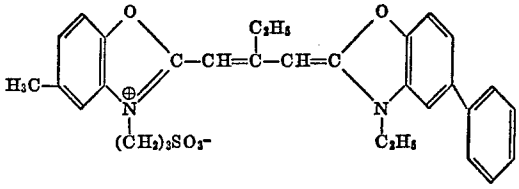
wherein R_5 and R_6 each represents an alkyl group or a substituted alkyl group where the substituent is vinyl, acetoxy or hydroxy; R_7 and R_8 each represents an alkyl group, a substituted alkyl group wherein the substituent is vinyl acetoxy, hydroxy or carbamyl, an optionally neutralized sulfoalkyl group, or an alkoxy- or hydroxy-substituted alkyl group having an optionally neutralized sulfo group of the formula -alky(alkoxyl)$_p$SO$_3^-$ or



respectively, where p is 1 or 2; at least one of said R_7 and R_8 being a carbamylalkyl group, said sulfoalkyl group or said substituted alkyl group having a sulfo group; R_9, R_{10}, R_{11} and R_{12} each represents a hydrogen atom, an alkylsufonyl group, an alkylsulfamoyl group, an N-di-substituted amino-sulfonyl group, an alkylcarbamoyl group, an N-di-substituted carbamoyl group, a cyano group, a trifluoromethyl group, or a halogen atom; X_2^- represents an acid anion group; and m is 1 or 2, m being 1 when at least one of R_7 and R_8 is a substituent having a sulfogroup; with the proviso that when R_9, R_{10}, R_{11} and R_{12} are simultaneously hydrogen or halogen or mixtures thereof, at least one of R_5 and R_6 is said substituted alkyl group or at least one of said R_7 and R_8 is said carbamyl group or said alkoxy- or hydroxy-substituted alkyl group having an optionally neutralized sulfo group; and with the further proviso that when said R_3 and R_4 are simultaneously phenyl, said R_9, R_{10}, R_{11} and R_{12} may not simultaneously be hydrogen or chlorine.

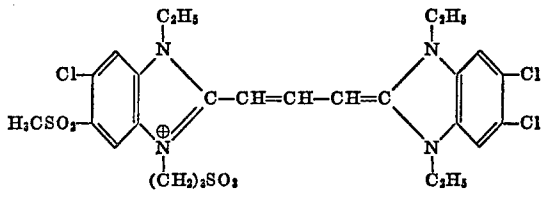
2. The silver halide photographic emulsion of claim 1, wherein the substituted alkyl group of R_5, R_6, R_7 and R_8 is acetoxypyropyl, hydroxyethyl, carbamylethyl or allyl; wherein said alkoxy- or hydroxy-substituted alkyl group having an optionally neutralized sulfo group is a 2-(3-sulfopropoxy) ethyl group, a 2-[2-(3-sulfopropoxy) ethoxy] ethyl group or a 2-hydroxy-3-sulfo-propyl group; wherein the N-di-substituted amino sulfonyl group is morpholino sulfonyl; and wherein the N-di-substituted carbamoyl group is morpholinocarbamoyl; wherein the halogen atom of R_3, R_4, R_9 and R_{10} is a chlorine atom; wherein said alkyl group of A is ethyl.

3. A silver halide photographic emulsion containing a sensitizing dye of the formula

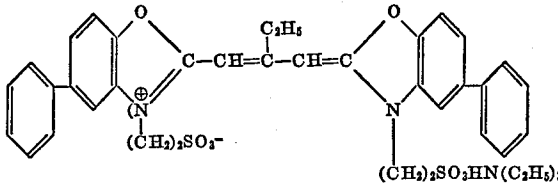


and at least one sensitizing dye represented by formula II as in claim 1.

4. A silver halide photograph emulsion as in claim 3, wherein the sensitizing dye represented by formula II is a dye of the formula

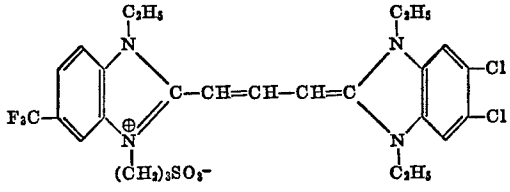


5. A silver halide photographic emulsion containing a sensitizing dye of the formula

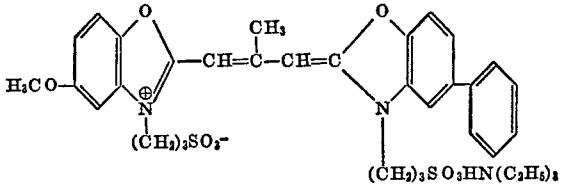


and at least one sensitizing dye represented by formula II as in claim 1.

6. A silver halide photographic emulsion as in claim 5 wherein the sensitizing dye represented by formula II is a dye of the formula

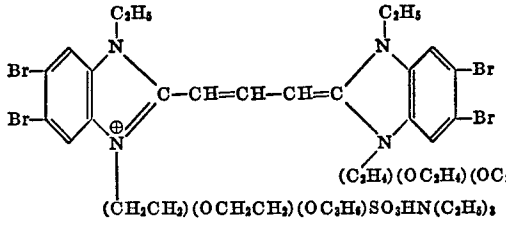


7. A silver halide photographic emulsion containing a sensitizing dye of the formula

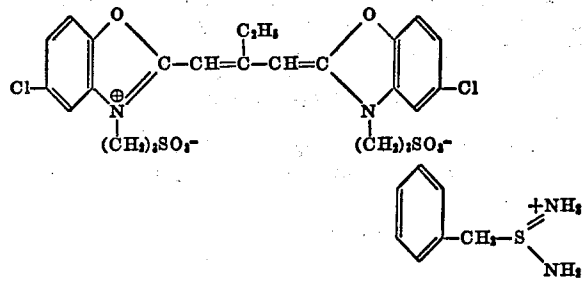


and at least one sensitizing dye represented by formula II as in claim 1.

8. A silver halide photographic emulsion as in claim 7 wherein the sensitizing dye represented by Formula II is a dye of the formula

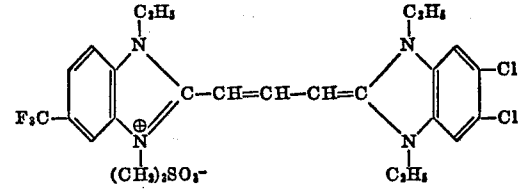


9. A silver halide photographic emulsion containing a sensitizing dye of the formula

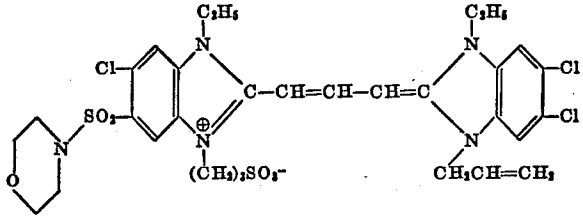


and at least one sensitizing dye represented by formula II as in claim 1.

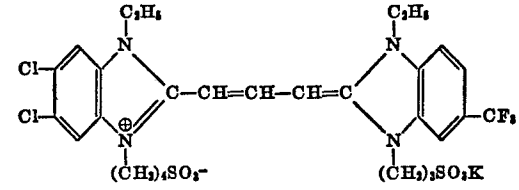
10. A silver halide photographic emulsion as in claim 9, wherein the sensitizing dye represented by formula II is a dye of the formula



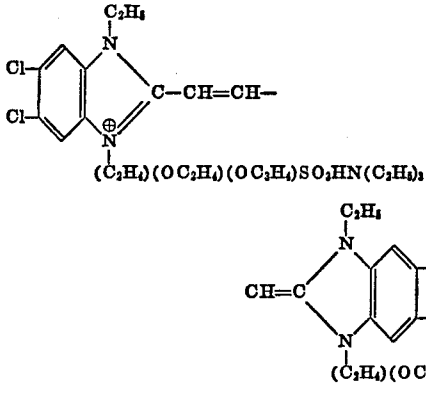
11. A silver halide photographic emulsion as in claim 9, wherein the sensitizing dye represented by formula II is a dye of the formula



12. A silver halide photographic emulsion as in claim 9, wherein the sensitizing dye represented by formula II is a dye of the formula



13. A silver halide photographic emulsion containing at least one sensitizing dye represented by formula I in claim 1 and a sensitizing dye of the formula

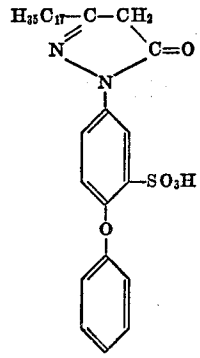


14. A silver halide photographic emulsion as in claim 1, which contains from 10^{-6} to 10^{-3} mole of each of the sensitizing dyes of formulae I and II per 1 mole of silver halide.

15. A silver halide photographic emulsion as in claim 1, wherein the molar concentration ratio of the sensitizing dye of formula I to the sensitizing dye of formula II is within the range 1:10 to 10:1.

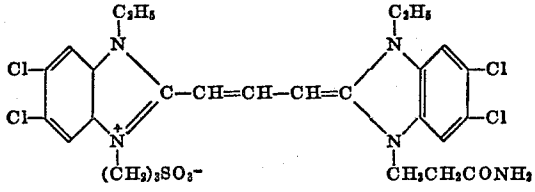
16. A silver halide photographic emulsion as in claim 1, wherein at least one magenta coupler is incorporated therein.

17. A silver halide photographic emulsion as in claim 16, wherein said magenta coupler is represented by the formula



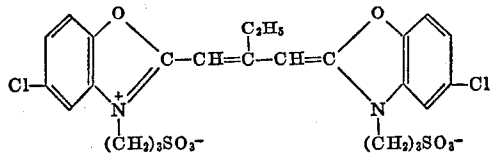
18. A photographic silver halide light-sensitive element comprising a support having thereon at least one layer containing the silver halide emulsion of claim 1.

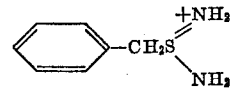
19. A silver halide photographic emulsion containing a sensitizing dye of the formula:



and at least one sensitizing dye represented by formula I as claimed in claim 1.

20. A silver halide photographic emulsion as in claim 19 wherein the sensitizing dye represented by formula I is a dye of the formula:





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J. TRAVIS BROWN, Primary Examiner

U.S. Cl. X.R.

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