United States Patent [19]

Sato et al.

[11] **3,770,440**

[45] **Nov. 6, 1973**

[54] **SPECTRALLY SENSITIZED PHOTOGRAPHIC SILVER HALIDE EMULSION**

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

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[21] Appl. No.: **149,276**

[30] **Foreign Application Priority Data**

June 2, 1970 Japan 45/47381

[52] **U.S. Cl.** **96/139,** 260/309.2

[51] **Int. Cl.** **G03c 1/10**

[58] **Field of Search** 96/120, 129, 139

[56] **References Cited**

UNITED STATES PATENTS

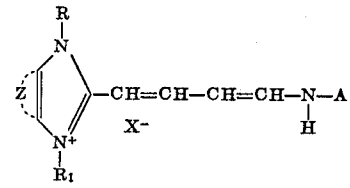
2,298,732	10/1942	Brooker et al.	96/139
2,369,509	2/1945	White	96/139
2,553,989	5/1951	Dormael	96/139
3,490,910	1/1970	Rauch et al.	96/139

Primary Examiner—J. Travis Brown

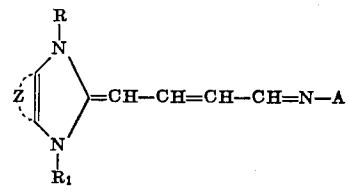
Attorney—Sughrue, Rothwell, Mion, Zinn and Macpeak

[57] **ABSTRACT**

A photographic silver halide emulsion containing at least one sensitizing dye represented by the formula (I) or (II):



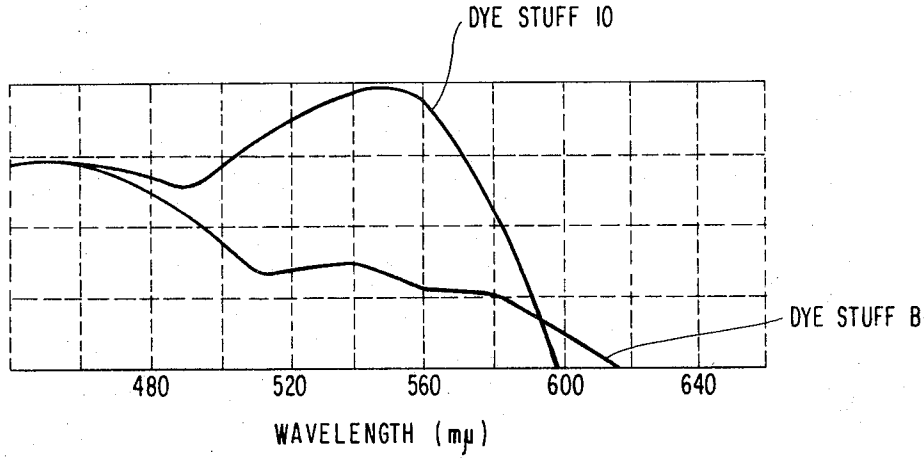
(I)



(II)

wherein Z represents an atomic group necessary to complete a benzene ring, the hydrogen atom of which may be substituted; R and R_1 each represent a member selected from the group consisting of the same or different alkyl groups and a substituted alkyl group except a sulfoalkyl group; and A represents an aryl group and X represents an acid anion.

6 Claims, 1 Drawing Figure



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SPECTRALLY SENSITIZED PHOTOGRAPHIC SILVER HALIDE EMULSION

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a photographic silver halide emulsion containing a new sensitizing dye and more particularly, it is concerned with a silver halide emulsion having a high spectral sensitivity in the ortho-region.

2. Description of the Prior Art

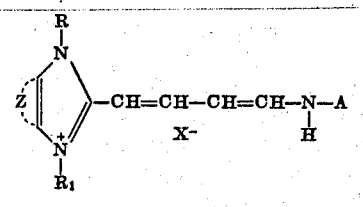
It has been well known in the technique for making a photographic silver halide emulsion that, when a sensitizing dye is added to a silver halide emulsion, it is spectrally sensitized and its light-sensitive wavelength region is enlarged. The spectral sensitivity is often affected by the chemical structure of a sensitizing dye. In particular, a strong sensitivity near the spectral sensitivity maximum due to the J-aggregate of a sensitizing dye adsorbed on surfaces of silver halide grains is liable to be affected because the formation of a J-aggregate depends on the chemical structure of the sensitizing dye; for example, the kind of heterocyclic ring or substituent. Therefore, it is very important in practice to select a sensitizing dye to be used in the case of sensitizing strongly the light-sensitive wavelength region required by a photographic light-sensitive material.

Moreover, when a photographic silver halide material containing a sensitizing dye is subjected to ordinary processings such as developing, fixing, stabilizing and water washing, staining often occurs due to coloring by the sensitizing dye remaining in the emulsion layer.

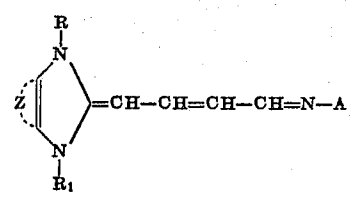
SUMMARY OF THE INVENTION

It is the principal object of this invention to provide a silver halide emulsion which has a high spectral sensitivity in the ortho-region and which does not retain stains after development.

The above mentioned object of the invention can be accomplished by incorporating a new sensitizing dye represented by the following general formula (I) or (II) in a silver halide emulsion.



(II)



In these formulas, Z represents an atomic group necessary for forming a benzene ring, the hydrogen atom of which may be substituted for by conventional substituents for benzimidazolo cyanine dyes. Substituents in this case are those well known for benzimidazolocarbocyanines, such as halogen atoms, e.g. fluorine, chlorine, bromine and iodine, a trifluoromethyl group, a trifluoromethylsulfonyl group, an alkylsulfonyl group, such as methylsulfonyl group, sulfamoyl group, an alkylaminosulfonyl group such as a methylaminosulfonyl

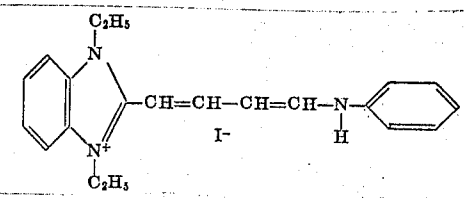
or ethylaminosulfonyl group, a dialkylaminosulfonyl group, such as a dimethylaminosulfonyl, diethylaminosulfonyl, piperidinosulfonyl, morpholinosulfonyl or a pyrrolidinosylfonyl group, a cyano group, a carboxyl group and an alkoxycarbonyl group, such as a methoxycarbonyl or an ethoxycarbonyl group. R and R_1 represent the same or different alkyl groups, such as methyl, ethyl, n-propyl and n-butyl groups, and substituted alkyl groups conventionally used as nitrogen substituents in benzimidazolo cyanine dyes, except a sulfoalkyl group, such as hydroxy alkyl (e.g. β-hydroxyethyl, γ-hydroxypropyl), acetoxyalkyl (e.g. β-acetoxyethyl, γ-acetoxypropyl) carboxyalkyl (e.g. carboxymethyl, β-carboxyethyl, γ-carboxypropyl, δ-carboxybutyl), cyanoalkyl (e.g. β-cyanoethyl, γ-cyanopropyl, δ-cyanobutyl), carbamoylalkyl (e.g. β-carbamoylethyl, γ-carbamoyl-propyl, δ-carbamoylbutyl, β-N-ethylcarbamoylethyl-, γ-N-ethylcarbamoylpropyl, δ-N-methylcarbamoylbutyl), sulfamoylalkyl (e.g. γ-sulfamoylpropyl, δ-sulfamoylbutyl), aminosulfonylalkyl (e.g. γ-N-ethylaminosulfonylpropyl, δ-N-ethylaminosulfonylbutyl), allyl (e.g. vinylmethyl) and aralkyl (e.g. phenethyl) groups. A represents aryl groups, such as a phenyl group, a methoxyphenyl, a tolyl or a chlorophenyl group. X represents an acid anion, such as a chloride, bromide, iodide, thiocyanate, perchlorate, benzenesulfonate, p-toluene-sulfonate, methylsulfate or ethylsulfate ion.

DETAILED DESCRIPTION OF THE INVENTION

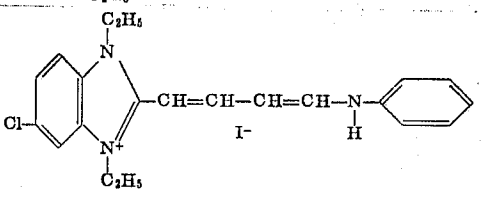
The feature of the sensitizing dyes of this invention, at least with regard to chemical structure resides in the fact that they are limited by general formulas (I) or (II) to a tetramethinehemicyanine or tetramethinehemicyanine base having a benzimidazole nucleus which tends to form a J-aggregate. In particular, these dyes are effective for raising the spectral sensitivity in the ortho-region. As compared with this, tetramethinehemicyanines or tetramethinehemicyanine bases having benzothiazole, benzoselenazole or benzoxazole nucleus, mentioned in U.S. Pat. Nos. 2,369,509 and 2,369,509 are difficult to form the J-aggregate and have a low spectral sensitivity.

The chemical structural formulas of typical examples of the new sensitizing dyes represented by general formulas (I) or (II) are shown below, but are not limited to such:

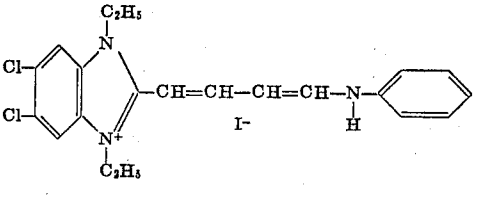
Dye 1



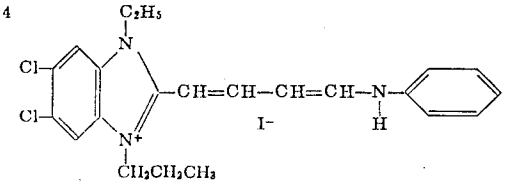
Dye 2



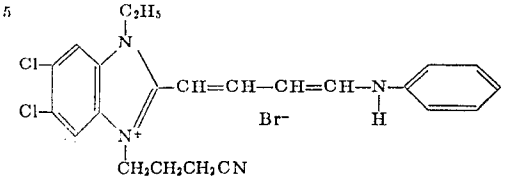
Dye 3



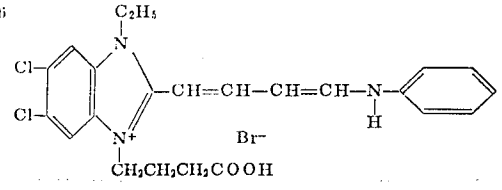
Dye 4



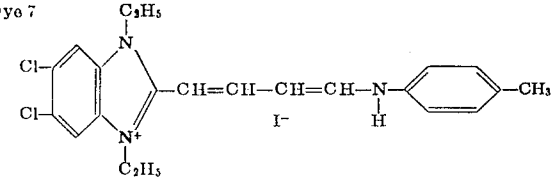
Dye 5



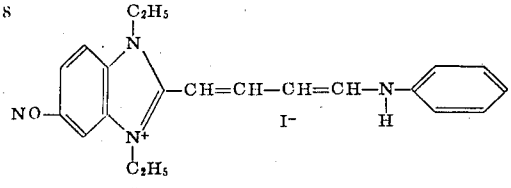
Dye 6



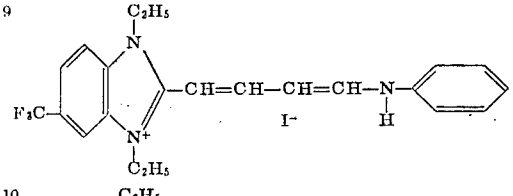
Dye 7



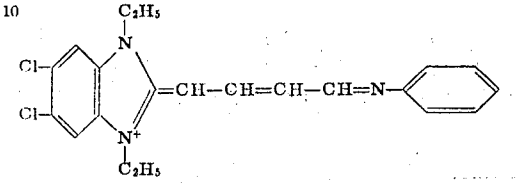
Dye 8



Dye 9



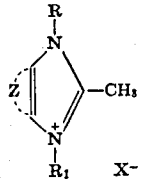
Dye 10



The sensitizing dyes of this invention, represented by general formulas (I) or (II) can be synthesized with reference to British Pat. No. 355,693 or U.S. Pat. No. 2,298,732.

The sensitizing dyes represented by general formulas (I) can be obtained by heating and melting a compound represented by general formula (III) and β-anilinoacroleinanil:

(III)



(Z, R, R_1 and X being defined as above), or heating in acetic anhydride to synthesize an acetanilide intermediate followed by hydrolysis. Moreover, the sensitizing dyes represented by general formula (II) are obtainable by treating the sensitizing dye (I) with an aqueous akaline solution and removing the HX.

SYNTHESIS EXAMPLE 1

3.8 g of 5,6-dichloro-1,3-diethyl-2-methylbenzimidazolium iodide and 2.2 g of β-anilinoacroleinanil are heated at 170°C for 6 hours in 50 ml of acetic anhydride on an oil bath. The reaction solution is cooled and mixed with ether in large excess to deposit a product. The ether is removed by decantation and the product is washed with ether. The product is recrystallized from ethanol to obtain 2.2 g of acetanilide intermediate melting at 225–228°C. The acetanilide intermediate is dissolved in methanol and then mixed with 4N caustic soda and with water to deposit a crystal which is then filtered, washed with water and recrystallized from methanol to obtain 1.5 g of Dye 3melting at 274°C.

SYNTHESIS EXAMPLE 2

1 g of Dye 3 is suspended in 100 ml of acetone and mixed with 4N caustic soda to dissolve the crystal. Water is added thereto to deposit a product which is then washed with water and extracted with benzene to obtain 0.3 g of Dye 10 melting at 174°C.

Other dyes can be obtained in a similar manner mentioned above.

The sensitizing dyes used in this invention are capable of spectrally sensitizing a silver halide photographic emulsion, and in particular, effectively enlarging the light-sensitive region of a gelatino-silver halide photographic emulsion. They can also sensitize other photographic emulsions containing a hydrophilic colloid besides gelatin. Illustrative of these are agar colloidion, cellulose derivatives, polyvinyl alcohol or a natural hydrophilic resin.

For the emulsion of this invention there are used various silver salts, such as mixed silver halides, such a s silver iodobromide, silver chlorobromide, a silver chloroiodobromide, and silver bromide.

For the preparation of a photographic emulsion sensitized according to the invention, the sensitizing dye may be added to a photographic emulsion in a conventional manner. Ordinarily the sensitizing dye is dissolved in a suitable solvent, such as methanol and added to an emulsion in the form of a solution. The quantity of the sensitizing dye to be incorporated in the emulsion may be varied within a wide range of 5–200 mg per 1 kg of the emulsion according to the desired effect.

Furthermore, to the photographic emulsion of this invention may be added known sensitizing dyes as well as commonly used additives, such as sensitizers, stabilizers, color tone regulators, hardeners, surfactants, fog inhibitors, plasticizers, development accelerators, color couplers, fluorescent whitening agents and ultraviolet ray absorbers.

The photographic emulsion of this invention may be coated in a conventional manner onto a suitable support member, such as glass, a cellulose derivative film, a synthetic resin film, baryta paper, a resin laminated paper or synthetic paper.

A better understanding of the present invention will be attained from the following examples which are merely illustrative and not limitative of the present invention.

EXAMPLES

A photographic silver halide emulsion was prepared by adding the following sensitizing dye of this invention to a gelatino-silver iodobromide emulsion (AgI : AgBr = 6 mols : 94 mols) or gelatino-silver chlorobromide emulsion (AgBr : AgCl = 40 mols : 60 mols).

This emulsion was coated onto a cellulose triacetate film base, dried, exposed to a light source of daylight color of 64 luxes (corresponding to 5,400°K) through a Fuji No. 3 Filter (yellow filter) and then developed. For the gelatino-silver iodobromide emulsion, there was employed a developer having the composition shown in Table 1 and for the gelatino-silver chlorobromide emulsion, there was employed another developer as shown in Table 2.

TABLE 1

metol	2 g
sodium sulfite	100 g
hydroquinone	5 g
borax	2 g
Water to 1000 ml	

TABLE 2

metol	3.1 g
sodium sulfite	45 g
hydroquinone	12 g
anhydrous sodium carbonate	67.5 g
potassium bromide	1.9 g
water to 1000 ml	

In Table 3 are shown the spectral sensitivity and sensitization maximum wavelengths obtained when the foregoing sensitizing dyes of this invention and comparative sensitizing dyes were added to a silver chlorobromide emulsion. In addition, the absorption maximum wavelengths of the sensitizing dyes of this invention in methanol are also noted. In Table 4, there are shown the spectral sensitivity and sensitization maximum wavelengths in the case of a silver iodobromide emulsion.

TABLE 3

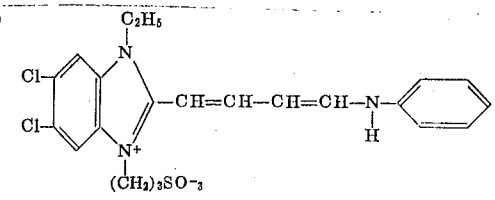
Dye No.	Amt. of dye added 2×10^{-3} mol conc. ml./kg. emulsion	Absorption max. wavelength mμ (in methanol)	Sensitization wavelength maximum mμ	Relative spectral sensitivity
1	40	439	520	120
2	40	450	540	276
3	40	461	550	379
4	40	462	550	346
5	40	466	545	174
6	40	466	550	200
7	40	469	540	256
8	40	468	545	282
9	20	463	545	276
10	40	461	550	363
A (comparison)	40		520	30
B (comparison)	40		555	100
C (comparison)	40		545	110

Dye No.	Amt. of dye added 1×10^{-3} mol conc. ml./kg. emulsion	Sensitization maximum wavelength mμ	Relative spectral sensitivity
2	80	550	312
3	80	550	460
4	80	550	500
5	80	550	500
6	160	550	460
7	40	560	228
8	80	550	260
9	80	550	300
10	80	550	500
A	80		80
B	80	*535	100

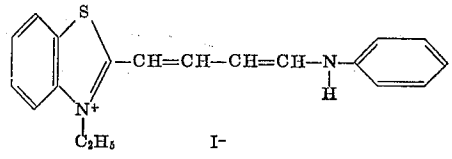
*M band.

The spectral sensitivity is a specific sensitivity when the spectral sensitivity of the sensitizing dye B is 100 when exposed using a Fuji No. 3 Filter (yellow filter). The chemical structural formulas of the sensitizing dyes used for the comparison are as follows:

(A)



(B)



(C)

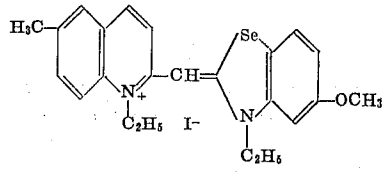
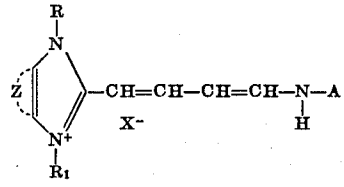


FIG. 1 shows spectrograms of the sensitizing dye **10**, a typical example of the new sensitizing dyes according to this invention, (solid line) and the dye B for comparison (broken line)

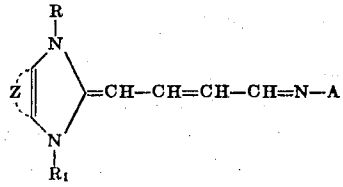
It will be understood from the drawing that the sensitizing dye of this invention forms a J-aggregate. This is a very excellent attribute as disclosed earlier.

What is claimed is:

1. A photographic silver halide emulsion containing at least one sensitizing dye represented by the formula (I) or (II):



(I)



(II)

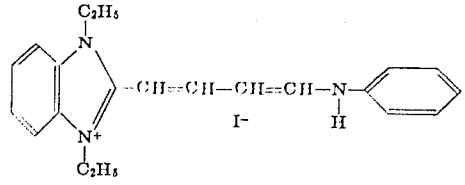
wherein Z represents an atomic group necessary to complete a benzene ring, which may be substituted or unsubstituted, said substituents being selected from the group consisting of halogen, trifluoromethyl, trifluoromethylsulfonyl, alkylsulfonyl, sulfamoyl, alkylaminosulfonyl, dialkylaminosulfonyl, cyano, carboxyl, and alkoxycarbonyl; R and R_1 each represents a member selected from the group consisting of the same or a different alkyl group and a substituted alkyl group selected from the group consisting of hydroxyalkyl, acetoxyalkyl, carboxyalkyl, cyanoalkyl, carbamoylalkyl, sulfamoylalkyl, aminosulfonylalkyl, allyl and aralkyl; A represents an aryl group, and X represents an acid anion.

2. The photographic silver halide emulsion of claim

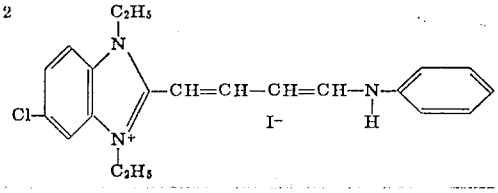
1, wherein the amount of the sensitizing dye present ranges from 5 to 200 mg per 1 kg of the emulsion.

3. The photographic silver halide emulsion of claim 1, wherein the sensitizing dye is selected from the group consisting of

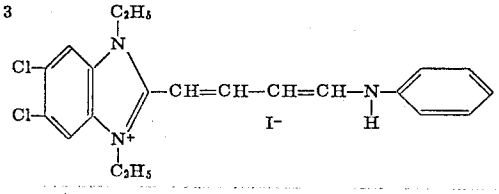
Dye 1



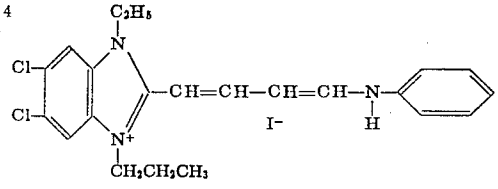
Dye 2



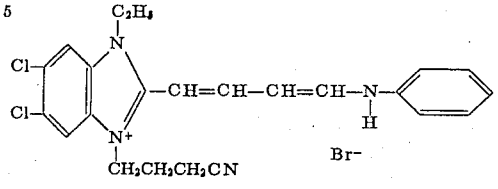
Dye 3



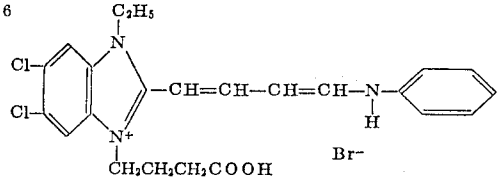
Dye 4



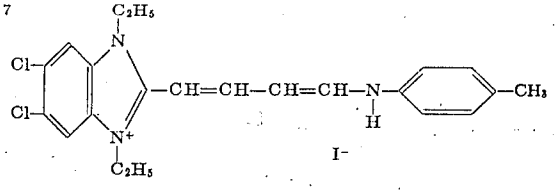
Dye 5



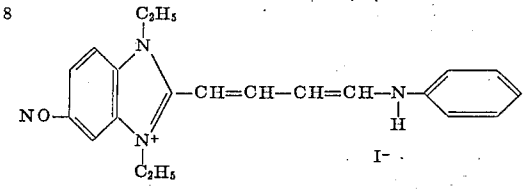
Dye 6



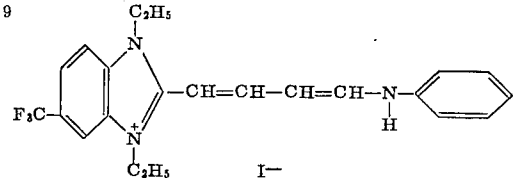
Dye 7



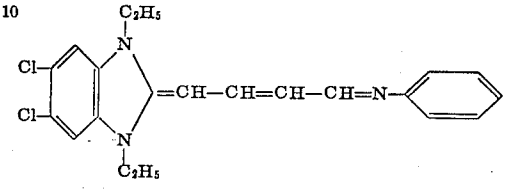
Dye 8



Dye 9



Dye 10



4. A photographic light-sensitive element having at least one layer which comprises the silver halide emulsion of claim 1.

5. The photographic silver halide emulsion of claim 1, wherein A is phenyl, methoxyphenyl, tolyl, or chlorophenyl.

6. The photographic silver halide emulsion of claim 1, wherein X is halide, thiocyanate, perchlorate, benzene sulfonate, p-toluene sulfonate, methyl sulfate, or ethyl sulfate.

* * * * *