United States Patent

Kimura et al.

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[54] **PHOTOGRAPHIC SILVER HALIDE EMULSION**

[72] Inventors: **Shiro Kimura; Yoshiyuki Nakazawa; Akira Sato; Yasuharu Nakamura,** all of Kanagawa, Japan

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

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[21] Appl. No.: **755,745**

[30] **Foreign Application Priority Data**

Aug. 29, 1967 Japan....................................42/55439

[52] **U.S. Cl.**..**96/127,** 96/102
[51] **Int. Cl.**..**G03c 1/10**
[58] **Field of Search**.......................................96/106, 102, 87

[56] **References Cited**

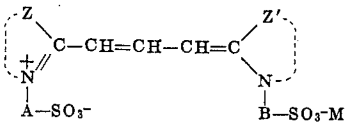
UNITED STATES PATENTS

2,912,329 11/1959 Jones et al. 96/100

Primary Examiner—Norman G. Torchin
Assistant Examiner—Edward C. Kimlin
Attorney—Sughrue, Rothwell, Mion, Zinn & Macpeak

[57] **ABSTRACT**

A photographic silver halide emulsion containing at least one unsymmetrical benzimidazolocarbocyanine sensitizing dye represented by the general formula:



Z and Z′ are non-metallic groups necessary to complete a benzimidazole nucleus, A and B are polymethylene groups or alkylpolymethylene groups, and M is a cation. Preferred dyes are set out in the specification.

7 Claims, No Drawings

PHOTOGRAPHIC SILVER HALIDE EMULSION

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates generally to a photographic silver halide emulsion containing a novel sensitizing dye, and more particularly to a photographic silver halide emulsion containing an unsymmetrical benzimidazolocarbocyanine dye in which the substituents of the nitrogen atoms in both heterocyclic rings are sulfoalkyl groups.

2. Description of the Prior Art

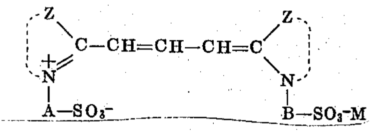
It is well known in the techniques of manufacturing photographic silver halide emulsions that by adding a sensitizing dye to a silver halide emulsion, the light-sensitive wavelength region of the emulsion is enlarged. However, the addition of a sensitizing dye to a silver halide emulsion generally tends to be accompanied by an increase in photographic fog caused by the presence of the dye. Accordingly, the sensitizing dye must be selected in view of the restrictions that the sensitivity of the desired spectral region be high and the formation of fog be low.

A benzimidazolocarbocyanine dye can provide a high spectral sensitivity to a silver halide emulsion, but the formation of fog is generally increased by the addition of such a dye.

It is known that when the nitrogen atoms of both heterocyclic rings of the benzimidazolocarbocyanine dye are substituted with sulfoalkyl groups, the formation of fog is markedly reduced. However, the prior art benzimidazolocarbocyanine dyes having sulfoalkyl groups at the nitrogen atoms of both heterocyclic rings thereof are all symmetrical dyes. Although some unsymmetrical benzimidazolocarbocyanine dyes are disclosed in the specifications of Belgian patents 659,415; 659,853; and 660,650, they have a sulfoalkyl group at the nitrogen atom of only one of the heterocyclic rings as the substituent of the nuclei. Symmetrical benzimidazolocarbocyanine dyes having sulfoalkyl groups at the nitrogen atoms in both heterocyclic rings are disclosed in the specifications of U. S. Pat. No. 2,912,329 and Belgian patents 648,981 and 669,308. However, unsymmetrical benzimidazolocarbocyanine dyes having sulfoalkyl groups at the nitrogen atoms in both heterocyclic groups thereof have never been known.

SUMMARY OF THE INVENTION

A photographic silver halide emulsion having a high sensitivity over the spectral over the spectrally sensitized wavelength region is obtained by incorporating therein at least one unsymmetrical benzimidazolocarbocyanine sensitizing dye represented by the formula:



wherein Z and Z' each represent a non-metallic atomic group necessary to complete the benzimidazole nucleus; A and B each represents a member selected from the group consisting of a polymethylene group, and an alkylpolymethylene group; and M represents a cation. For most commercial usage, about 5 mg. to 150 mg. of dye per kilogram of emulsion will suffice.

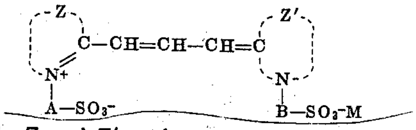
A photographic light-sensitive element containing the above-described emulsion shows greatly improved results.

Preferred dyes and the various moities operable are set out in the descriptive portion of the specification.

An object of this invention is to provide a photographic silver halide emulsion having a high sensitivity over the spectral sensitizing wavelength region by using a novel sensitizing dye which does not increase photographic fog caused by the sensitizing dye.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The object of the present invention can be attained by incorporating a novel sensitizing dye represented by general formula (I) in a photographic silver halide emulsion:



(I)

wherein Z and Z' each represents non-metallic atoms necessary to complete the benzimidazole nucleus; A and B, which may be the same or different, each represents a polymethylene group, such as an ethylene group, a trimethylene group, and a tetramethylene group, or an alkylpolymethylene group such as a methyltrimethylene group; and M represents a hydrogen cation, a metallic ion necessary for forming a salt of sulfonic acid, such as, a potassium ion, a sodium ion, and the like, or a cation of an organic amine, such as a triethylammonium ion, a pyridinium ion, an S-benzylthiuronium ion, and the like.

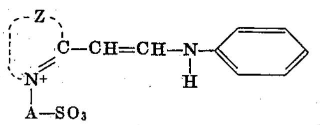
As shown in the above formula, the sensitizing dye used in the present invention is an unsymmetrical benzimidazolocarbocyanine dye having sulfoalkyl groups as substituents at the nitrogen atoms in both heterocyclic rings.

As examples of the benzimidazole nucleus formed by aforesaid atomic groups Z or Z', there are: 1-ethylbenzimidazole, 1-phenylbenzimidazole, 1-methyl-5-chlorobenzimidazole, 1-ethyl-5-chlorobenzimidazole, 1-methyl-5,6-dichlorobenzimidazole, 1-ethyl-5,6-dichlorobenzimidazole, 1-(β-hydroxyethyl)-5,6-dichlorobenzimidazole, 1-(γ-acetoxypropyl)-5,6-dichlorobenzimidazole, 1-ethyl-5,6-dibromobenzimidazole, 1-ethyl-5-chloro-6-bromobenzimidazole, 1-ethyl-5-phenylbenzimidazole, 1-ethyl-5-fluorobenzimidazole, 1-ethyl-5,6-difluorobenzimidazole, 1-ethyl-5-cyanobenzimidazole, 1-(β-acetoxyethyl)-5-cyanobenzimidazole, 1-ethyl-5-chloro-6-cyanobenzimidazole, 1-ethyl-5-cyano-6-chlorobenzimidazole, 1-ethyl-5-fluoro-6-cyanobenzimidazole, 1-ethyl-5-carboxybenzimidazole, 1-ethyl-5-carboethoxybenzimidazole, 1-ethyl-5-acetylbenzimidazole, 1-ethyl-5-sulfamylbenzimidazole, 1-ethyl-5-N-ethylsulfamylbenzimidazole, 1-ethyl-5-morpholinosulfonylbenzimidazole, 1-ethyl-5-morpholinosulfonyl-6-chlorobenzimidazole, 1-ethyl-5-methylsulfonyl-benzimidazole, 1-ethyl-5-trifluoromethylbenzimidazole, and the like.

As stated, the sensitizing dye of the present invention is an unsymmetrical benzimidazolocarbocyanine dye which has sulfoalkyl groups at the nitrogen atoms in both heterocyclic rings thereof in combination with properly selected substituents in both heterocyclic rings. The sensitivity of the desired spectral wavelength region of a photographic silver halide emulsion can be increased by adding the sensitizing dye described thereto without increasing the formation of fog to any significant extent.

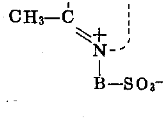
The sensitizing dye used in this invention also has great merit that the alkyl groups of the nitrogen atoms in both heterocyclic rings of the dye and the alkylene chains of the sulfoalkyl groups may be selected from a large class.

The novel sensitizing dye represented by general formula (I) may be prepared by reacting an anilinovinyl intermediate compound having a sulfoalkyl group as a substituent of the nitrogen atom in the heterocyclic ring as shown by general formula (II):



(II)

(wherein Z and A are defined in connection with general formula (I)) with acetic anhydride in nitrobenzene, to provide an acetoanilidovinyl intermediate product, and condensing the intermediate product in the presence of an organic base, such as triethylamine, with an intermediate represented by general formula (III):

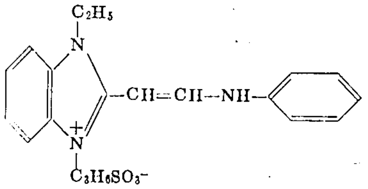


(III)

(wherein Z′ and B are as defined in connection with general formula (I)).

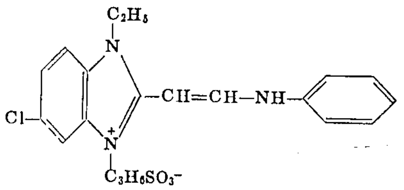
General methods for preparing the intermediate products and the dyes used in this invention are shown below, but it should be understood that the invention is not to be limited to them.

Intermediate 1



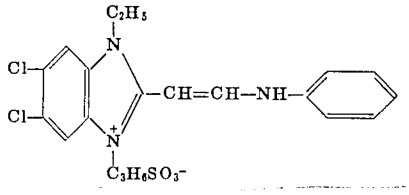
Two grams (2 g.) of anhydro-1-ethyl-2-methyl-3-(3-sulfopropyl)benzimidazolium hydroxide and 2.8 g. of diphenylformamidine were fused and reacted by heating for 20 minutes. The reaction product produced was washed with acetone and then with water and finally recrystallized from an alcohol to provide 1 g. of intermediate 1, having a melting point of 145° C.

Intermediate 2



Three grams (3g.) of anhydro-5-chloro-1-ethyl-2-methyl-3-(3-sulfopropyl)benzimidazolium hydroxide and 3.7 g. of diphenylformamidine were fused and reacted by heating for 20 minutes. The reaction product was washed with acetone and then with water and finally recrystallized from a mixed solvent of methanol and dimethylformamide to provide 1.3 g. of intermediate 2, having a melting point of 304° C.

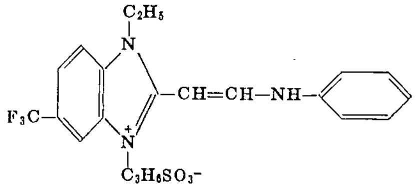
Intermediate 3



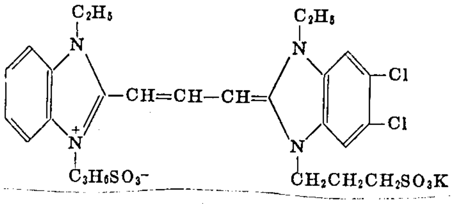
A mixture of 4 g. of 6-chloro-4-methyl quinoline and 6 g. of ethyl iodide was heated for 6 hours under refluxing. After cooling, acetone was added to the product, and the resulting mixture was stirred to form crystals, which were then recovered by filtration. 7.5 g. of the crystals of the iodide, having a melting point of 171°–173° C, were obtained.

Three grams (3 g.) of anhydro-5,6-dichloro-1-ethyl-2-methyl-3-(3-sulfopropyl)benzimidazolium hydroxide and 3.2 g. of diphenylformamidine were fused and reacted by heating for 20 minutes. The reaction product was washed with acetone and then with water and thereafter recrystallized from methanol to provide intermediate 3, having a melting point of 288° C.

Intermediate 4

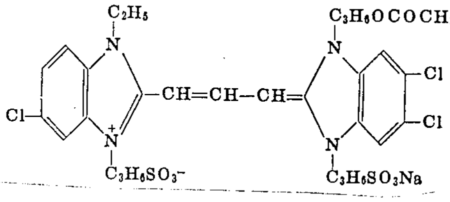


3.4 g. of anhydro-1-ethyl-2-methyl-3-(3-sulfopropyl)-5-trichloromethylbenzimidazolium hydroxide and 4 g. of diphenyl-formamidine were fused and reacted by heating for 30 minutes. The reaction product was washed with acetone and then with water and thereafter recrystallized from methanol to provide 2.3 g. of intermediate 4, having a melting point greater than 300° C.



1.5 g. of anhydro-2-(β-anilinovinyl)-1-ethyl-3-(3-sulfopropyl)benzimidazolium hydroxide were heated and refluxed in a mixture of 15 ml. of nitrobenzene and 2 ml. of acetic anhydride for five minutes. The solution thus prepared was mixed with 1.5 g. of anhydro-5,6-dichloro-1-ethyl-2-methyl-3(3-sulfobutyl)benzimidazolium hydroxide and 2 ml. of triethylamine and the resulting mixture was reacted under refluxing by heating. After the reaction was finished, ether was added to the reaction product mixture to precipitate the dye, which was recovered by filtration and treated with an aqueous solution of potassium acetate to provide dye 1. The spectral absorption maximum of the dye in methanol was 511 m. μ.

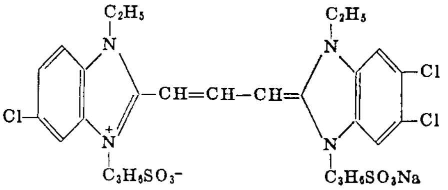
Dye 2



In a mixture of 30 ml. of nitrobenzene, 1.5 ml. of acetic anhydride, and 0.2 ml. of triethylamine, the following materials were reacted for ten minutes under refluxing by heating: 4.2 g. of anhydro-2-(β-anilinovinyl)-5-chloro-1-ethyl-3-(3-sulfopropyl) benzimidazolium hydroxide. The solution thus prepared was mixed with 4 g. of anhydro-1-(3-acetoxypropyl)-5,6-dichloro-2-methyl-3-(3-sulfopropyl)benzimidazolium hydroxide and 2 ml. of triethylamine and this mixture was reacted for ten minutes under refluxing by heating.

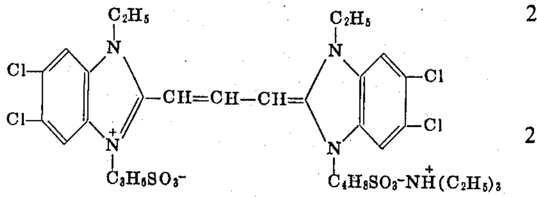
After reaction was completed, ether was added to the reaction product to precipitate the dye, which was recovered, washed with ether, and mixed with water to be crystallized. The dye obtained was dissolved in ethanol and an aqueous sodium iodide solution was added to the resultant solution to convert the dye into the sodium salt thereof. When the sodium salt of the dye was recrystallized from a mixed solvent of methanol and iso-propanol, 0.8 g. of the crystal of dye 2, having a melting point of 260° C., was obtained. The spectral absorption maximum of the dye in methanol was 515 m. μ.

Dye 3



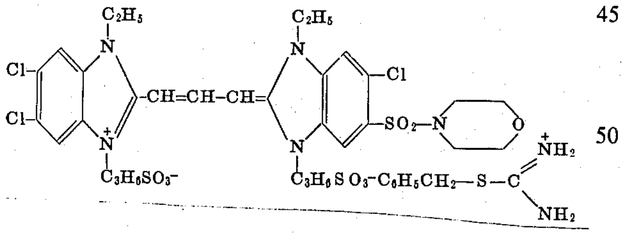
In a mixture of 15 ml. of nitrobenzene and 2 ml. of acetic anhydride there was reacted 2 g. of anhydro-2(β-anilinovinyl)-5,6-dichloro-1-ethyl-3-(3sulfopropyl)benzimidazolium hydroxide for five minutes under refluxing by heating. The solution thus prepared was mixed with 2 g. of anhydro-5-chloro-1-ethyl-2-methyl-3-(3-sulfopropyl)-benimidazolium hydroxide, 1.5 ml. of triethylamine, and 0.1 ml. of acetic acid, and the resultant mixture was reacted for 5 minutes under refluxing by heating. After the reaction was finished, ether was added to the reaction product to precipitate the dye, which was recovered by filtration, washed with ether, and treated with an aqueous sodium iodide solution to convert the dye into the sodium salt of the dye. When the sodium salt of the dye was recrystallized from methanol, 0.5 g. of the crystal of dye 3, having a melting point of 277° C., was obtained. The spectral absorption maximum of the dye in methanol was 515 m. μ.

Dye 4



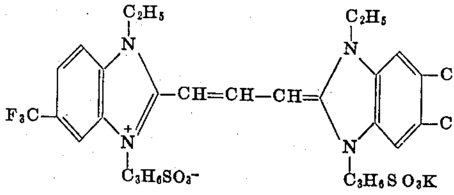
In a mixture of 20 ml. of nitrobenzene and 2.5 ml. of acetic anhydride there was reacted 3 g. of anhydro-2-(β-anilinovinyl)-5,6-dichloro-1ethyl-3-(3-sulfopropyl)benzimidazolium hydroxide for 5 minutes under refluxing by heating. The solution obtained was mixed with 3 g. of anhydro-5,6-dichloro-1-ethyl-2-methyl-3-(4-sulfobutyl)benzimidazolium hydroxide and 1.5 ml. of triethylamine, and the resultant mixture was reacted for 10 minutes under refluxing by heating. After the reaction was finished, ether was added to the reaction product to precipitate the dye, which was recovered by filtration, washed with ether and recrystallized from ethanol to provide 1.2 g. of dye 4, having a melting point of 235° C. The spectral absorption maximum of the dye in methanol was 519 m. μ.

Dye 5



In a mixture of 25 ml. of nitrobenzene and 4 ml. of acetic anhydride there was reacted 3 g. of anhydro-2-(β-anilinovinyl)-5,6-dichloro-1-ethyl-3-(3-sulfopropyl)benzimidazolium hydroxide for five minutes under refluxing by heating. The solution thus prepared was mixed with 3 g. of anhydro-6-chloro-1-ethyl-2-methyl-5-morpholino-sulfonyl-3-(3-sulfopropyl)benzimidazolium hydroxide and 2 ml. of triethylamine, and the resultant mixture was reacted for 15 minutes under refluxing by heating. After the reaction was finished, ether was added to the reaction product to precipitate the dye, which was recovered by filtration, washed with ether, and treated with an aqueous potassium acetate solution to convert the dye into the potassium salt thereof. The potassium salt of the dye was dissolved in a mixed solvent of water and a small proportion of ethanol, and an aqueous solution of S-benzylthiuronium chloride was added to the solution thus prepared. The S-benzylthiuronium salt of the dye thus precipitated was recrystallized from a mixed solvent of methanol, ethanol, and chloroform, to provide 12 g. of the crystal of dye 5, having a melting point of 213° C. The spectral absorption maximum of the dye in methanol was 522 m. μ.

Dye 6



In a mixture of 30 ml. of nitrobenzene, 4 ml. of acetic anhydride, and 0.1 ml. of triethylamine there was reacted 2 g. of anhydro-2-(β-anilinovinyl)-1-ethyl-3-(3-sulfopropyl)-5-trifluoromethylbenzimidazolium hydroxide for 5 minutes under refluxing by heating. The solution prepared was mixed with 2 g. of anhydro-5,6-dichloro-1-ethyl-2-methyl-3-(3-sulfopropyl)-benzimidazolium hydroxide and 4 ml. of triethylamine and the resultant mixture was reacted for 15 minutes under refluxing by heating. After the reaction was finished, ether was added to the reaction product to precipitate the dye, which was recovered by filtration, washed with ether and then treated with an aqueous solution of potassium acetate to convert the dye into the potassium salt of the dye. When the potassium salt was recrystallized from a mixed solvent of methanol and isopropanol, 0.7 g. of the crystal of dye 6, having a melting point greater than 300° C., was obtained. The spectral absorption maximum of the dye in methanol was 512 m. μ.

The novel sensitizing dye used in the present invention can spectrally sensitize silver halide emulsions and in particular, the dye is very effective for enlarging the spectrally sensitive region of a gelatino silver halide emulsion. The sensitizing dye can also sufficiently sensitize photographic silver halide emulsions containing hydrophilic colloids other than gelatin, such as, agar agar, collodion, water-soluble cellulose derivatives, polyvinyl alcohol, and other natural or synthetic hydrophilic resins. In the photographic silver halide emulsion of this invention, such silver salts as silver chloride, silver bromide, silver iodobromide, silver chlorobromide, and silver chloro-iodobromide may be employed.

For preparing the photographic silver halide emulsion of this invention, one or more of the aforesaid novel sensitizing dyes may be incorporated in a photographic silver halide emulsion by any conventional method. In practice, the dye is usually added to a photographic emulsion as a solution thereof in a solvent such as methanol or ethanol. The amount of the sensitizing dye to be incorporated in the photographic emulsion may be varied within a very wide range, but for most commercial uses, it has been found that from 5 mg. to 150 mg. per kilogram of emulsion, according to desired end result, is suitable.

The photographic silver halide emulsion of this invention may further be subjected to super sensitization and hyper sensitization. Moreover, in the photographic silver halide emulsion of this invention, there may be added the usual additives such as a chemical sensitizer, a stabilizer, an antibronzing agent, a hardening agent, a surface active agent, an antifoggant, a plasticizer, a developing accelerator, a color coupler, and a fluorescent whitening agent. Any conventional methods may be used for the addition.

The photographic silver halide emulsion of this invention may be applied to a support such as a glass plate, a cellulose derivative film, a synthetic resin film, or a baryta paper by any conventional methods to provide photographic light-sensitive elements.

The present invention will be more practically explained by referring to the following example. EXAMPLE

A photographic silver halide emulsion was prepared by adding the sensitizing dye of this invention mentioned above to a silver iodobromide emulsion (AgI : AgBr = 7 mol : 93 mol). The photographic emulsion was applied to a triacetyl cellulose film and dried. The photographic light sensitive film was exposed to a lamp (color temperature 2,660° K.) and after development, the spectral sensitizing characteristics were measured by means of a diffraction grating spectrometer.

The composition of the developer used above was as follows:

N-methyl-p-aminophenol sulfate	20 g.
Hydroquinone	5.0 g.
Sodium sulfite	100 g.
Borax	20 g.
Water to make	1 liter

The sensitization maximums when various sensitizing dyes of this invention were used are shown in Table 1, and the fog densities of the photographic light-sensitive elements prepared by using the photographic silver halide emulsions of this invention are shown in Table 2 together with those of comparative light-sensitive elements using other photographic silver halide emulsions containing conventional control sensitizing dyes shown below.

TABLE 1

Sensitizing Dye	Mg-mol/kg-Emulsion	Kind of Emulsion	Sensitizing Maximum m. μ.
1	0.08	AgBr/I	560
2	"	"	570
3	"	"	580
4	"	"	582
5	"	"	565
6	"	"	575

TABLE 2

Sensitizing Dye	Mg-mol/kg-Emulsion	Kind of Emulsion	Fog
1	0.08	AgBr/I	0.04
7*	"	"	0.11
4	"	"	0.04
8*	"	"	0.27
6	"	"	0.04
9*	"	"	0.09
10*	"	"	0.06

* Conventional sensitizing dyes utilized for comparison purposes represented by the following formulas:

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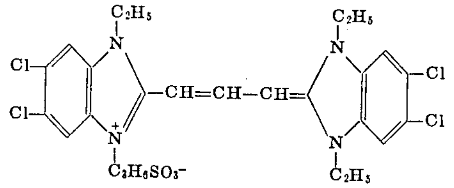

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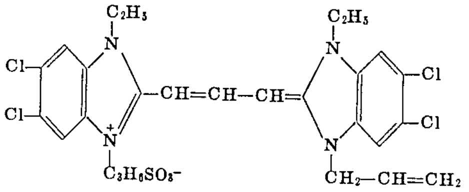

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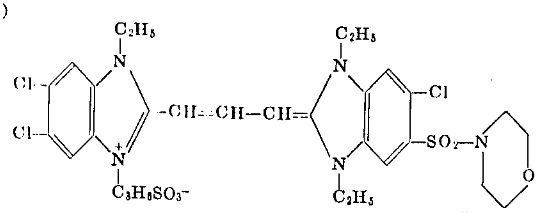

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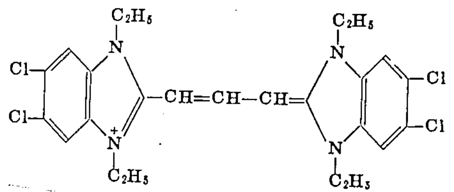
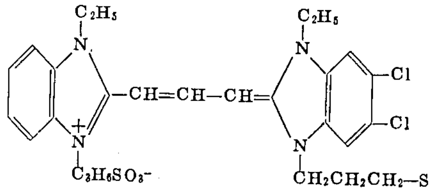
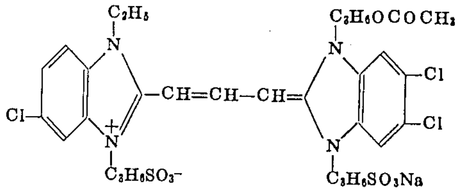
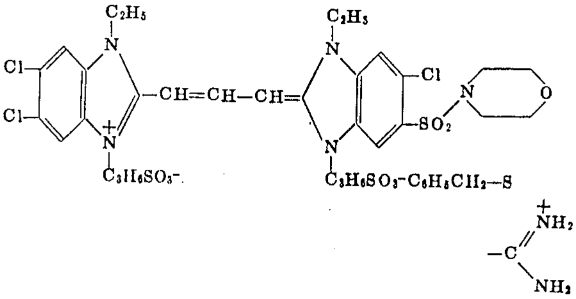


What is claimed is:

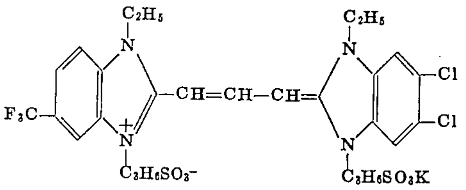
1. A photographic silver halide emulsion containing at least one unsymmetrical benzimidazolocarbocyanine sensitizing dye selected from the group consisting of







and



2. The photographic silver halide emulsion of claim 1 wherein said dye is (A).

3. The photographic silver halide emulsion of claim 1 wherein said dye is dye (B).

4. The photographic silver halide emulsion of claim 1 wherein said dye is dye (c).

5. The photographic silver halide emulsion of claim 1 wherein said dye is dye (D).

6. The photographic silver halide emulsion of claim 1 wherein the amount of said sensitizing dye is from about 5 mg. to about 150 mg. per kilogram of emulsion.

7. A photographic light-sensitive element which comprises a layer of photographic silver halide emulsion claimed in claim 1.

* * * * *