# United States Patent

[11] 3,615,632


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[45] Patented **Oct. 26, 1971**
[73] Assignee **Fuji Photo Films Co., Ltd. Kanagawa, Japan**
[32] Priority **July 29, 1967**
[33] **Japan**
[31] **42/48761**


[54] **SUPERSENSITIZED PHOTOGRAPHIC SILVER HALIDE LIGHT-SENSITIVE ELEMENTS**
**6 Claims, No Drawings**


[52] **U.S. Cl.** ..... **96/122**
[51] **Int. Cl.** ..... **G03c 1/28**
[50] **Field of Search** ..... 96/104, 82; 8/1.1



[56] **References Cited**

UNITED STATES PATENTS

2,875,058 2/1959 Carroll et al. ..... 96/104

OTHER REFERENCES

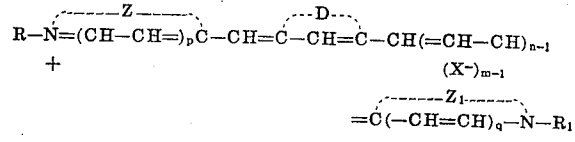
Moore " Bleaching Goods for Dyeing & Finishing in the Continuous Open-Width Peroxide System" June 2, 1949 American Dyestuff Reporter pages 497, 498, 499, 504. (8/111)



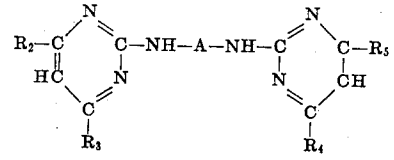
*Primary Examiner*—J. Travis Brown
*Attorney*—Sughrue, Rothwell, Mion, Zinn and Macpeak



**ABSTRACT:** A photographic silver halide light-sensitive element containing a support bearing thereon, a silver halide emulsion containing at least one sensitizing dye having the structure,



and at least one compound of the structure



# SUPERSENSITIZED PHOTOGRAPHIC SILVER HALIDE LIGHT-SENSITIVE ELEMENTS

## BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a photographic silver halide light-sensitive element and more particularly to a photographic silver halide light-sensitive element having improved preservability and a high spectral sensitivity.

2. Description of the Prior Art

It is well known in the production of photographic sensitive elements that when a sensitizing dye is incorporated into a silver halide photographic emulsion, the light-sensitive wavelength region of the emulsion will be enlarged, i.e., spectrally sensitized.

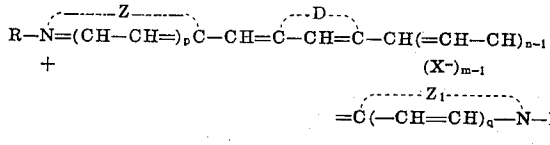
Although there are many well-known sensitizing dyes that possess very high sensitizing characteristics for silver halide emulsions, these known dyes are also sensitive to humidity and if stored under conditions of high humidity, the sensitivity of the light-sensitive elements will be undesirably reduced. Accordingly, such conventional sensitizing dyes cannot be used practically.

It is therefore an object of the present invention to provide a photographic silver halide light-sensitive element containing a sensitizing dye having high-sensitizing characteristics, which has a greater degree of preservability than conventional sensitizing dyes and which is not affected to as large a degree as such conventional dyes.

## SUMMARY OF THE INVENTION

These and other objects are attained by incorporating into the light-sensitive emulsion layer of a photographic silver halide light-sensitive element at least one sensitizing dye represented by the general formula I below and at least one compound represented by the general formula II below.

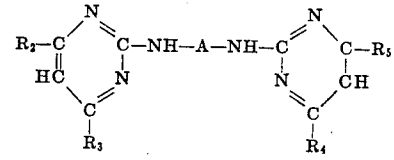
GENERAL FORMULA I



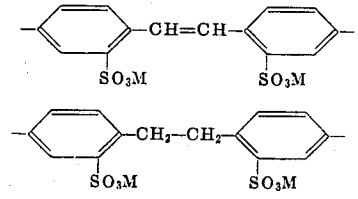
wherein $R$ and $R_1$ each represent alkyl groups and preferably lower alkyl groups such as methyl, ethyl, or propyl, or each represents a substituted alkyl group, such as 2-hydroxyethyl, 2-methoxyethyl, carboxymethyl, 2-carboxyethyl, 3-carboxypropyl, 2-sulfoethyl, 3-sulfopropyl, 4-sulfobutyl, carboethoxymethyl, 2-carbomethoxyethyl, 2-carboethoxyethyl and the like; and $D$ represents a nonmetallic atomic group necessary for forming a six-membered ring comprising three methylene groups; $X^1$ represents an anion, such a chlorine ion, a bromine ion, an iodine ion, a perchloric acid ion, a p-toluene sulfonic acid ion, an ethyl sulfate ion, or the like; $Z$ and $Z_1$ each represent nonmetallic atomic groups necessary for forming a heterocyclic ring containing one or more nitrogen atoms, such as benzothiazole, 5-chlorobenzothiazole, 6-chlorobenzothiazole, 4-methylbenzothiazole, 5-methylbenothiazole, 6-methylbenzothiazole, 5-phenylbenzothiazole, 6-methoxybenzothiazole, 4-ethoxybenzothiazole, 5-methoxybenzothiazole, 5-hydroxybenzothiazole, 6-hydroxybenzthiazole, 5,6-dimethoxybenzothiazole, 5,6-dimethylbenzothiazole, and the like or naphthothiazoles, such as $\alpha$-naphthothiazole, $\beta$-naphthothiazole and the like, or benzoselenzoles, such as benzoselenazole, 5-chlorobenzoselenazole, 6-methbenzoselenazole, 6-methoxybenzoselenazole, and the like or the naphthoselenazoles, such as $\alpha$-naphthoselenazole, $\beta$-naphthoselenazoles, and the like, or the benzoxazoles, such as benzoxazole, 5-methylbenzoxazole, 6-methoxybenzoxazole, 5-phenlbenzoxazole, and the like, or the naphthoxazoles, such as $\alpha$-naphthoxazole, $\beta$-naphthoxazole, and the like, or the 2-quinolines, such as 2-quinoline, 6-methyl-2-quinoline, 6-chloro-2-quinoline, 5-ethoxy-2-quinoline, and the like, or the 4-quinolines, such as 4-quinoline, 6-methyl-4-quinoline, 8-methyl-4-quinoline, and the like, or the 3,3-dialklindolenines, such as 3,3-dimethylindolenine, 3,3-dimethyl-5-methylindolenine, and the like; and wherein $p$ and $q$ each represent 0 or 1; wherein $m$ represents 1, when the dye forms and intermolecular salt, or 2; and $n$ represents 1 or 2 and the general formula II is



GENERAL FORMULA II



wherein $R_2$, $R_3$, $R_4$, and $R_5$ each represent halogen atoms, hydroxyl groups, aryloxy groups, arylthio groups, or arylamino groups, or mixtures thereof; and $A$ represents a group shown by the following formula



wherein $M$ represents a hydrogen atom, and alkali or an ammonium group.

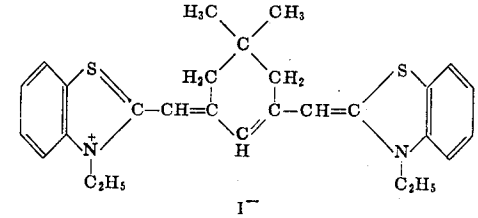
By using at least one sensitizing dye represented by the aforesaid general formula I (hereinafter called sensitizing dye I) together with at least one compound represented by the aforesaid general formula II (hereinafter called compound II), in the photographic silver halide emulsion, the reduction of light-sensitivity characteristics of conventional dyes on storage is avoided without increasing the formation of fog.

It has further been found that the combinations of sensitizing dyes I and compounds II will not only scarcely reduce the spectral sensitivity of the silver halide emulsion layer containing them but will in many instances greatly increase the spectral sensitivity and in some combinations demonstrate synergistic sensitization.

Moreover, the combination of compound II with sensitizing dye I, not only does not increase dye fog (fogs caused by the addition of dye) as in conventional dyes, but in many instances actually decreases fog.

The typical examples of sensitizing dye I used in the present invention are illustrated below although the invention is clearly not limited to these preferred species.

(I-1)



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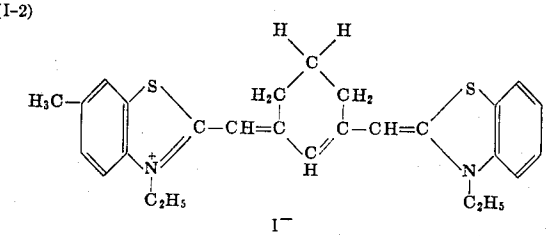
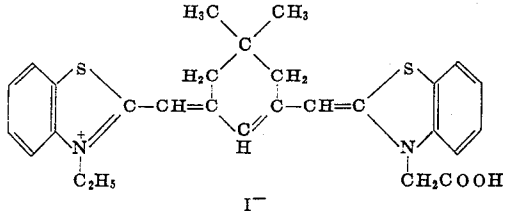
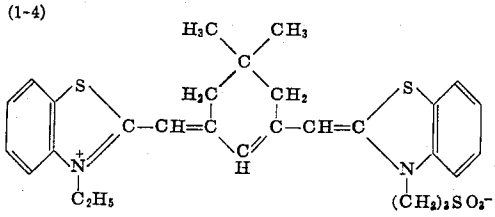


(I-3)



(I-4)



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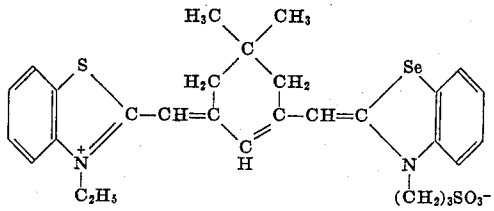
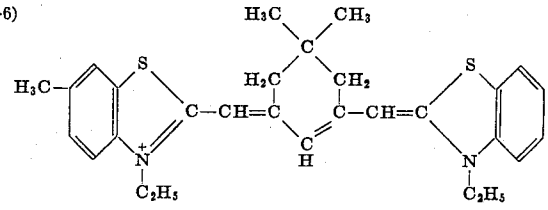
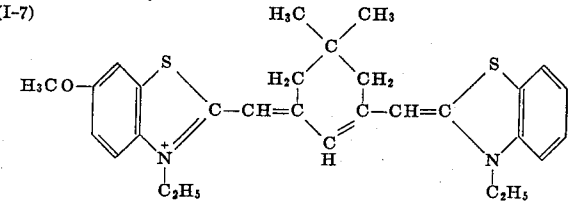


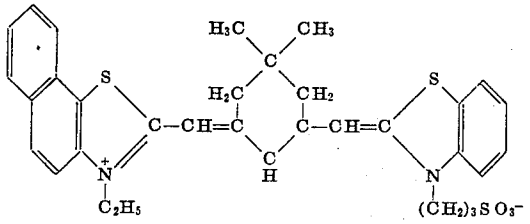
(I-6)



(I-7)



(I-8)



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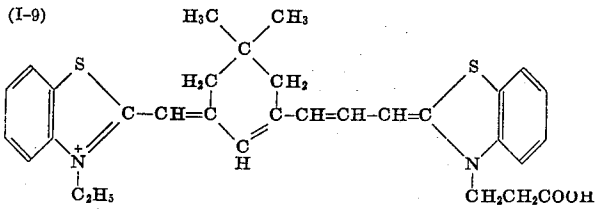
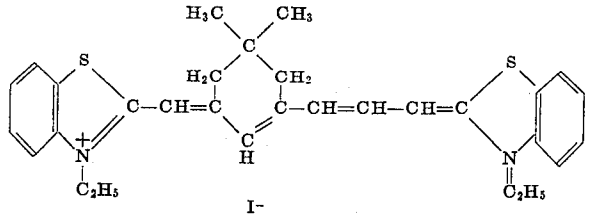
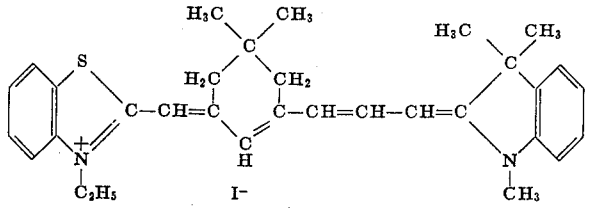




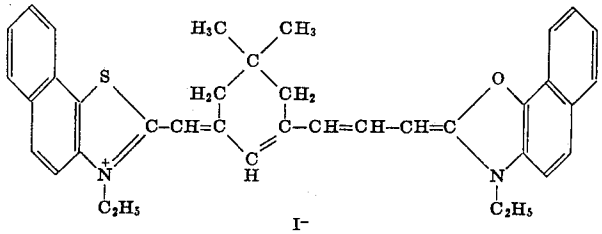
(I-10)



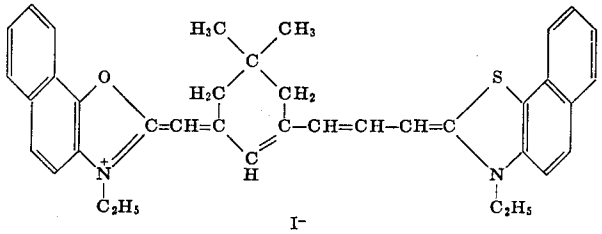
(I-11)



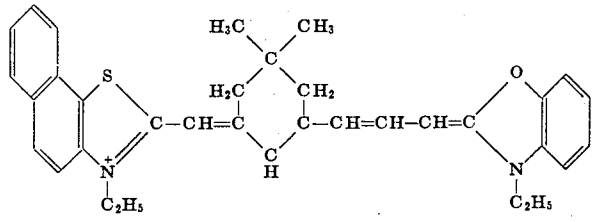
(I-12)



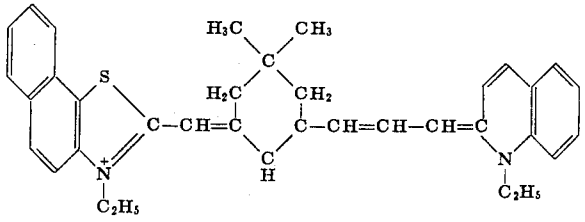
(I-13)



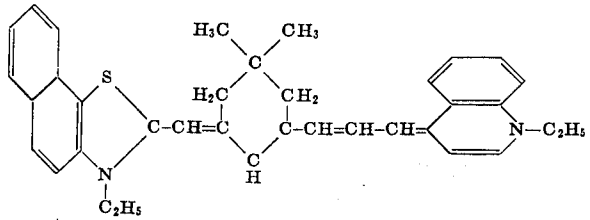
(I-14)



(I-15)



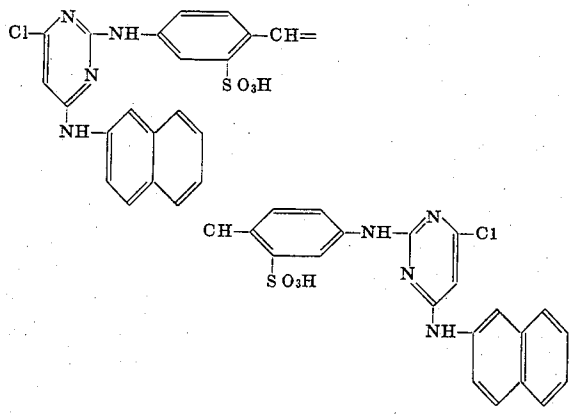
(I-16)



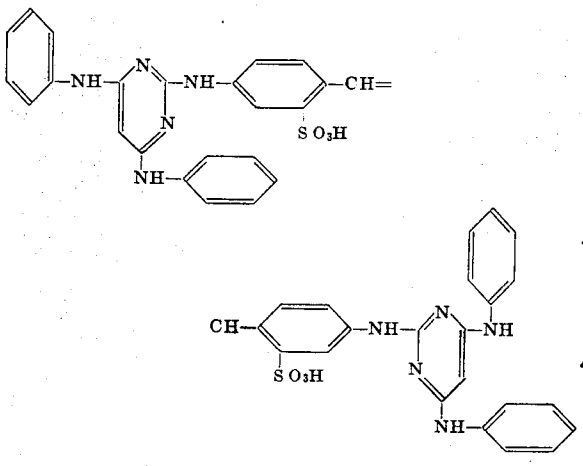
Sensitizing dye I used in this invention may be easily prepared by known processes, for example, the processes described in British Patents 595,784 and 774,779.

Typical examples of compound II used in this invention can be represented by the following preferred species.

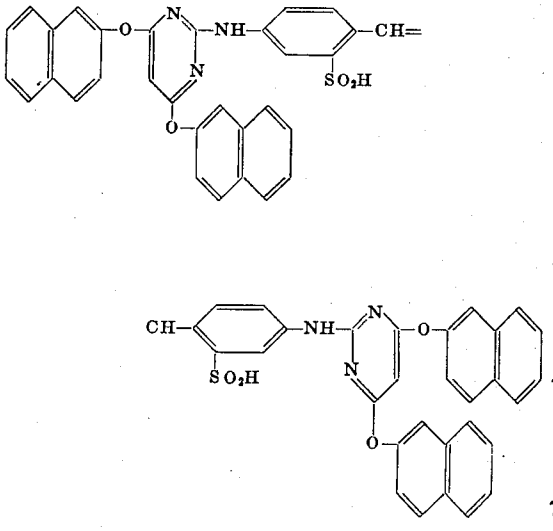
(II-1)



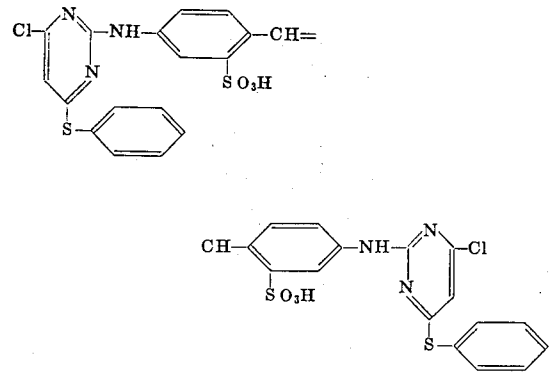
(II-2)



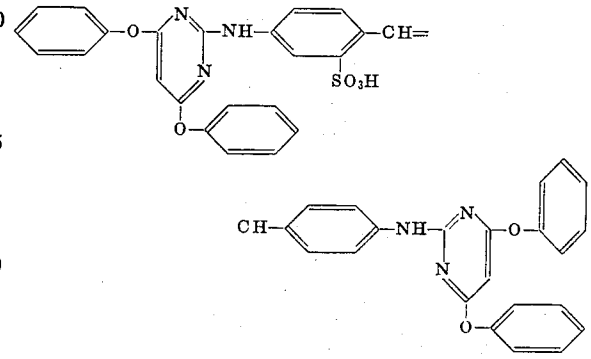
(II-3)



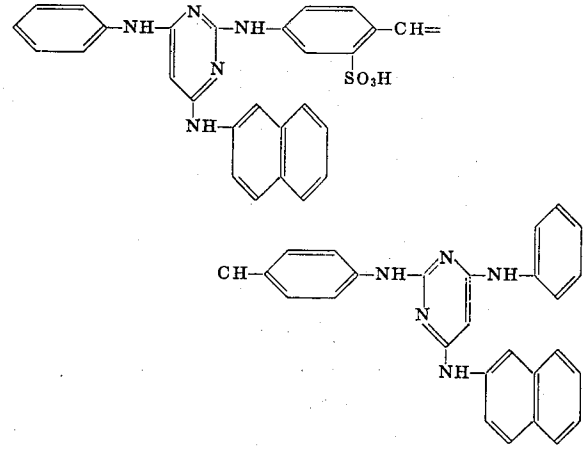
(II-4)



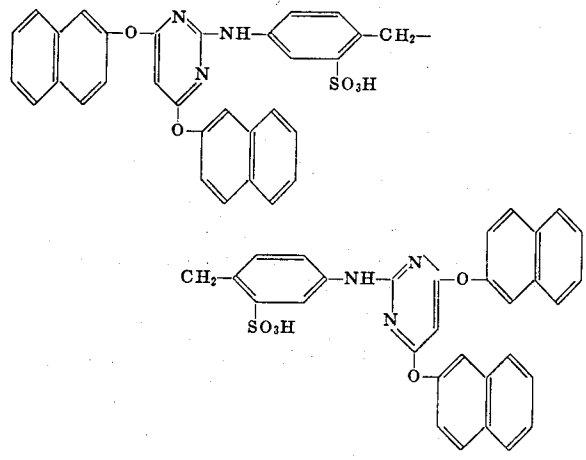
(I-5)



(II-6)



(II-7)

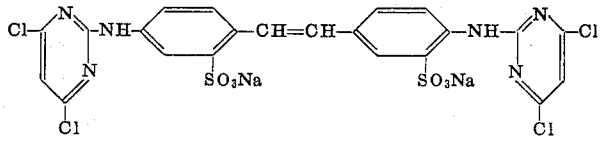


Shown below are several examples of the preparation compound II used in the present invention. It should be clearly understood, however, that other compounds than those illustrated in the following examples may be prepared in a similar manner to those shown.

### 1. PREPARATION OF COMPOUND II-0

To a mixture of 100 ml. of acetone and 100 ml. of water were added 12.4 g. of sodium 4,4'-diaminostilbene-2,2'-disulfonate and 11.0 g. of 2,4,6trichloropyrimidine. The mixture was stirred at 55°–65° C. During reaction the mixture was maintained in a weak acidic state by neutralization of the hydrochloric acid formed during reaction by dropwise addition of an aqueous 10 percent solution of sodium carbonate. After the reaction was complete, the reaction product was cooled by ice and the crystals thus precipitated were recovered by filtration to provide the compound represented by the following formula II-0.

(II-0)



### 2. PREPARATION OF COMPOUND II-2

A dimethylformamide solution (100 ml.) containing 17.8 g. of compound II-0 was prepared as above and 5.7 g. of β-naphthylamine was refluxed by heating for 3–4 hours in a nitrogen gas stream. After allowing the reaction product to cool, it was filtered to remove salts and the filtrate was neutralized by an aqueous 10 percent sodium carbonate solution. The unreacted amine was removed by benzene-extraction and the dimethylformamide-water solvent was removed by a reduced pressure distillation. The residue (200 g.) was refluxed by heating for about three hours in 100 ml. of aniline, the reaction product was poured into about 250 ml. of methanol, and the crystals thus precipitated were recovered by filtration and dried to an objective compound.

### 3. PREPARATION OF COMPOUND II-3

Into 70 ml. of dimethyl formamide was refluxed by heating for about 2.5 hours, 14.1 g. of compound II-0, 13.3 g. of sodium-β-naptholate, and 1.0 g. of 1,4-diaza-2:2:2-bicyclo-octane. After allowing the mixture to cool, the precipitate formed was removed by filtration and dimethyl formamide in the filtrate was removed by distillation under reduced pressure. The residue was dissolved in a mixed solvent of water and acetone, about 5 ml. of concentrated hydrochloric acid was added to the resulting solution, and the crystals thus precipitated were recovered by filtration. The crystals were washed first with a small amount of acetone and then with water, followed by drying to provide the objective compound.

### 4. PREPARATION OF COMPOUND II-4

In a mixed solvent of 70 ml. of water and 20 ml. of dioxane was refluxed by heating 14.1 g. of compound II-0, 4.4 g. of thiophenol, and 1.6 g. of sodium hydroxide. After the reaction was finished about 5 ml. of concentrated hydrochloric acid was added to the reaction product to precipitate the product, which was recovered by filtration under suction. The product thus recovered was first washed with water and then washed with methanol and dried.

The sensitizing dye I of this invention is suitably used in a concentration of 0.02–0.2 g. per 1-g. molecule of silver halide in a silver halide emulsion and the compound II is in a concentration of 0.02–10 g. per 1-g. molecule of silver halide therein. The preferable concentration ratio of sensitizing dye I to compound II is from 1:2 to 1:200.

Sensitizing dye I may be added to a silver halide emulsion by any conventional manner known in the field. Also, compound II may be added to a silver halide emulsion as a solution in an organic solvent such as methanol, ethanol, and the like if necessary water, acetone or an alkaline aqueous solution, etc., may be added to the solution to increase the solubility of the compound.

It is preferable to add sensitizing dye I and compound II to a silver halide emulsion directly before coating. Sensitizing dye I may be added to the emulsion before or after the addition of compound II or may be added as a mixture with compound II.

As the silver halide in the silver halide emulsion of this invention, there may be used various silver halides such as silver chloride, silver bromide, silver iodide, silver chlorobromide, silver iodobromide, and silver chloroiodo-bromide. Furthermore, the photographic silver halide emulsion of this invention may further contain the usual additives such as a chemical sensitizers, hardening agents, antifoggants, wetting agents, and stabilizers, developing accelerators, color-toning agents, and the like, and may also contain a coupler capable of forming a dye by color development.

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

The invention will now be described by reference to the following examples which are presented for purposes of illustration only.

### EXAMPLE 1

A photographic silver halide emulsion containing sensitizing dye I was applied to cellulose acetate film. Also, a photographic silver halide emulsion containing sensitizing dye I and compound II was applied to a cellulose acetate film. Each of the light-sensitive films thus prepared were red-exposed to a light source of 2,666° K. in color temperature through Fuji No. 7 Filter (passing the light having wavelengths longer than 590 millimicrons; made by Fuji Photo Film Co. in Japan) and thereafter the emulsion layer thus exposed was developed for 6 minutes at 20° C. in a developer having the following composition,

| | |
|---|---|
| N-Methyl-p-aminophenol sulfate | 2.0 g. |
| Hydroquinone | 4.0 g. |
| Sodium sulfite | 40.0 g. |
| Sodium carbonate (monohydrate) | 28.0 g. |
| Potassium bromide | 1.0 g. |
| Water to make | 1 l. |

The film developed was preserved for 30 days at a relative humidity of 60 percent. The results shown in the following table.

*red sensitivity directly after coating
**fog directly after coating
***red sensitivity after preservation
****fog directly after preservation

| Sensitizing Dye I (mg./gram mol of silver halide) | Compound II | * | ** | *** | **** |
|---|---|---|---|---|---|
| (a) I-4 (50) | | 100 | 0.06 | 70 | 0.06 |
| (b) I-4 (50) | II-3 (1,280) | 150 | 0.06 | 125 | 0.06 |
| (c) I-7 (60) | | 100 | 0.07 | 60 | 0.07 |
| (d) I-7 (60) | II-3 (1,280) | 145 | 0.07 | 130 | 0.07 |
| (e) I-9 (12) | | 100 | 0.13 | 60 | 0.14 |
| (f) I-9 (12) | II-2 (40) | 100 | 0.08 | 80 | 0.08 |
| (g) I-9 (12) | II-3 (40) | 70 | 0.11 | 65 | 0.11 |
| (h) I-12 (10) | | 100 | 0.13 | 60 | 0.13 |
| (i) I-12 (10) | II-3 (40) | 70 | 0.06 | 70 | 0.06 |
| (j) I-6 (60) | | 100 | 0.04 | 85 | 0.04 |
| (k) I-6 (60) | II- 3 (600) | 150 | 0.04 | 150 | 0.04 |
| (l) I-7 (60) | | 100 | 0.04 | 80 | 0.04 |
| (m) I-7 (60) | II-3 (600) | 150 | 0.04 | 150 | 0.04 |
| (n) I-13 (15) | | 100 | 0.04 | 70 | 0.04 |
| (o) I-13 (15) | II-3 (300) | 112 | 0.04 | 85 | 0.04 |
| (p) I-15 (15) | | 100 | 0.04 | 55 | 0.04 |

| | | | | | |
|---|---|---|---|---|---|
| (q) I-15 (15) | II-3 (300) | 140 | 0.04 | 110 | 0.04 |
| (r) I-16 (15) | | 100 | 0.04 | 50 | 0.04 |
| (s) I-16 (15) | II-3 (300) | 100 | 0.04 | 78 | 0.04 |

(a)–(i): silver iodobromide emulsion
(j)–(s): silver chlorobromide emulsion

## EXAMPLE 2

A silver chlorobromide emulsion containing sensitizing dye I and a dispersion of the coupler having the below-showing structure was mixed with a hardening agent and a wetting agent and the resulting mixture was applied to a baryta paper followed by drying.

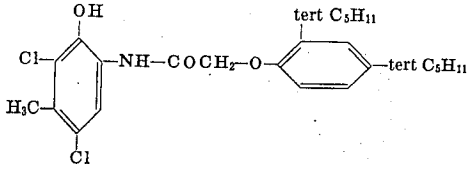
Further, a silver chlorobromide emulsion containing sensitizing dye I, compound II, and the dispersion of the aforesaid coupler was also mixed with the same hardening agent and a wetting agent as above and the resulting mixture was applied to a baryta paper followed by drying.

Each of the emulsion layers thus formed was exposed and developed by a color developer having the following composition:

Benzyl alcohol 30 ml.
sodium chloride 0.7 g.
Sodium bromide 0.5 g.
Sodium sulfite 2.0 g.
Sodium carbonate (monohydrate) 30.0 g.
Sodium sulfate 3.0 g.
Hydroxylamine sulfate 2.4 g.
N,N-diethyl-2-methyl-p-phenylene-diamine hydrochloride 5.2 g.
Water to make 1 l.

The emulsion layer thus color developed was further subjected to the usual processing such as fixing, water washing, bleaching, water washing, hardening, water washing, and stabilizing in this order. The film was then stored for ten days at 40° C. and at a relative humidity of 70 percent. The results shown in the following table.

The structure of the coupler used:



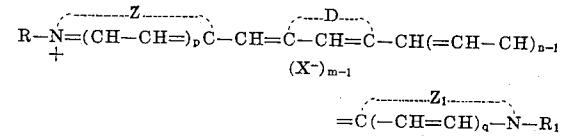

*red sensitivity directly after coating
**fog directly after coating
***red sensitivity after preservation
****fog directly after preservation

| Sensitizing Dye I mg./gram mol of silver halide) | Compound II | * | ** | *** | **** |
|---|---|---|---|---|---|
| (a) I-4 (45) | | 100 | 0.04 | 55 | 0.06 |
| (b) I-4 (45) | II-1 (600) | 150 | 0.04 | 130 | 0.06 |
| (c) I-4 (45) | II-2 (600) | 100 | 0.04 | 90 | 0.06 |
| (d) I-4 (45) | II-3 (600) | 180 | 0.04 | 165 | 0.06 |
| (e) I-4 (45) | II-4 (600) | 180 | | 0.04 | 0.06 |
| (f) I- 4 (45) | II-5 (600) | 145 | 0.04 | 110 | 0.06 |
| (g) I-4 (45) | II-7 (600) | 175 | 0.04 | 160 | 0.06 |
| (h) I-5 (45) | | 100 | 0.08 | 60 | 0.08 |
| (i) I-5 (45) | II-3 (1,200) | 150 | 0.08 | 120 | 0.08 |
| (j) I-8 (50) | | 100 | 0.08 | 80 | 0.08 |
| (k) I-8 (50) | II-3 (2,400) | 130 | 0.08 | 97 | 0.08 |

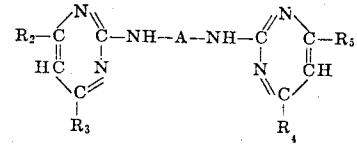
the emulsion of (a)–(g) were from the same batch and (h)–(k) were from another same batch.

We claim:

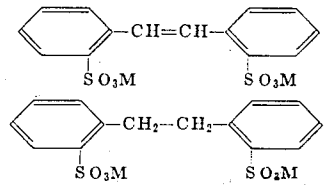
1. A photographic silver halide light-sensitive element comprising a support bearing thereon a silver halide emulsion layer containing at least one sensitizing dye represented by the general formula I




wherein $R$ and $R_1$ each represent members selected from the group consisting of an alkyl group and an alkyl group substituted with a member selected from the class consisting of a hydroxy group, an alkoxy group, a carboxy group, a sulfo group and a carboalkoxy group; $D$ represents a nonmetallic atomic group necessary for forming a six-membered ring comprising three methylene groups; $X$ represents an anion; $Z$ and $Z_1$ each represent nonmetallic atomic groups necessary for forming a member from the group consisting of naphthothiazole; benzothiazole benzothiazole substituted with a member from the class consisting of a chloro group, an alkoxy group, an alkyl group, a phenyl group and an hydroxy group, benzoselenazole; benezoselenazole substituted with a member from the class consisting of chloro group, an alkyl group and an alkoxy group; naphthoselenazole benzoxazole; benzoxazole substituted with a member from the class consisting of an alkyl group, and alkoxy group and an phenyl group; naphthoxazole; quinoline; quinoline substituted with a member selected from the class consisting of an alkyl group, a chloro group and an alkoxy group; and a dialkylindoleine $p$ and $q$ is 0 or 1 and $m$ and $n$ each is 1 or 2 and at least one compound represented by the general formula II




wherein $R_2$, $R_3$, $R_4$ and $R_5$ represent members selected from the groups consisting of halogen, hydroxyl, aryloxyl, arylthio and arylamino; and $A$ represents a member selected from the group consisting of

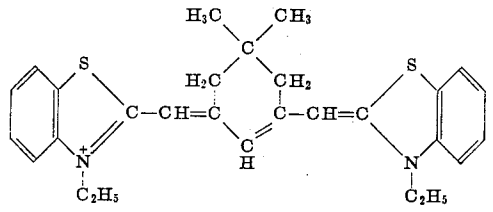



wherein M represents a member selected from the group consisting of hydrogen, an alkali metal and an ammonium group.

2. The photographic silver halide light-sensitive element as claimed in claim 1 wherein the amount of said sensitizing dye I in a silver halide in the emulsion is 0.02–0.2 g. per 1 g. mol of silver halide in the emulsion and the amount of said compound II is 0.02–10 g. per 1 g. mol of silver halide.

3. The photographic silver halide light-sensitive elements as claimed in claim 1 wherein the ratio of said sensitizing dye I to said compound II is from 1:2 to 1:200.

4. The photographic silver halide light-sensitive element as claimed in claim 1 wherein said sensitizing dye represented by the general formula 1, is a compound selected from the group consisting of



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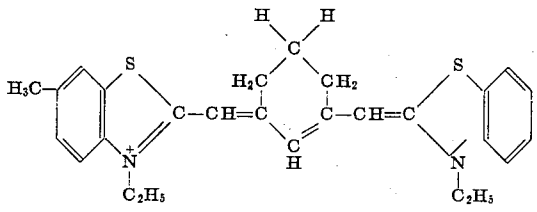

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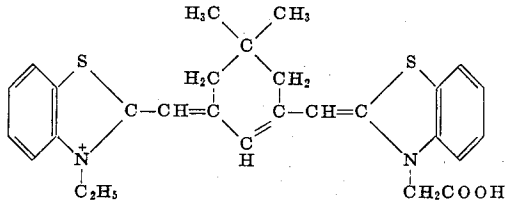

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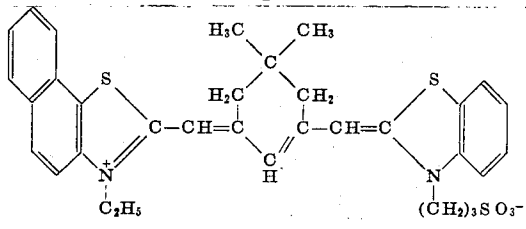

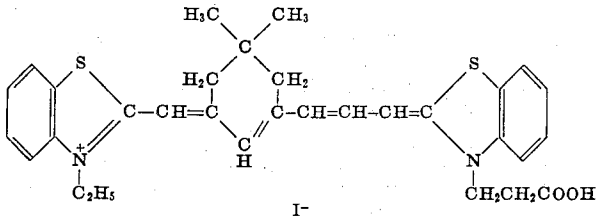

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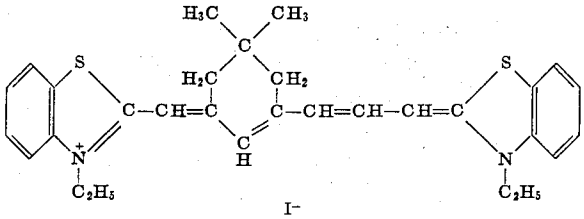

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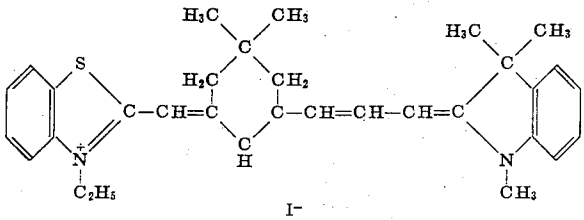

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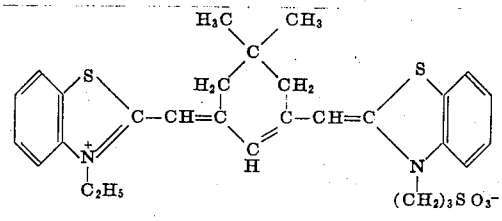



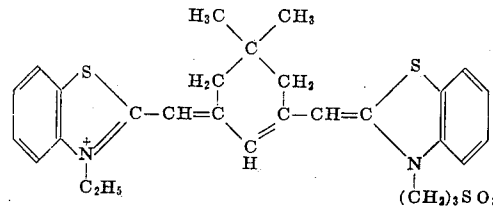

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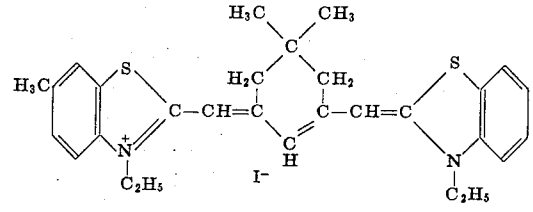

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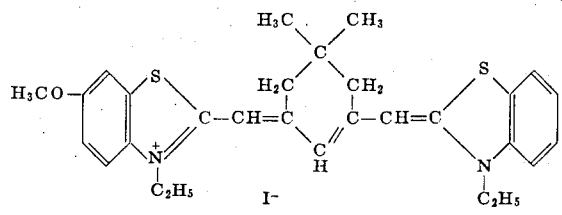

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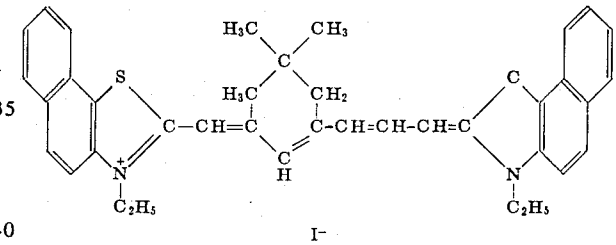

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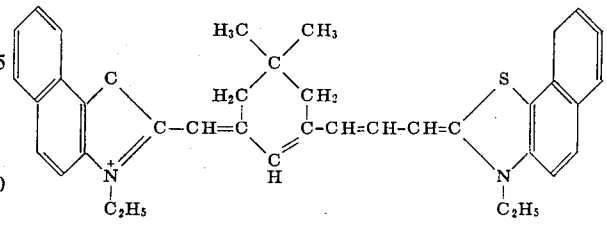

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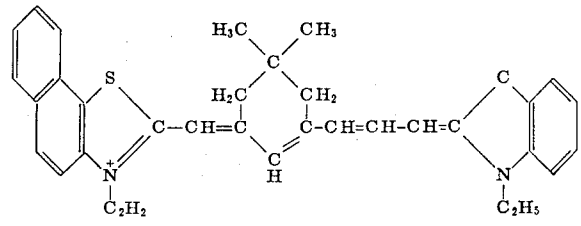

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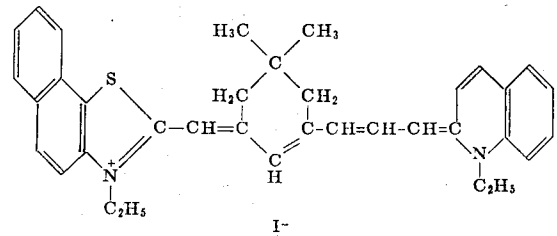

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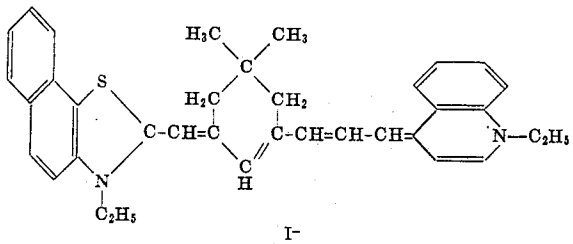
and



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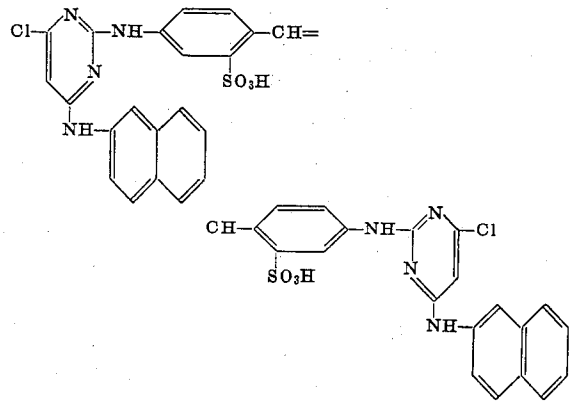
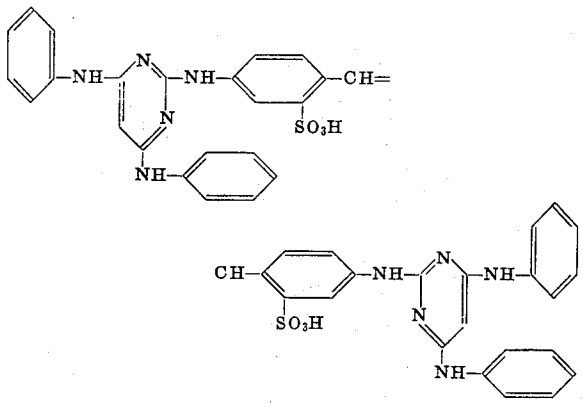
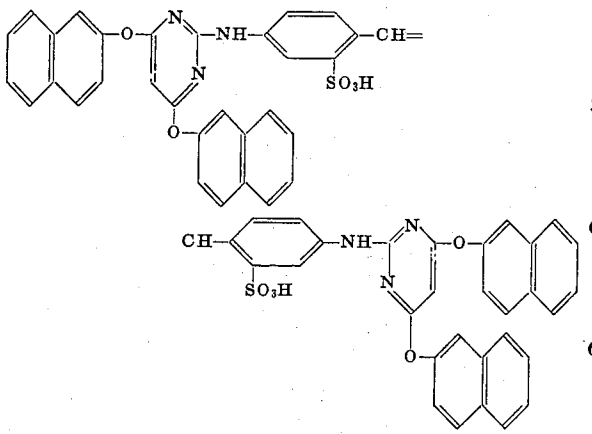
5. the photographic silver halide light-sensitive element as claimed in claim 1 wherein said compound, represented by the general formula II, is a compound selected from group consisting of

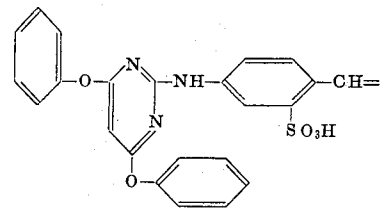


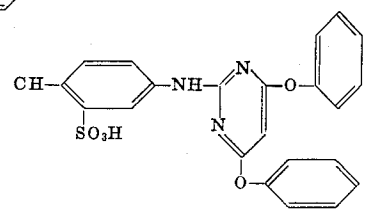


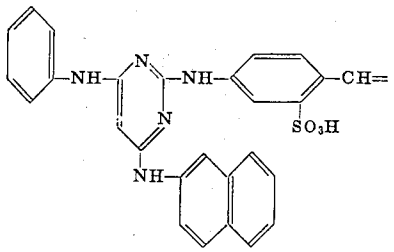


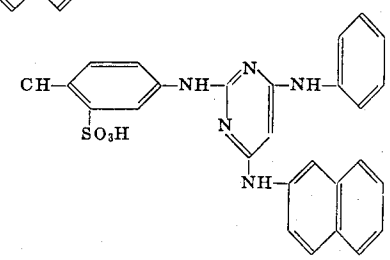












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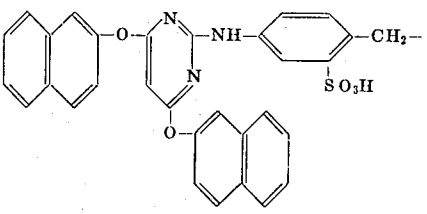

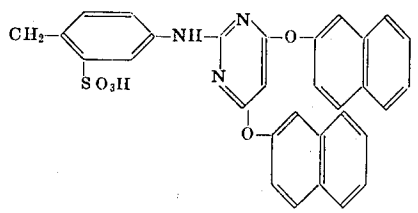

6. The photographic silver halide light-sensitive elements as claimed in claim 1 wherein $R$ and $R_1$ each represent a member selected from the group consisting of methyl, ethyl, propyl, 2-hydroxyethyl, 2-methoxyethyl, carboxymethyl, 2-carboxyethyl, 3-carboxypropyl, 2-sulfoethyl, 3-sulfopropyl, 4-sulfobutyl, carboethoxymethyl, 2-carbomethoxyethy, and a 2-carboethoxyethyl group; $X^1$ represents a member selected from the group consisting of a chlorine ion, a bromine ion, and iodine ion, a perchloric acid ion, a p-toluene sulfonic acid ion, and an ethyl sulfate ion; and $Z$ and $Z_1$ each represent the non-metallic group atomic groups necessary for forming a heterocyclic ring selected from the group consisting of benzothiazole, 5-chlorobenzothiazole, 6-chlorobenzothiazole, 4-methylbenzothiazole, 5-methylbenzothiazole, 6-methylbenzothiazole, 5-phenylbenzothiazole; 6-methoxybenzothiazole, 4-ethoxybenzothiazole, 5-methoxybenzothiazole, 5-hydroxybenzothiazole, 6-hydrox-

ybenzothiazole, 5,6-dimethoxybenzothiazole, 5,6-dimethylbenzothiazole, α-naphthothiazole β-naphthothiazole, benezoselenazole 5-chlorobenzoselenazde, 6-methylbenzoselenazole, 6-methoxybenzoselenazole, β-naphthoselenazole, β-naphthoselenazole, benzoxazle, 5-methylbenzoxzzole, 6-methoxybenzoxazole, 5-phenylbenzoxazole, α-naphthoxazole, β-naphthoxazole 2-quinoline, 6-methyl-2-6-methoxybenzoxazole, 5-phenylbenzoxazole, α-naphthoxazole, β-naphthoxazole 2-quinoline, 6-methyl-2-quinoline, 6-chloro-2-quinoline, 5-ethoxy-2-quinoline, 4-quinoline, 6-methyl-4-quinoline, 8-methyl-4-quinoline, 3,3-dimethylindolenine, and 3,3-dimethyl-5-methyl-indolenine.

* * * * *