United States Patent

[11] 3,617,296

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Leverkusen, Germany

[32] Priority **May 22, 1967**
[33] **Germany**
[31] **A 55 772**

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[54] **OPTICALLY SENSITIZED LIGHT-SENSITIVE SILVER HALIDE MATERIAL**
7 Claims, No Drawings

[52] **U.S. Cl.** **96/140,** 96/120, 260/240
[51] **Int. Cl.** **G03c 1/08**
[50] **Field of Search** 96/102, 106; 260/240

[56] **References Cited**

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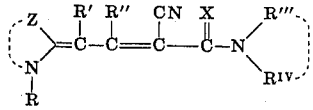
Primary Examiner—J. Travis Brown
Attorney—Connolly and Hutz

ABSTRACT: This invention relates to light-sensitive layers, in particular to silver halide emulsion layers, spectrally sensitized with sensitizing dyes which contain a thiocarbamoyl or selenocarbamoyl group.

OPTICALLY SENSITIZED LIGHT-SENSITIVE SILVER HALIDE MATERIAL

It has been known for a long time that the sensitivity of light-sensitive layers, especially silver halide emulsion layers, may be increased by adding substances which increase the spectral sensitivity range of the light-sensitive substances. Numerous substances which mainly belong to the class of cyanine dyes have been described for sensitizing silver halide emulsion layers. These known substances, however, often have disadvantages in that their sensitizing effect is inadequate or they cause the layer to be discolored, or adversely influence the photographic process itself. This applies in particular to special photographic processes or special photographic materials. The adsorption of the sensitizers on the silver halide should be so strong that the sensitizing effect will be impaired as little as possible by the other necessary additives such as wetting agents and emulsifiers, stabilizers, color couplers, dyes that can be bleached out, white toners etc. It must also be possible to carry out sensitization under extreme conditions such as elevated temperature and high moisture-content. Furthermore, the sensitizing dyes must not increase the fog as is the case with the known basic cyanine dyes. For these reasons, there is considerable interest in finding new sensitizing dyes.

It is among the objects of the present invention to provide sensitizing dyes for spectrally sensitizing light-sensitive layers, especially silver halide emulsion layers, which do not have the above-mentioned disadvantages. We now have found that light-sensitive materials, especially silver halide emulsion layers, can be spectrally sensitized with cyanine dyes of the following formula:



wherein:

X = sulfur or selenium

Z = the nonmetallic ring members necessary for completing 5- or 6-membered heterocyclic rings which may have a benzene or naphthalene ring fused thereto; these heterocyclic rings include the usual heterocyclic rings of cyanine chemistry, such as those of the benzothiazole series, e.g. benzothiazole, 4-chloro-benzothiazole, 5-chloro-benzothiazole, 6-chloro-benzothiazole, 7-chloro-benzothiazole, 4-methyl-benzothiazole, 5-methyl-benzothiazole, 6-methyl-benzothiazole, 6-bromo-benzothiazole, 4-phenyl-benzothiazole, 5-phenyl-benzothiazole, 4-methoxy-benzothiazole, 5-methoxy-benzothiazole, 6-methoxy-benzothiazole, 5-iodo-benzothiazole, 6-iodo-benzothiazole, 6-ethoxy-benzothiazole, 5-ethoxy-benzothiazole, tetrahydrobenzothiazole 5,6-dimethoxy-benzothiazole, 5,6-methylene-dioxy-benzothiazole, 5-hydroxy-benzothiazole, 6-hydroxy-benzothiazole, etc.); those of the naphthothiazole series (e.g. α-naphthothiazole, β-napthothiazole, 5-methoxy-β-napthothiazole, 5-ethoxy-β-naphthothiazole, 7-methoxy-β-naphthothiazole, 8-methoxy-α-naphthothiazole); those of the selenazole series (e.g. 4-methylselenazole, 4-phenyl-selenazole); those of the benzoselenazole series (e.g. benzoselenazole, 5-chloro-benzeselenazole, 5-methoxy-benzoselenazole 5-hydroxy-benzoselenazole, tetrahydrobenzoselenazole); those of the naphthoselenazole series (e.g. β-naphthoselenazole); those of the thiazoline series (e.g. thiazoline, 4-methylthiazoline); those of the pyrroline, piperidine or homopiperidine series, those of the 2-quinoline series (e.g. quinoline, 3-methylquinoline, 5-methylquinoline, 7-methylquinoline, 6-chloroquinoline, 8-chloroquinoline, 6-methoxyquinoline, 8-methylquinoline); those of the 3,3-dialkylindolenine series (e.g. 3,3-dimethylindolenine; those of the pyridine series (e.g. pyridine, 3-methylpyridine, 4-methylpyridine, 5-methylpyridine, 3,4-dimethylpyridine, 3,5-dimethylpyridine, 3,6-dimethylpyridine, 4,5-dimethylpyridine, 4-chloropyridine, 5-chloropyridine, 6-chloropyridine, 3-hydroxypyridine 4-hydroxypyridine, 5-hydroxypyridine, 4-phenylpyridine, 6phenylpyridine); those of the 4-pyridine series (e.g. 2-methylpyridine, 3-methylpyridine, 2-chloropyridine, 3-chloropyridine, 2,3-dimethylpyridine, 2-hydroxypyridine, and 3-hydroxypyridine; those of the oxazole series e.g. 4-phenyloxazole, 4,5-diphenyloxazole and 4-methylbenzoxazole; those of the benzoxazole series e.g. benzoxazole, 5-methylbenzoxazole, 6-methylbenzoxazole, 5,6-dimethylbenzoxazole, 5-methoxybenzoxazole, 6-dialkylaminobenzoxazole, 5-phenylbenzoxazole, 5-carboxylic acid benzoxazole, 5-acrylic acid benzoxazole, 5-sulphonamido benzoxazole, 5-sulfonic acid benzoxazole and 5-chlorobenzoxazole; those of the naphthoxazole series e.g. 4,5-benzobenzoxazole, 5,6-benzobenzoxazole, and 6,7-benzobenzoxazole; those of the thiodiazole, oxodiazole, imidazole or benzimidazole series (e.g. 5-chlorobenzimidazole, 5,6-dichlorobenzimidazole or 5-trifluoromethylbenzimidazole) or those of the pyrimidine or triazine or benzothiazine series;

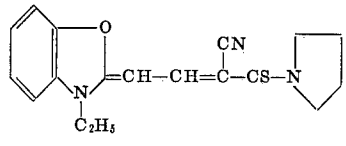
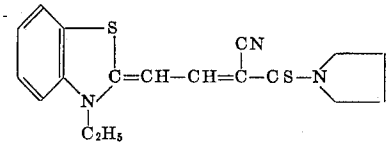
R = a saturated or olefinically unsaturated aliphatic group, preferably with up to five carbon atoms, e.g. methyl, ethyl, or allyl, which may be substituted with halogen such as chlorine, or hydroxyl, alkoxy, sulfonamide, carbamoyl or by acid groups such as sulfo, phosphoric acid or carboxyl, e.g. ω-sulfopropyl, ω-sulfobutyl, ω-sulfoethyl, ω-carboxypropyl, ω-carboxybutyl, ω-carboxyethyl, 2-chloro-3-sulfopropyl, or 2-hydroxy-3-sulfopropyl; or R may also represent a cycloalkyl such as cyclohexyl, aralkyl such as benzyl or phenylethyl, or aryl such as phenyl;

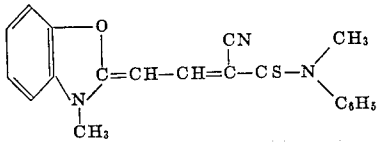
R′, R″ = hydrogen or alkyl, preferably with up to three C atoms;

R‴, R^{IV} = hydrogen, a saturated or olefinically unsaturated aliphatic group, preferably with up to six C atoms, cycloalkyl such as cyclohexyl, aryl preferably phenyl or naphthyl, aralkyl, preferably benzyl or phenylethyl, or a heterocyclic group; R‴ and ^{IV} together represent the ring members necessary for completing a saturated 5-, 6- or 7-membered heterocyclic ring, e.g. a pyrrolidine, piperidine, hexamethylene-imine, piperazine, morpholine, thiomorpholine or isoindolenine ring.

The heterocyclic rings or aryl groups contained in the above formula can be further substituted in any way, e.g. with alkyl, preferably with up to 3 C atoms, such as methyl or ethyl, halogen such as chlorine or bromine, hydroxyl, alkoxy with preferably up to 3 C atoms such as methoxy or ethoxy, hydroxyalkyl, mercaptoalkyl, aryl such as phenyl or aralkyl such as benzyl, amino, substituted amino and the like.

Suitable dyes include those of the following formulas:

		Sensitization, maximum mμ	Melting point, ° C.
I		497	188–190
II		525	218–221

III. 

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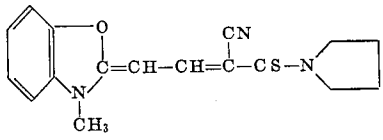
IV. 

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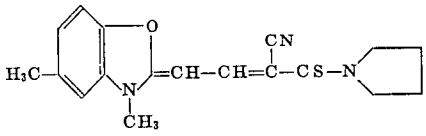
V. 

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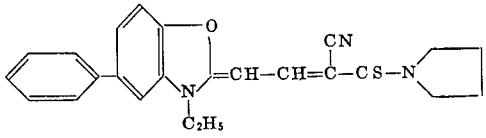
VI. 

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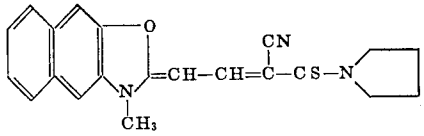
VII. 

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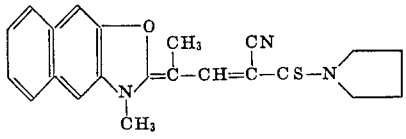
VIII. 

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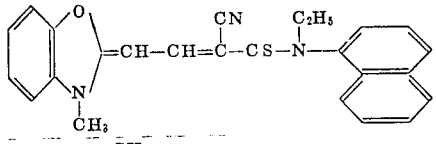
IX. 

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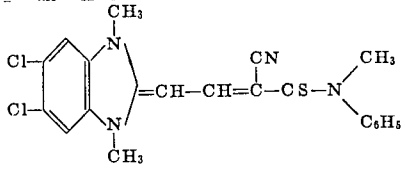
X. 

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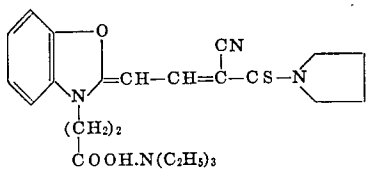
XI. 

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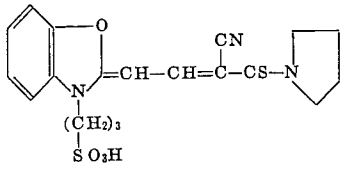
XII. 

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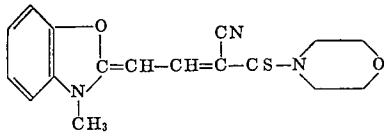
XIII. 

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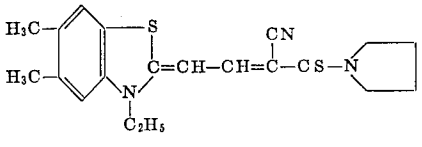
XIV. 

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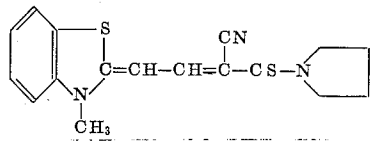
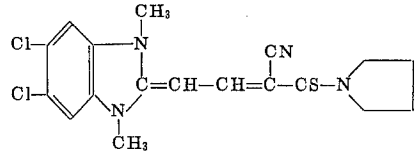
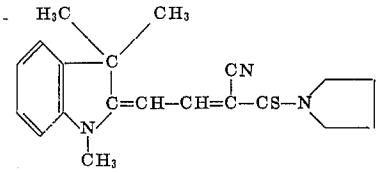
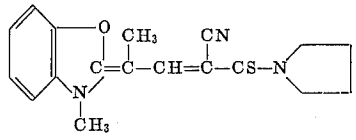
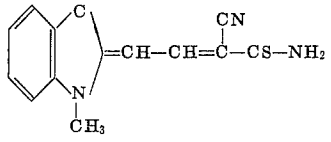
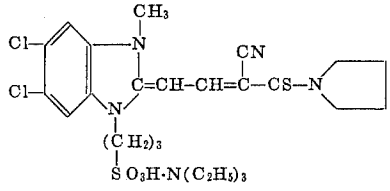
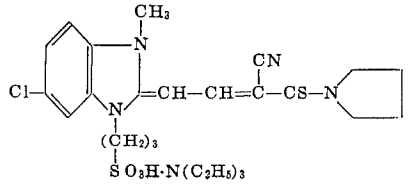
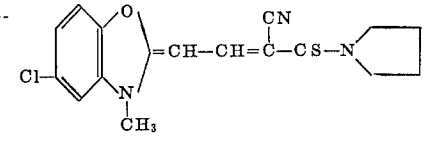
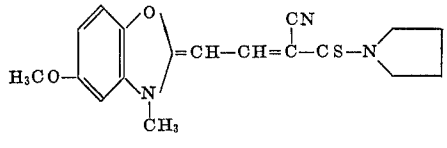
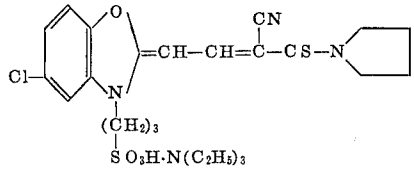
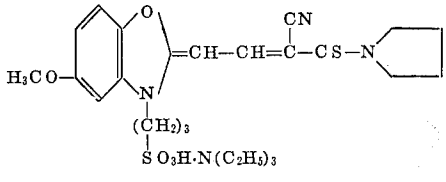
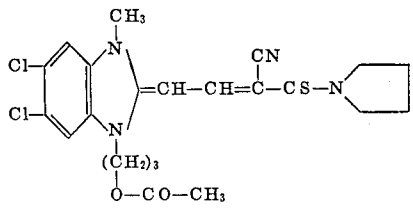
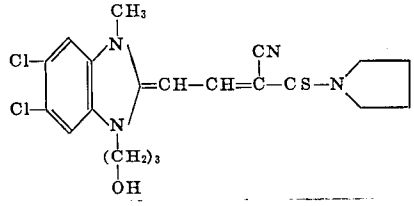
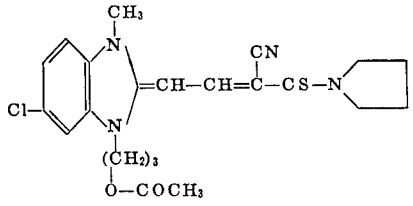
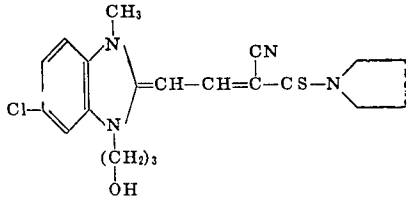
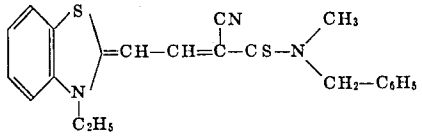
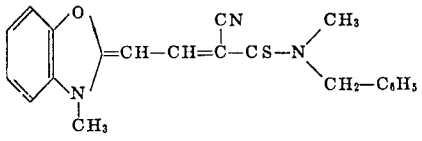
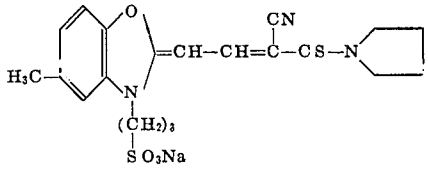
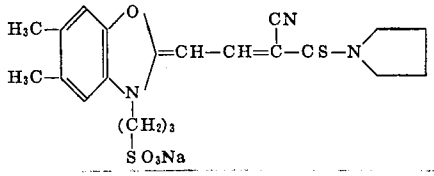
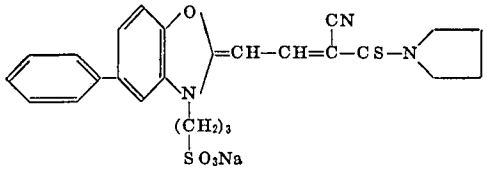
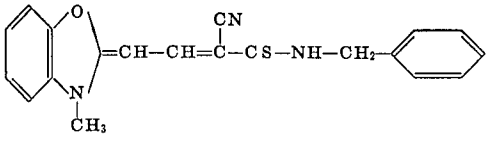
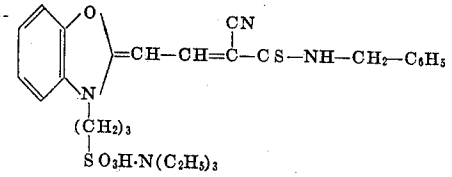
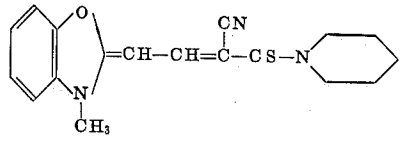
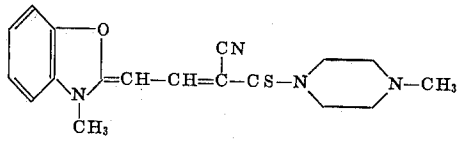
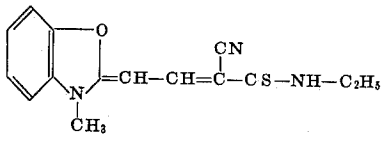
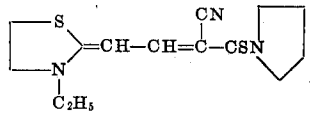
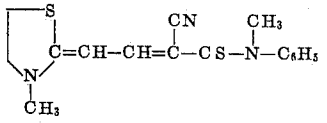
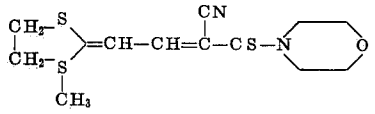
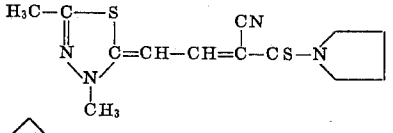
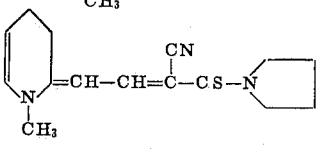
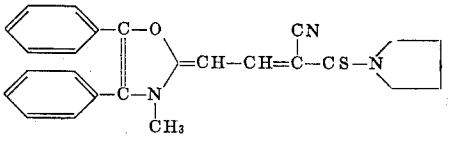
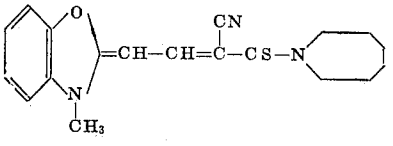
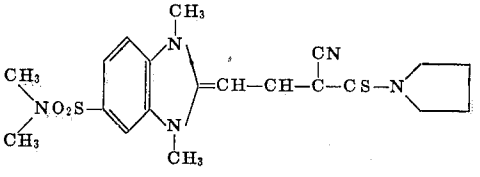
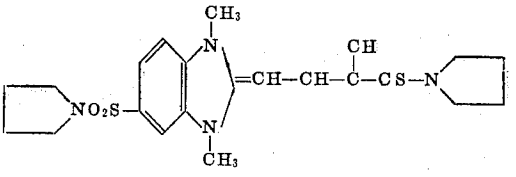
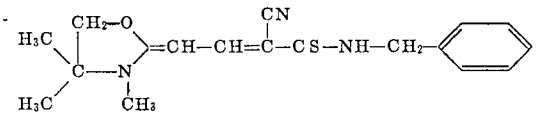
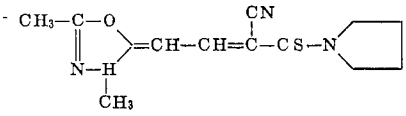
XV		540	
XVI		502	>290
XVII		518	193-195
XVIII		510	204-206
XIX		502	208-209
XX		503	266-267
XXI		498	254-256
XXII		500	241-245
XXIII		510	240-242
XXIV		500	205-208
XXV		508	188-190

XXVI		510	>236
XXVII		508	248
XXVIII		497	214–215
XXIX		496	224–226
XXX		528	164–165
XXXI		498	201–203
XXXII		498	>290
XXXIII		502	>290
XXXIV		509	>290
XXXV		508	176–179

XXXVI		507	249–251
XXXVII		514	215–217
XXXVIII		508	193–195
XXXIX		499	225
XL		480	153
XLI		482	118–120
XLII		486	157–159
XLIII		508	220–222
XLIV		512	195–198
XLV		509	161–164
XLVI		503	155–157
XLVII		503	295–297
XLVIII		503	274–276

XLIX		453	207–208
L		471	204–206

The sensitizers for use according to the invention are prepared by methods known per se, for example, by condensation of a quaternary salt of an acetanilidovinyl substituted heterocyclic base with a cyanothioacetamido- or cyanoselenoacetamido compound in pyridine, or in alcohol, with the addition of a base such as triethylamine.

Cyanothioacetamides and cyanoselenoacetamides can be easily obtained by sulfurization of the corresponding cyanoacetamides with phosphorus pentasulfide or phosphorus pentaselenide with or without the addition of an inert solvent such as toluene or xylene. Unsubstituted cyanothioacetamide can be prepared according to Chem. Ber. 93, 1559 (1960) by addition of hydrogen sulfide to malonitrile.

The preparation of compound I is described in detail below;

4.8 g. of N-ethyl-2-β-acetanilido-vinyl-benzoxazolium-tosylate are heated with 1.4 g. of cyanothioacetic acid pyrrolidide in 30 ml. of acetic acid anhydride with 2 ml. of triethylamine on an oil bath for 5 minutes at reflux. The dye precipitates on cooling. Recrystallized from methanol, m.p. 188° to 190° C. yield 2.8 g. Absorption maximum 455 millimicrons (in methanol).

Cyanothioacetic acid pyrrolidide can be prepared as follows: 69 g. of cyanoacetic acid pyrrolidide with 50 g. of phosphorus pentasulfide in 600 ml. of xylene are heated to 110° to 120° C. (internal temperature) for 1 hour on an oil bath with stirring, and then stirred for a further 30 minutes at this temperature. The reaction mixture is filtered hot to remove the residue, and the product which precipitates on cooling is separated by suction filtration and washed with petroleum ether. When recrystallized from ethyl acetate, the substance melts at 106° to 108° C. Yield 46.8 g.

The preparation of photographic silver halide emulsions substantially comprises three steps:

1. Precipitation of the silver halide in the presence of a protective colloid and physical ripening.
2. Removal from the emulsion of excess water-soluble salts introduced during precipitation, generally by washing, and
3. Chemical ripening or after-ripening, which serves to impart the desired sensitivity to the emulsion.

The sensitizing dyes according to the present invention can be used in any silver halide emulsions. Suitable silver halides are silver chloride, silver bromide or mixtures thereof, if desired containing a small amount of silver iodide up to 10 mols percent. The silver halides may be dispersed in the usual hydrophilic compounds, for example, carboxymethylcellulose, polyvinyl alcohol, polyvinyl pyrrolidone, alginic acid and its salts, esters or amides or preferably gelatin.

The sensitizing dyes to be used according to the present invention are advantageously added to the photographic emulsion after the chemical ripening and before casting. The methods employed for this are generally known to persons skilled in this art. The sensitizing dyes are generally incorporated in the emulsion in the form of solutions, e.g., in alcohol or mixtures of alcohol and water. The solvents must, of course, be compatible with gelatin and must not have any adverse effects on the photographic properties of the emulsion. Water, methanol or mixtures thereof are generally used as solvents. The quantity of sensitizing dye added may vary within wide limits, e.g., between 2 and 200 mg. preferably between 10 and 60 mg. per kg. of the silver halide emulsion. The concentration of dye may be adapted to the particular requirements, depending on the type of emulsion, the desired sensitizing effect etc. The most suitable concentration for any given emulsion can easily be determined by the usual tests employed in the art of emulsion making.

The emulsions may also contain chemical sensitizers, e.g., reducing agents such as stannous salts, polyamines such as diethylentriamine, or sulfur compounds as described in U.S. Pat. No. 1,574,944. Furthermore, salts of noble metals, such as ruthenium rhodium, palladium, iridium, platinum or gold may be contained in the emulsions for chemical sensitization, as described in the article by R. Koslowsky, Z. Wiss. Phot. 46, 65–72 (1951). The emulsions may also contain, as chemical sensitizers, polyalkylene oxides, especially polyethylene oxide and derivatives thereof.

The emulsions according to the present invention may contain the usual stabilizers such as homopolar or salt-type compounds of mercury with aromatic or heterocyclic rings, such as mercaptotriazoles, simple mercury salts, sulfonium mercury double salts and other mercury compounds. Other suitable stabilizers are azaindenes, especially tetra- or pentaaza-indenes, in particular those that are substituted with hydroxyl or amino groups. Compounds of this type are described in the article by Birr, Z. Wiss. Phot. 47, 2–58 (1952). Other suitable stabilizers include heterocyclic mercapto compounds, e.g., phenylmercaptotetrazole, quaternary benzothiazole derivatives and benzotriazole.

The emulsions may be hardened in the usual manner, for example, with formaldehyde or by use of halogen-substituted aldehydes which contain a carboxyl group, e.g., mucobromic acid, diketones, methanesulfonic acid esters and dialdehydes.

The emulsions according to the invention may be used for all sorts of different photographic processes, for example, for copying materials, for reproduction photography, for X-ray films, for materials which are suitable for use in the silver salt diffusion process, for color photographic materials for the silver dye bleaching process, etc.

The sensitizers to be used according to the invention may also be used in the spectral sensitization of electrophotographic layers, especially layers which contain photoconductive zinc oxide distributed in an insulating binder.

EXAMPLE

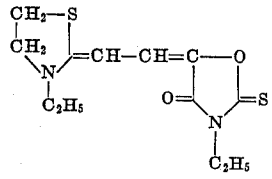
30 mg. of a sensitizing dye identified in the following table are added to a conventional photographic silver chlorobromide gelatine emulsion containing 80 mol percent of silver-bromide. The emulsion is applied onto a barytacoated paper support and dried.

The light-sensitive layer is exposed for 10 seconds in a sensitometer customarily employed in the art behind a step wedge ($\sqrt[3]{2}$ wedge), and development is performed for 2 minutes in a developer of the following composition:

Water	1,000 ml.
p-methylaminophenol	1 g.
hydroquinone	3 g.
sodium sulfite, anhydrous	13 g.
sodium carbonate, anhydrous	26 g.
potassium bromide	1 g.

The excellent intensity of sensitization of the dyes is shown in the following table. In order to demonstrate the excellent stability of the dyes under tropical conditions, the table also shows the number of steps obtained under similar conditions but after storage of the unexposed emulsion layer under tropi-

cal conditions (7 days, 40° C. relative humidity 85 percent). The dye of the following formula:



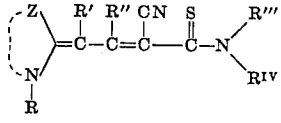
which is known to be highly effective was used for comparison.

TABLE

Dye	Steps in fresh sample	Steps after storage under tropical conditions
comparison dye	23	19
Dye No. 4	24	24
Dye No. 16	24	24
Dye No. 22	25	25
Dye No. 25	25	25
Dye No. 35	25	25
Dye No. 43	23	23

We claim:

1. A spectrally sensitized photographic silver halide emulsion spectrally sensitized by a sensitizer of the following formula:



wherein:

Z represents the nonmetallic ring members necessary for completing a heterocyclic ring of the thiazole-, oxazole-, imidazole-, thiadiazole-, pyridine-, dialkylindolenine-, oxazoline-, selenazole and thiazoline- series;

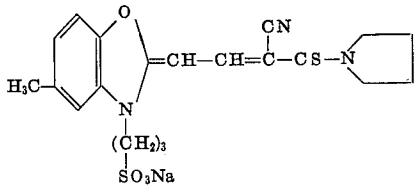
R represents a saturated or olefinically unsaturated aliphatic group, cycloalkyl, aralkyl or phenyl;

R', R'' represent hydrogen or alkyl;

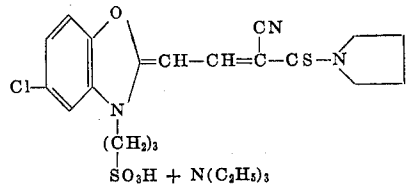
R''', R^{IV} represent hydrogen, a saturated or olefinically unsaturated aliphatic group, cycloalkyl, aryl or aralkyl group; R''' and R^{IV} together may represent the ring member necessary for completing a heterocyclic ring selected from the group consisting of pyrolidine, piperidine, morpholine, piperazine and mexamethyleneimine

2. A silver halide emulsion as defined in claim 1 wherein Z represents the ring members necessary for completing a benzoxazole-, benzthiazole- or benzimidazole group.

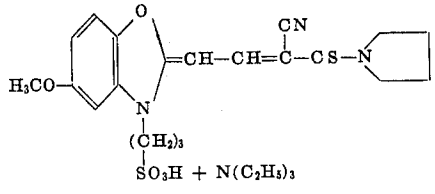
3. A silver halide emulsion as defined in claim 1 in which the sensitizer has the following formula:



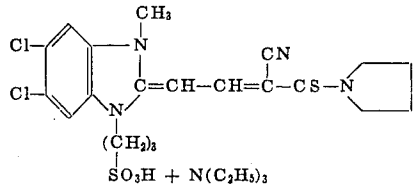
4. A silver halide emulsion as defined in claim 1 in which the sensitizer has the following formula:



5. A silver halide emulsion as defined in claim 1 in which the sensitizer has the following formula:



6. A silver halide emulsion as defined in claim 1 in which the sensitizer has the following formula:



7. A silver halide emulsion as defined in claim 1 in which the sensitizer has the following formula: