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3,796,580

SPECTRALLY SENSITIZED LIGHT SENSITIVE SILVER HALIDE MATERIAL

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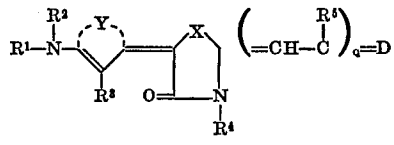
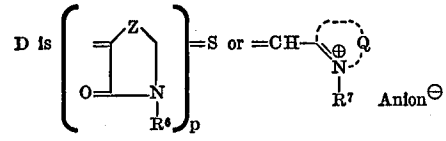
Claims priority, application Germany, Apr. 10, 1970, P 20 17 206.9
Int. Cl. G03c 1/10
U.S. Cl. 96—127 1 Claim

ABSTRACT OF THE DISCLOSURE

Excellent spectral sensitization of silver halide photographic materials with improved stability to elevated temperature and moisture is effected by trimethine hemioxonoles if the three carbon atoms of the trimethine chain form part of a 5- or 6-membered isocyclic ring. The sensitizing dyes have the formula:



wherein



and the other symbols have the meaning given in the description.

The present invention relates to light-sensitive photographic materials which are spectrally sensitized with new types of sensitizing dyes, and more particularly to materials of this type which contain silver halide emulsion layers.

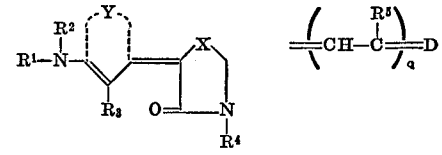
It has already been known for a long time to increase the sensitivity of light sensitive photographic materials, especially those materials which contain silver halide emulsion layers, by adding substances which increase the spectral range of sensitivity of the light sensitive substances. Numerous substances for the sensitization of silver halide emulsion layers have already been described; these substances mainly belong to the class of cyanine dyes. These known substances, however, often have disadvantages, for example their sensitization effect may be insufficient or they may impart an unwanted color to the layer or they may adversely affect the photographic process itself. This applies more particularly to specialized photographic materials. The adsorption on the silver halide should be of such a strength that the sensitizing effect is disturbed very little by other necessary additives such as wetting agents and emulsifiers, stabilizers, color couplers, dyes which can be bleached or white toners. Moreover, the sensitization should be reliable even under extreme conditions such as conditions of high temperature and moisture and the sensitizing dyes should not increase the basic fogging as is occasionally the case with basic cyanine dyes. The sensitizing dyes are also required to have certain sensitization properties such as sufficient intensity or sensitization in the sensitization range and above all a very steep drop in sensitization in the transition to light of longer wavelengths. For these reasons, there is considerable interest in finding new sensitization dyes which do not have the preceding disadvantages.

It has been known for a long time that trimethine hemioxonols have a very good sensitizing effect in silver

halide emulsions. However, this sensitization effect has been found to be unstable at elevated temperature and elevated moisture conditions, and these compounds have, therefore, not been used in practice as spectral sensitizers.

It has now been found that considerably more stable sensitization can be achieved with such trimethine hemioxonols if the three methine carbon atoms of the trimethine chain form part of a 5-membered or 6-membered isocyclic ring.

This invention therefore relates to a light sensitive photographic material comprising at least one silver halide emulsion layer, which contains a sensitizing dye of the following general formula:

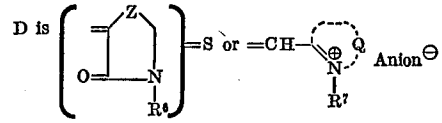


in which the symbols have the following meaning:

Y is an aliphatic hydrocarbon radical required for completing a 5-membered or 6-membered ring, e.g.

$$-(CH_2)_2-$$

$$-(CH_2)_3- \text{ or } -CH_2-CR^3{}_2-CH_2-;$$



R^1 and R^2 are (1) hydrogen (2) saturated or unsaturated aliphatic hydrocarbon groups which preferably have up to 6 C atoms and which may be substituted e.g. with phenyl, hydroxyl, alkoxy, amino, quaternary ammonium, halogen, cyanogen or carboxyl, (3) cycloalkyl, for example cyclohexyl or (4) aryl, especially phenyl; and can be the same or different; furthermore, R^1 and R^2 may represent a heterocyclic ring together with nitrogen atom, e.g. a pyrrolidine, piperidine, hexamethyleneimine, morpholine, thiomorpholine, piperazine, phenomorpholine or tetrahydroquinoline ring;

R^3 is hydrogen or saturated or unsaturated aliphatic hydrocarbon groups, preferably having up to 6 C atoms, for example methyl, ethyl, propyl or butyl; or aryl, especially phenyl;

R^4, R^6 and R^8 are (1) hydrogen (2) saturated or olefinically unsaturated aliphatic hydrocarbon groups preferably having up to 6 C atoms which may be substituted, e.g. with phenyl, hydroxyl or carboxyl, (3) cycloalkyl, example cyclohexyl, or (4) aryl, especially phenyl; and can be the same or different;

R^5 is hydrogen, alkyl, alkoxy or alkylthio preferably having up to 3 C atoms, for example methyl, methoxy or methylthio; or aryl, for example phenyl;

R^7 is (1) saturated or unsaturated aliphatic hydrocarbon groups preferably having up to 6 C atoms, which groups may be substituted, e.g. with phenyl, hydroxyl, halogen, amino, carboxyl, sulfo, sulfonyl amino, sulfamyl, carbonamido, carbamyl, carbalkoxy, sulfate or thiosulfate (2) cycloalkyl such as cyclohexyl or (3) aryl, especially phenyl;

X and Z may be identical or different and may represent —O—, —S—, —NR^8— or —CO—NR^8—

p and *q* are identical or different and represent 0 or 1;

Anion$^\ominus$ is any anion, e.g. a halide, such as chloride, bromide or iodide, perchlorate, sulfate, methylsulfate, p-toluenesulfonate and the like; the anion is not present in cases where R^7 contains an acid group in the anionic form so that a betaine is present;

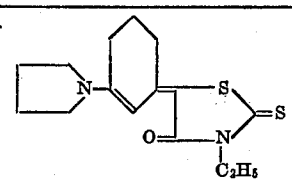
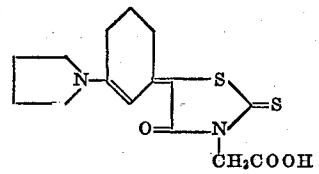
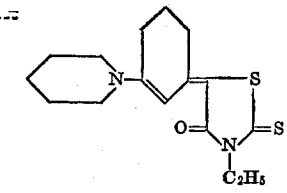
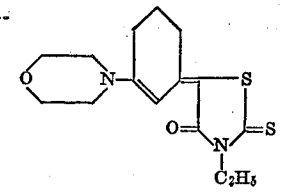
Q=a radical required for completing a heterocyclic group comprising a 5-membered or 6-membered heterocyclic

ring; the heterocyclic group may contain a condensed benzene or naphthalene ring and other substituents; suitable heterocyclic groups include those commonly found in cyanine chemistry,

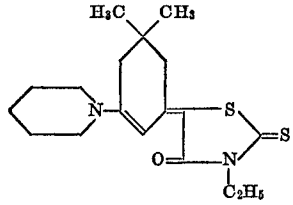
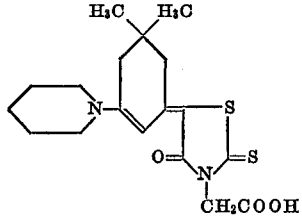
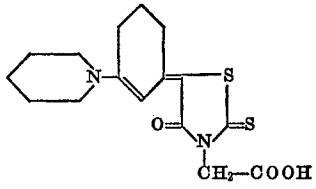
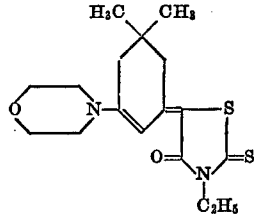
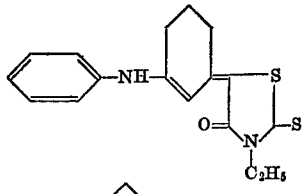
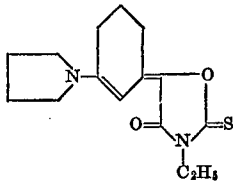
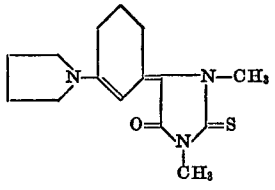
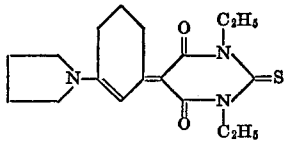
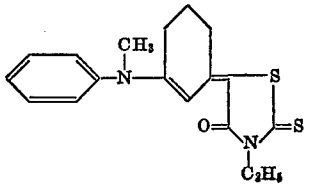
for example those of the thiazole series (e.g. thiazole, 4-methylthiazole, 5-methylthiazole, 4,5-dimethylthiazole, 4-phenylthiazole, 5-phenylthiazole, 4,5 - diphenylthiazole, benzothiazole, 4 - chlorobenzothiazole, 5 - chlorobenzothiazole, 6 - chlorobenzothiazole, 7 - chlorobenzothiazole, 6 - bromobenzothiazole, 5 - iodobenzothiazole, 6 - iodobenzothiazole, 4 - methylbenzothiazole, 5 - methylbenzothiazole, 6 - methylbenzothiazole, 5,6 - dimethylbenzothiazole, 4 - phenylbenzothiazole, 5-phenylbenzothiazole, 6 - phenylbenzothiazole, 5-hydroxybenzothiazole, 6 - hydroxybenzothiazole, 4 - methoxybenzothiazole, 5-methoxybenzothiazole, 6 - methoxybenzothiazole, 5 - ethoxybenzothiazole, 6 - ethoxybenzothiazole, 5,6 - dimethoxybenzothiazole, 5,6 - methylenedioxybenzothiazole, 5 - diethylaminobenzothiazole, 6 - diethylaminobenzothiazole, 5-carboxybenzothiazole, 5 - sulfobenzothiazole, tetrahydrobenzothiazole, 7 - oxotetrahydrobenzothiazole, naphtho[1,2-d]thiazole, naphtho[2,1-d]thiazole, 5-methoxynaphtho[2,1-d]thiazole, 5 - ethoxynaptho[2,1-d]thiazole, 7-methoxynaphtho[2,1-d]thiazole or 8 - methoxynaphtho[1,2-d]thiazole thiazoline or 4-methyl thiazoline); those of the selenazole series (e.g. 4-methylselenazole or 4-phenylselenazole, benzoselenazole, 5 - chlorobenzoselenazole, 5,6 - dimethylbenzoselenazole, 5 - hydroxybenzoselenazole, 5 - methoxybenzoselenazole, tetrahydrobenzoselenazole, naphtho[1,2-d]selenazole or naphtho[2,1-d] selenazole); those of the oxazole series (e.g. oxazole, 4-methyloxazole, 4 - phenyloxazole, 4,5-diphenyloxazole, benzoxazole, 5 - chlorobenzoxazole, 6-chlorobenzoxazole, 5,6 - dimethylbenzoxazole, 5 - phenylbenzoxazole, 5-hydroxybenzoxazole, 5 - methoxybenzoxazole, 5 - ethoxybenzoxazole, 6 - dialkylaminobenzoxazole, 5 - carboxybenzoxazole, 5 - sulfonbenzoxazole, 5 - sulfonamidobenzoxazole, 5 - β - carboxyvinylbenzoxazole, naphtho[1,2-d] oxazole, naphtho[2,1-d]oxazole or naphtho[2,3-d]oxazole); those of the imidazole series including benzimidazoles and naphthimidazoles (e.g. 1 - methylimidazole, 1 - ethyl - 4 - phenyl - imidazole, 1 - butyl-,4,5-dimethylimidazole, 1 - methylbenzimidazole, 1 - butyl - 4 - methylbenzimidazole, 1 - ethyl - 5,6 - dichlorobenzimidazole, 1 - ethyl - 5 - trifluoromethylbenzimidazole, 1 - methylnaphtho[1,2-d]imidazole or 1 - ethyl - naphtho[2,3-d] imidazole; those of the 3,3 - dialkylindolenine series (e.g. 3,3 - dimethylindolenine, 3,3,5-trimethylindolenine or 3,3-dimethyl - 5 -methoxyindolenine); those of the pyridine series (e.g. pyridine, 3 - methylpyridine, 4 - methylpyridine, 5 - methylpyridine, 6 - methylpyridine, 3,4-dimethylpyridine, 3,5 - dimethylpyridine, 3,6 - dimethylpyridine, 4,5 - dimethylpyridine, 4,6 - dimethylpyridine, 4 - chloropyridine, 5 - chloropyridine, 6 - chloropyridine, 3 - hydroxypyridine, 4 - hydroxypyridine, 5 - hydroxypyridine, 6 - hydroxypyridine, 3 - phenylpyridine, 4 - phenylpyridine or 6 - phenylpyridine, 3 - chloropyridine or 3 - hydroxypyridine); those of the quinoline series (e.g. quinoline, 3 - methylquinoline, 5 - methylquinoline, 7 - methylquinoline, 8 - methylquinoline, 6 - chloroquinoline, 8-chloroquinoline, 6 - methoxyquinoline, 6 - ethoxyquinoline, 6-hydroxyquinoline, 8 - hydroxyquinoline or 5 - oxo-5,6,7,8-tetrahydroquinoline); those of the isoquinoline series (e.g. isoquinoline or 3,4 - dihydroisoquinoline); and those of the pyrroline, tetrahydropyridine, thiadiazole, oxadiazole, pyrimidine, triazine or benzothiazine series.

The heterocyclic groups may in addition be substituted by any other substituents, e.g. by additional alkyl groups which preferably have up to 3 C atoms, e.g. methyl or ethyl, or halogen such as chlorine or bromine, hydroxyl, alkoxy, preferably with up to 3 C atoms such as methoxy or ethoxy, hydroxyalkyl, alkylthio, aryl such as phenyl, or aralkyl such as benzyl, amino, substituted amino and the like.

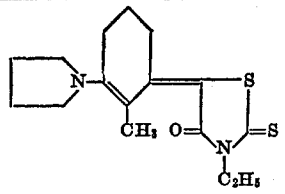
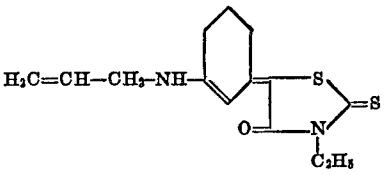
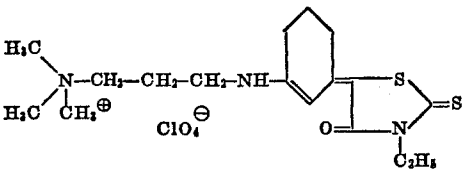
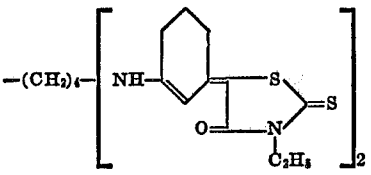
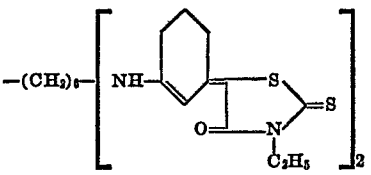
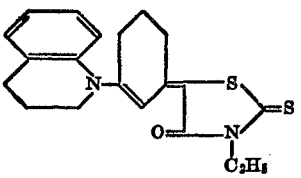
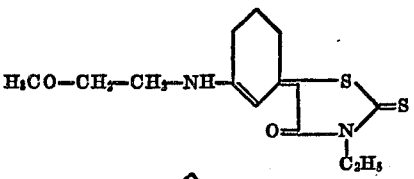
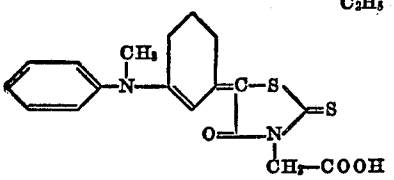
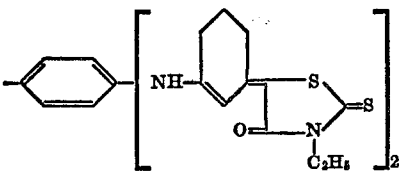
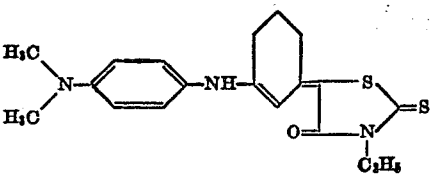
The following are examples of suitable compounds. The absorption maxima were measured in methanolic solution unless otherwise indicated. DMF in the following table denotes dimethylformamide, and nm. denotes millimicrons.

No.	Dye	Absorption maximum (nm.)	Sensitization maximum (nm.)
1		484	535
2		482	532
3		488	535
4		480	540

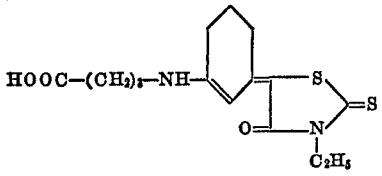
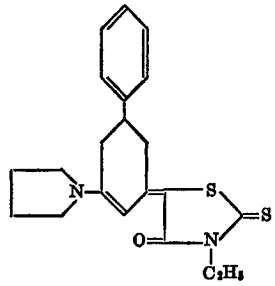
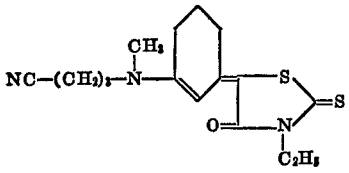
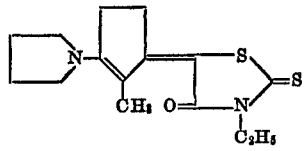
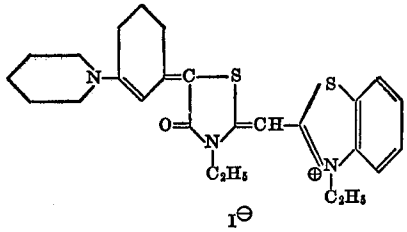
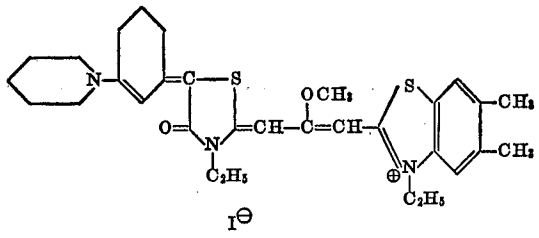
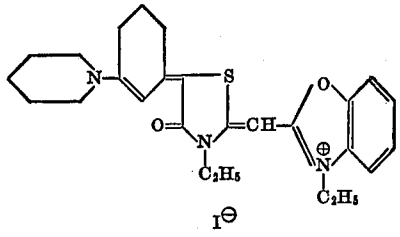
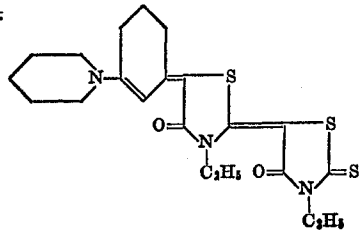
TABLE—Continued

No.	Dye	Absorption maximum (nm.)	Sensitization maximum (nm.)
5		490	584
6		488	538
7		486	535
8		481	535
9		467 (CHCl3)	535
10		451	503
11		463	502
12		451	465
13		480 (CHCl3)	540

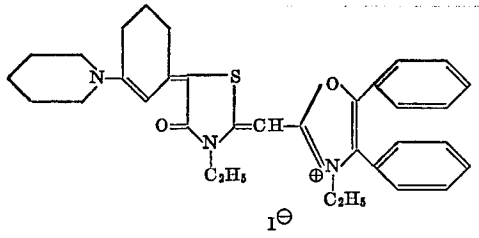
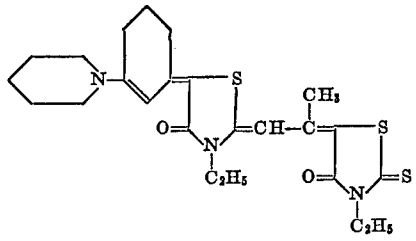
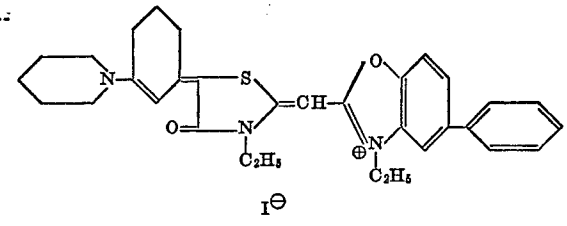
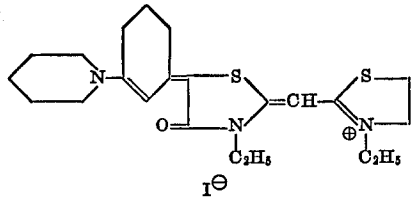
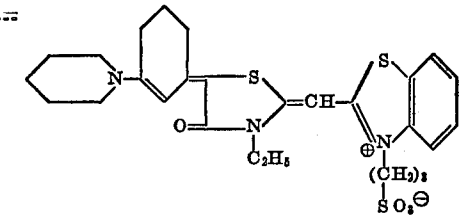
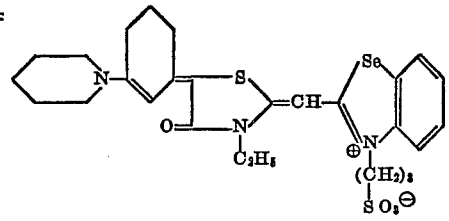
TABLE—Continued

No.	Dye	Absorption maximum (nm.)	Sensitization maximum (nm.)
14		492 ($CHCl_3$)	530
15		469	525
16		469	524
17		476	525
18		473 (DMF)	528
19		497 (DMF)	562
20		460	505
21		475	540
22		507 (DMF)	565
23		461	499

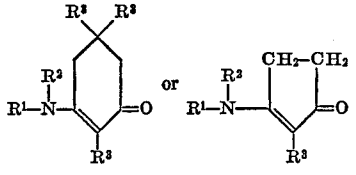
TABLE—Continued

No.	Dye	Absorption maximum (nm.)	Sensitization maximum (nm.)
24		471	520
25		485	539
26		476	531
27		467	515
28		556	590
		610	645
30		542	572
31		546 (CHCl$_3$)	600

TABLE—Continued

No.	Dye	Absorption maximum (nm.)	Sensitization maximum (nm.)
32		537	560
33		610 ($CHCl_3$)	705
34		547	580
35		533	558
36		558	588
37		560	590

The starting materials for the preparation of the dyes according to the invention are 1-aminocyclohexenone-3 or 1-aminocyclopentenone-3 represented by the following formulae:



in which R^1, R^2 and R^3 have the meaning already indicated. 1-aminocyclohexenone-3 and 1-aminocyclopentenone-3 can easily be prepared by the condensation of dihydroresorcinols or cyclopentadiones with amines.

1-pyrrolidino-cyclohexenone-3

A mixture of 112 g. of dihydroresorcinol and 71 g. of pyrrolidine in 1 l. of dry benzene is heated in an apparatus equipped with reflux condenser and water separator until 18 ml. of water have separated. The benzene is evaporated off under vacuum and the residue is recrystallized from ligroin. 98 g. of 1-pyrrolidino-cyclohexenone-3 of melting point 85° C. to 86° C. are obtained.

The dyes according to the invention are prepared by quaternizing 1-aminocycloalkenone-3 and condensing the resulting compound by known methods with ketomethyl-

ene compounds, for example with N-ethylrhodanine. The multi-nuclear dyes are obtained by again quaternizing the resulting hemioxonoles and reacting the resulting compounds with ketomethylene compounds or with 2-methyl-quaternary salts of heterocyclic bases.

The preparation of some of the dyes is described in detail below.

Dye 1: 1.6 g. of pyrrolidino-cyclohexenone-3 and 1 ml. of dimethylsulfate are heated in an oil bath to 100° C. the reaction temperature rising to 120° C. Without isolating the quaternary salt, the reaction mixture is heated on a steam bath for 5 minutes with 1.6 g. of N-ethylrhodanine in 15 ml. of ethanol with the addition of 2 ml. of triethylamine, the dye partly precipitating in the process. The mixture is cooled and the dye is isolated by suction filtration and recrystallized twice, each time from 40 ml. of ethanol with the addition of active charcoal. Yield 1.4 g., M.P. 179° C. to 180° C.

Dye 28: 3.2 g. of Dye 3 and 4.2 g. of ethyl p-toluenesulfonate are heated on an oil bath to 130° C. for 20 minutes. The mixture is cooled and heated on a steam bath for 10 minutes with 3.4 g. 2-methyl-3-ethyl-benzothiazolium-p-toluene sulfonate in 20 ml. of ethanol with the addition of 2 ml. of triethylamine. The mixture is cooled, the dye is precipitated in the form of an oil with ether, the solution is decanted and the residue is triturated with potassium iodide solution. The dye is isolated by suction filtration and recrystallized from methanol. 3.8 g., M.P. 199° C. to 201° C.

Dye 31: 3.2 g. of Dye 3 are quaternized by the method described for Dye 28 and heated on a steam bath for 10 minutes with 1.6 g. of N-ethylrhodanine in 20 ml. of alcohol and 2 ml. of triethylamine. The dye crystallizes on cooling. After recrystallization from 100 ml. of chloroform, 3.7 g. of the dye which has a melting point of 279 to 281° C. are obtained.

The sensitizing dyes according to the invention may be used in any silver halide emulsions. Suitable silver halides are silver chloride, silver bromide or mixtures of these salts, optionally with a small silver iodide content of 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 in gelatin.

The sensitizing dyes to be used according to the present invention are advantageously added to the photographic emulsion after chemical ripening and before casting. The methods used for this are generally known in the art. The sensitizing dyes are generally incorporated in the emulsion in the form of solutions. The solvents must, of course, be compatible with gelatin and must not have any adverse effect on the photographic properties of the emulsion. Water, methanol, ethanol, acetone or mixtures of these substances are generally used as solvents. The quantity of sensitizing dye added may vary within wide limits, e.g. between 10 and 1000 mg./mol of silver halide, and the amount used is preferably between 30 and 300 mg./mol of silver halide. The concentration of the dye may be adjusted to the individual requirements depending on the nature of the emulsion, and the sensitizing effect required. The most suitable concentration for any given emulsion can easily be determined by the usual tests employed in photography.

The emulsions may also be chemically sensitized, e.g. by the addition of compounds which contain sulfur at the stage of chemical ripening, for example compounds such as allylisothiocyanate, allylthiourea or sodium thiosulfate. Reducing agents, e.g. the tin compound described in Belgian Patents 493,464 and 568,687 or polyamines such as diethylenetriamine or aminomethylsulfinic acid derivatives, e.g. as described in British patent specification 789,823, may also be used as chemical sensitizers.

Noble metals and noble metal compounds, e.g. gold, platinum, palladium, iridium, ruthenium or rhodium are also suitable for use as chemical sensitizers. This method of chemical sensitization has been described in the article by R. Koslowsky, Z. Wiss. Phot. 46, 65–72 (1951).

The emulsions may also be sensitized with polyalkylene oxide derivatives, e.g. with polyethylene oxide having a molecular weight of between 1000 and 20,000, or with condensation products of alkylene oxide and aliphatic alcohols, glycols or cyclic dehydration products of hexitols or with alkyl substituted phenols, aliphatic carboxylic acids, aliphatic amines, aliphatic diamines and amides. The condensation products have a molecular weight of at least 700 and preferably more than 1000. These sensitizers may, of course, be combined to achieve special effects, as described in Belgian Pat. 537,278 and in British patent specification 727,982.

The emulsions may also contain other spectral sensitizers in addition, e.g. the usual polymethine dyes such as merocyanines, basic or acid carbocyanines, rhodacyanines, hemicyanines, styryl dyes, oxonoles and the like. Sensitizers of this type have been described in the work by F. M. Hamer "The Cyanine Dyes and Related Compounds," (1964).

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

The emulsions may be hardened in the usual manner, for example with formaldehyde or halosubstituted aldehydes which contain a carboxyl group, e.g. mucobromic acid, diketones, methanesulfonic acid esters or dialdehydes.

The emulsions according to the present invention may be used for various photographic recording materials, in printing materials, in film used for reproduction photography, in X-ray films, in materials which are suitable for the silver salt diffusion process, in color photographic materials or in photographic materials for the silver dye bleaching process.

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

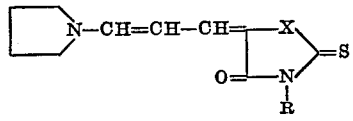
Example

30 mg. of each of the sensitizing dyes mentioned in the following table are added to a silver chlorobromide emulsion containing 29.5 g. of silver per kg. The emulsion is in each case cast on a baryta paper support in the usual manner and dried. The light sensitive layer thus formed is exposed behind a grey step wedge ($\sqrt[3]{2}$ steps) for 10 seconds and then developed for 2 minutes in a developer of the following composition:

	G.
p-Methylaminophenol	1
Hydroquinone	3
Anhydrous sodium sulfite	13
Anhydrous sodium carbonate	26
Potassium bromide	1
Water up to 1000 ml.	

The outstanding intensity of sensitization obtained with the dyes according to the invention is clear from the following table. The number of visible steps is a measure of the relative sensitivity of the sensitized emulsions. The excellent stability of the dyes under tropical conditions is also indicated in the table by the number of visible steps obtained when the materials had been stored in a tropical cupboard (4 days, 40° C., 85% relative humidity) before

being processed. For comparison, the known hemi-oxonols (I), (II) and (III) represented by the following formula were included in the table:

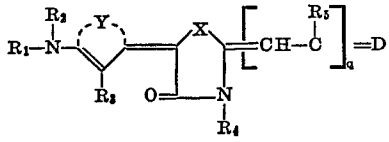


(I) X=S, R=C_2H_5,
(II) X=O, R=C_2H_5,
(III) X=NCH_3, R=C_6H_5.

Dye	Relative sensitivity ($\sqrt{2}$ steps) Fresh sample	After storage in tropical cupboard
Comparison dye I	27	26
Comparison dye II	25	22
Comparison dye III	25	23
Dye 1	28	28
Dye 10	25	24
Dye 11	25	25
Dye 4	28	28
Dye 7	27	28
Dye 27	26	27

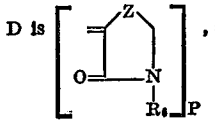
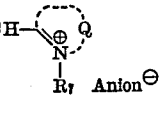
What is claimed is:

1. A photographic silver halide emulsion which contains an effective amount of a sensitizing dye of the following formula:



in which

Y is an aliphatic hydrocarbon required for completing a 5-membered or 6-membered ring;

D is  , =S, or =CH— 

R_1 and R_2 are (1) hydrogen, (2) saturated or unsaturated aliphatic hydrocarbon groups having up to 6 carbon atoms and which may be substituted with quaternary ammonium, alkoxy, carboxyl or cyano, (3) cycloalkyl and (4) aryl, and be the same or different, and together with the nitrogen atom to which they are linked represent a heterocyclic ring;

R_3 is hydrogen or saturated or unsaturated aliphatic hydrocarbon groups having up to 6 C atoms;

R_4, R_6 and R_8 are (1) hydrogen, (2) saturated or olefinically unsaturated aliphatic hydrocarbon groups having up to 6 C atoms, which may be substituted with carboxyl, (3) cycloalkyl or (4) aryl, and can be the same or different;

R_5 is hydrogen or alkyl, alkoxy or alkylthio having up to 3 C atoms or aryl;

R_7 is (1) a saturated or unsaturated aliphatic hydrocarbon group having up to 6 C atoms, which may be substituted with carboxyl or sulfo; (2) cycloalkyl or (3) aryl;

X and Z may be identical or different and represent O, S NR^8 or CO—NR^8;

p and *q* may be identical or different and represent 0 or 1;

Anion$^{\ominus}$ is an anion and can be the anion of an acid group on R_7; and

Q is a radical required for completing a heterocyclic group having a 5-membered or 6-membered heterocyclic ring.

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J. TRAVIS BROWN, Primary Examiner

U.S. Cl. X.R.

96—139, 140, 142; 260—240.1, 240.4