United States Patent [19]

Öhlschläger et al.

[11] **3,844,798**

[45] **Oct. 29, 1974**

[54] **SPECTRALLY SENSITIZED LIGHT-SENSITIVE SILVER HALIDE PHOTOGRAPHIC MATERIAL**

[75] Inventors: **Hans Öhlschläger,** Koeln; **Oskar Riester,** Leverkusen; **Johannes Götze,** Bergisch-Neukirchen; **Alfons Dorlars,** Leverkusen, all of Germany

[73] Assignee: **Agfa-Geveert Aktiengesellschaft,** Levenkusen, Germany

[22] Filed: **May 8, 1972**

[21] Appl. No.: **251,414**

Related U.S. Application Data

[63] Continuation of Ser. No. 47,157, June 17, 1970.

[30] **Foreign Application Priority Data**

July 10, 1969 Germany 1934891

[52] **U.S. Cl.** **96/127,** 96/139, 96/140, 260/240.1

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

[58] **Field of Search** 96/127, 139, 140

[56] **References Cited**

UNITED STATES PATENTS

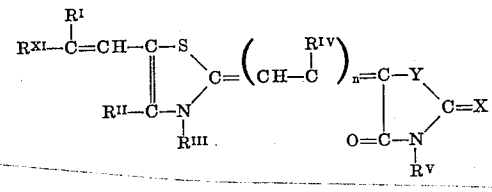
3,656,958	4/1972	Deporter et al.	96/139
3,672,897	6/1972	Sato et al.	96/140
3,702,767	11/1972	Ohlschlager et al.	96/127

Primary Examiner—J. Travis Brown

Attorney, Agent, or Firm—Connolly and Hutz

[57] **ABSTRACT**

Light-sensitive photographic materials, preferably containing light-sensitive silver halide emulsion layers, can be spectrally sensitized by new sensitizing dyes which are derivatives of 5-β-carboxyvinylthiazole and have the formula:



wherein the symbols R^{I}, R^{II}, R^{III}, R^{IV}, R^{V}, R^{XI}, X and *n* have the meaning given in the description.

5 Claims, No Drawings

SPECTRALLY SENSITIZED LIGHT-SENSITIVE SILVER HALIDE PHOTOGRAPHIC MATERIAL

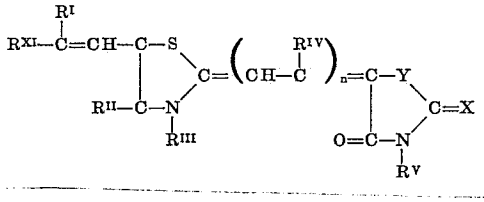
This application is a continuation of the copending, now abandoned, U.S. application Ser. No. 47,157 filed June 17, 1970 entitled "Spectrally Sensitized Light-Sensitive Photographic Material."

The invention relates to a light-sensitive photographic material, in particular to a photographic material containing silver halide emulsion layers, which are spectrally sensitized with new types of sensitizing dyes.

Increasing the sensitivity of light-sensitive layers, in particular of silver halide emulsion layers, by the addition of substances which widen the spectral sensitivity range of light-sensitive substances have been known for a long time. Many substances, mainly belonging to the class of cyanine dyes, have been proposed for sensitizing silver halide emulsion layers. These known substances, however, often have disadvantages, for example their sensitizing effect is insufficient, they impart an interfering color to the layer, or they adversely influence the photographic process. This applies particularly to special photographic processes or to special photographic materials. The absorption of silver halide should be sufficiently strong so that the sensitizing effect is as far as possible not altered by other necessary additives such as wetting agents and emulsifiers, stabilizers, color-forming couplers, dyes which can be bleached out and white toners. The sensitizing effect must also be ensured under extreme conditions such as elevated temperature and moisture. Furthermore, the sensitizing dyes must not cause any additional increase in the basic fog which is present, as is the case with basic cyanine dyes. Furthermore, the sensitizing dyes are required to have certain sensitizing properties, one of the most important of which, apart from an adequate intensity of sensitization, is a steep drop in the sensitization range. For the reasons mentioned above, there is considerable interest in finding new sensitizing dyes which do not have the above mentioned disadvantages.

It is the object of the invention to find sensitizing dyes for the sensitization of light-sensitive layers, in particular of silver halide emulsion layers, which do not have the disadvantage mentioned above.

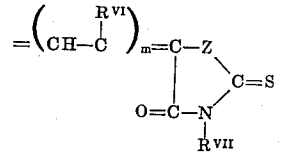
A photographic material comprising at least one spectrally sensitized silver halide emulsion layer has now been found which contains a sensitizer of the following formula:



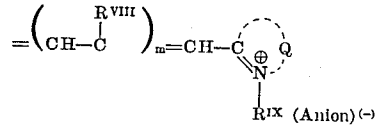
in which

X is a sulfur atom or groups of the following formulae:

(a)



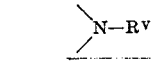
(b)



(c)

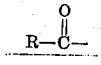


Y and Z which may be the same or different, are an oxygen or sulfur atom or a group



or $-CO-NR^{VII}-$;

R^{XI} is a nitrile or a



group;

R is a hydroxy group, an alkoxy group, preferably containing up to six carbon atoms, an amino group which may be substituted, e.g. with one or two short chain alkyl groups such as methyl, or a five-membered or six-membered saturated ring which is attached to the carbonyl group by a ring nitrogen atom, e.g. a pyrrolidinyl or piperidinyl group;

R^{I} is a hydrogen atom or a nitrile group;

R^{II} is a hydrogen atom or an alkyl group preferably containing up to six carbon atoms, a cycloalkyl group such as a cyclohexyl group, an aryl group, preferably a phenyl or naphthyl group, an aralkyl group, preferably a benzyl or phenylethyl group;

R^{III} and R^{IX} which may be the same or different are

1. a saturated or an olefinically unsaturated aliphatic group preferably containing up to six carbon atoms which may be substituted with phenyl, carboxyl, sulfonic acid, sulfonamide, carbamoyl, esterified carboxyl, sulfonic acid ester, hydroxyl, sulfato or amino group,
2. a cycloalkyl group such as a cyclohexyl or cyclopentyl group, or
3. an aryl group in particular a radical of the phenyl series;

R^{IV} is a hydrogen atom or an alkyl group preferably containing up to three carbon atoms;

R^{V} and R^{VII} which may be the same or different, are

1. a hydrogen atom,
2. a saturated or an olefinically unsaturated aliphatic group which may be substituted with phenyl, hydroxyl or carboxyl groups,
3. a cycloalkyl group such as a cyclohexyl or cyclopentyl group, or
4. an aryl group such as a phenyl or naphthyl group;

R^{VIII} is

1. a hydrogen atom;

2. a saturated or an olefinically unsaturated aliphatic group preferably containing up to three atoms;
3. a cycloalkyl group such as a cyclohexyl or cyclopentyl group;
4. an aryl group especially a phenyl group;
5. an alkoxy group preferably containing up to three carbon atoms, such as a methoxy or ethoxy group, or
6. an alkylthio group preferably containing up to three carbon atoms, e.g. a methylthio or ethylthio group;

R^X is a CN, carboxylic acid ester or thiocarboxylic acid amide group;

n is 0, 1 or 2; and

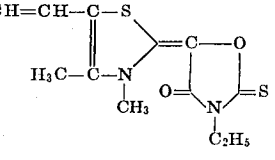
m is 0 or 1;

anion may be any anion and depends substantially on the nature of the method used for preparing the compound, suitable anions being e.g. halogen ions such as Cl^-, Br^- or I^-; the anion is absent if R^{IX} is an acid group such as carboxyl or sulfonic acid so that the radical is a betaine radical;

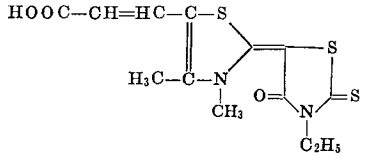
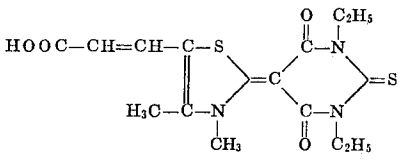
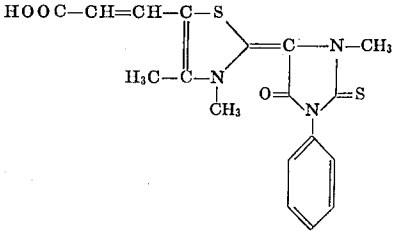
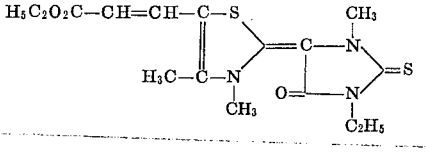
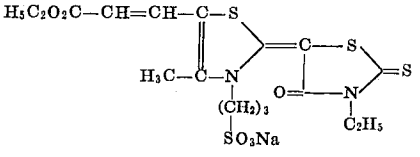
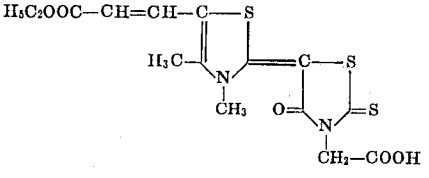
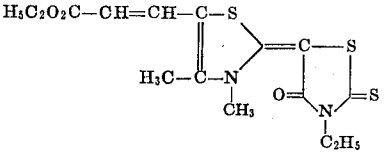
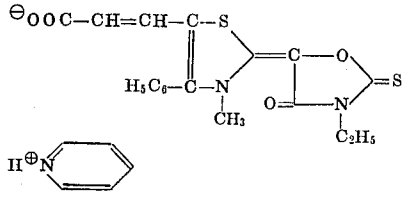
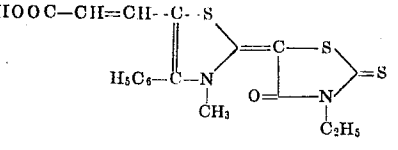
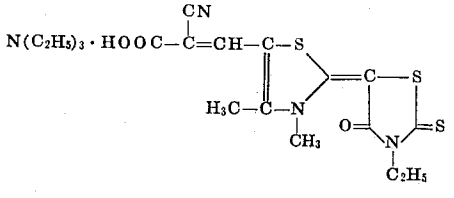
Q ia the non-metallic ring members required to complete a ring, preferably a five- or six-membered, but also a higher membered heterocyclic ring, which may contain a condensed benzene or naphthalene ring, and which may be further substituted, suitable are the heterocyclic rings of cyanine chemistry such as those of the thiazole series thiazole, 4-methylthiazole, 5-methylthiazole, 4-phenylthiazole, 4.5-diphenylthiazole, benzothiazole, 4-chlorobenzothiazole, 5-chlorobenzothiazole, 6-chlorobenzothiazole, 7-chlorobenzothiazole, 4-methylbenzothiazole, 5-methylbenzothiazole, 6-methylbenzothiazole, 5,6-dimethylbenzothiazole, 6-bromobenzothiazole, 4-phenylbenzothiazole, 5-phenylbenzothiazole, 4-methoxybenzothiazole, 5-methoxybenzothiazole, 6-methoxybenzothiazole, 5-iodobenzothiazole, 6-iodobenzothiazole, 6-ethoxybenzothiazole, 5-ethoxybenzothiazole, tetrahydrobenzothiazole, 5,6-dimethoxybenzothiazole, 5,6-methylene dioxybenzothiazole, 5-hydroxybenzothiazole, 6-hydroxybenzothiazole, 5- or 6-diethylaminobenzothiazole, 5-carboxybenzothiazole, 5-sulfobenzothiazole, α-naphthothiazole, β-naphthothiazole, 5-methoxy-β-naphthothiazole, 5-ethoxy-β-naphthothiazole, 7-methoxy-β-naphthothiazole, 8-methoxy-α-naphthothiazole, indenobenzthiazole, etc.), those of the selenazole series (e.g. selenazole, 4-methylselenazole, 4-phenylselenazole, benzoselenazole, 5-chlorobenzoselenazole, 5-methoxybenzoselenazole, 5,6-dimethylbenzoselenazole, 5-hydroxybenzoselenazole, tetrahydrobenzoselenazole, α-naphthoselenazole, β-naphthoselenazole, etc.), those of the thiazoline series (e.g. thiazole, 4-methylthiazoline, etc.), those of the 2-pyrroline or 2-piperidine or 2-homopiperidine series, those of the 2-quinoline series (e.g. quinoline, 3-methylquinoline, 5-methylquinoline, 7-methylquinoline, 6-chloroquinoline, 8-chloroquinoline, 6-methoxyquinoline, 6-ethoxyquinoline, 6-hydroxyquinoline, 8-hydroxyquinoline, etc.), those of the 4-quinoline series (e.g. quinoline, 6-methoxyquinoline, 7-methylquinoline, 8-methylquinoline, etc.), those of the 3,3-dialkylindolenine series (e.g. 3,3-dimethylindolenine, 3,3,5-trimethylindolenine, 3,-3-dimethyl-5-methoxyindolenine, etc.), those of the 2-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, 5-ethylpyridine, 4-chloropyridine, 5-chloropyridine, 6-chloropyridine, 3-hydroxypyridine, 4-hydroxypyridine, 5-hydroxypyridine, 2-phenylpyridine, 4-phenylpyridine, 6-phenylpyridine, etc.), those of the oxazole series (e.g. 4-phenyloxazole, 4,5-diphenyloxazole, benzoxazole, 4-methylbenzoxazole, 5-methylbenzoxazole, 6-methylbenzoxazole, 5,6-dimethylbenzoxazole, 5-methoxybenzoxazole, 6-dialkylaminobenzoxazole, 5-phenylbenzoxazole, 5-carboxybenzoxazole, 5-β-carboxyvinylbenzoxazole, 5-sulfonamidobenzoxazole, 5-sulfobenzoxazole, 5-chlorobenzoxazole, 4,5-benzobenzoxazole, 5,6-benzobenzoxazole, 6,7-benzobenzoxazole, etc.), those of the 4-pyridine series (e.g. 2-methylpyridine, 3-methylpyridine, 2-chloropyridine, 3-chloropyridine, 2,3-dimethylpyridine, 2-hydroxypyridine, 3-hydroxypyridine, etc.), those of the thiadiazole, oxadiazole, imidazole or benzimidazole, 5-chlorobenzimidazole, 5,6-dichlorobenzimidazole or 5-trifluoromethylbenzimidazole series or those of the pyrimidine, triazine or benzothiazine series.

The heterocyclic rings or aryl groups contained in the above formulae may themselves be substituted in any way, e.g. with alkyl groups, preferably alkyl groups containing up to three carbon atoms such as methyl or ethyl, halogen such as chlorine or bromine, hydroxyl, alkoxy, preferably alkoxy groups containing up to three carbon atoms such as methoxy or ethoxy, hydroxyalkyl, alkylthio, aryl such as phenyl or aralkyl such as benzyl, amino, substituted amino and the like.

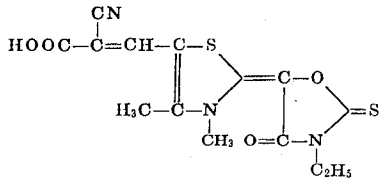
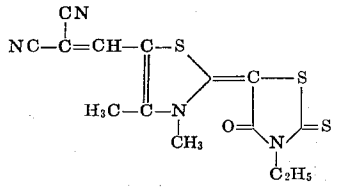
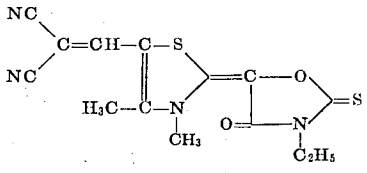
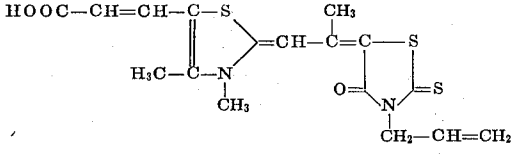
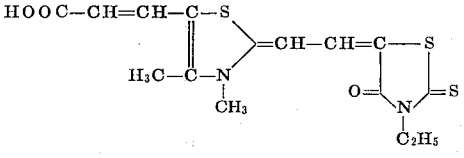
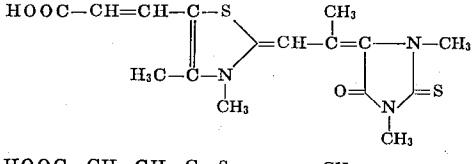
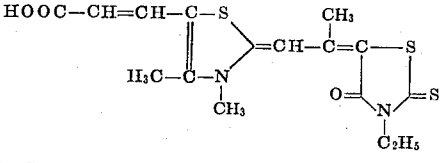
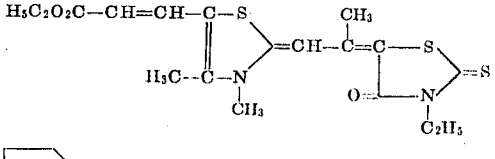
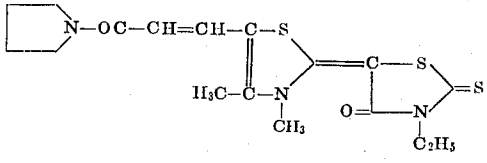
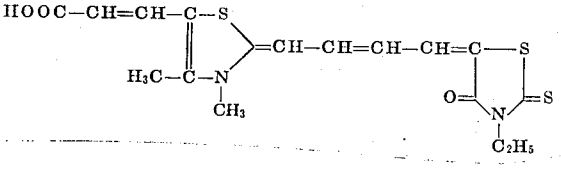
The following dyes, for example, are suitable: (Unless otherwise indicated, the absorption maxima were measured in methanol as solvent).

Dye	Absorption maximum in nm.
(1) 	444

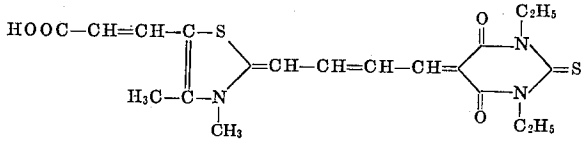
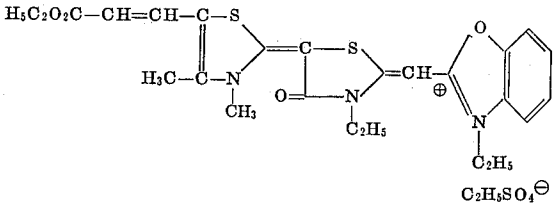
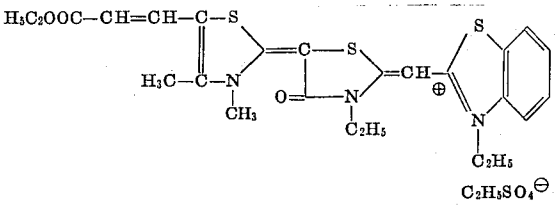
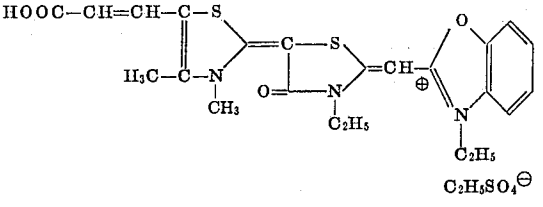
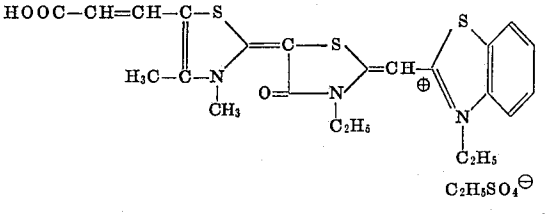
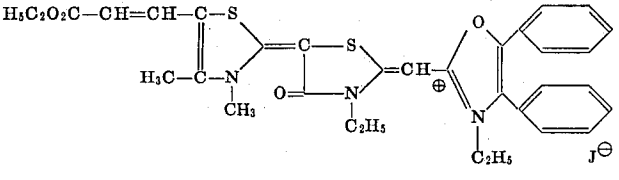
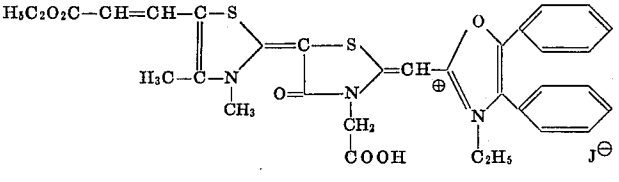
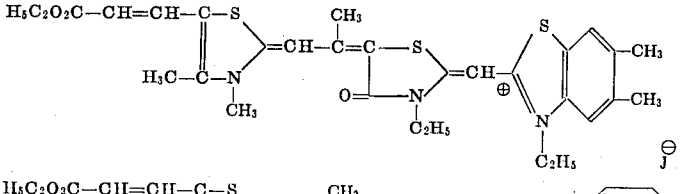
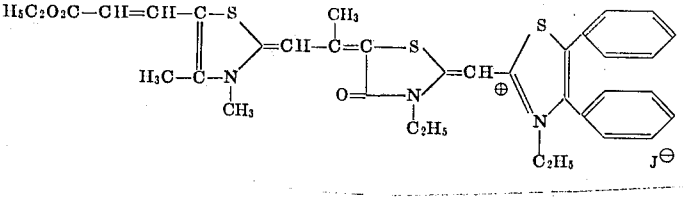
Continued

	Dye	Absorption maximum in nm.
(2)		459
(3)		406
(4)		455
(5)		457
(6)		460
(7)		461
(8)		460
(9)		1 499
(10)		1 462
(11)		483

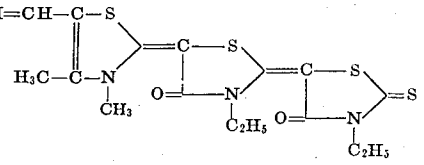
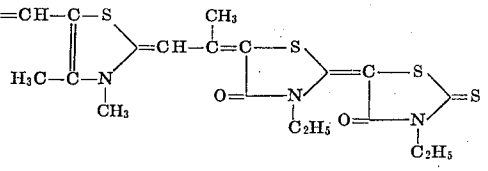
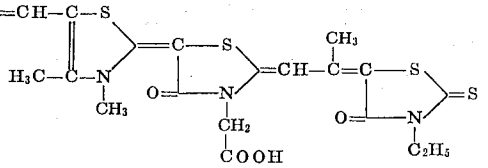
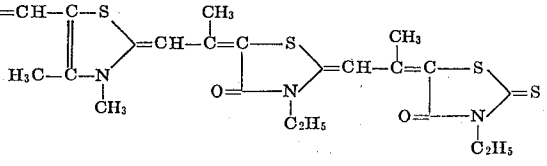
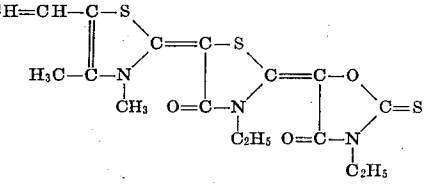
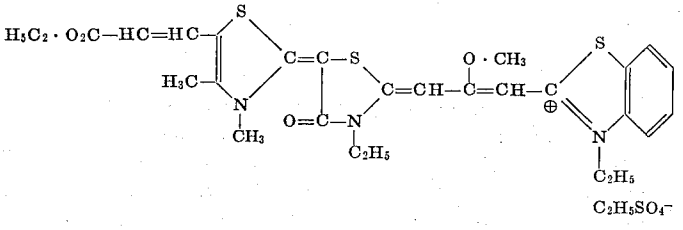
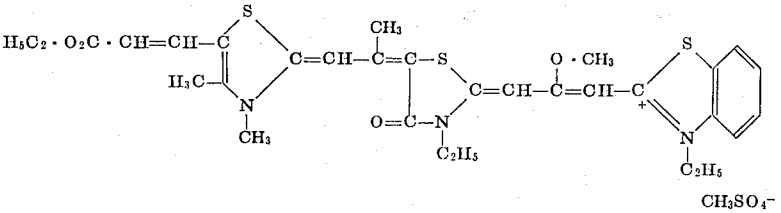
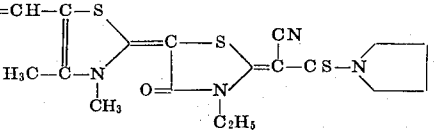
Continued

	Dye	Absorption maximum in nm.
(12)		478
(13)		1 510
(14)		1 500
(15)		560
(16)		562
(17)		548
(18)		560
(19)		565
(20)		462
(21)		648

Continued

	Dye	Absorption maximum in nm.
(22)		623
(23)		508
(24)		523
(25)		515
(26)		529
(27)		507
(28)		505
(29)		626
(30)		621

Continued

	Dye	Absorption maximum in nm.
(31)		[2] 517
(32)		[2] 614
(33)		[2] 577
(34)		[2] 671
(35)		[1] 505
(36)		580
(37)		672
(38)		[1] 480

[1] In dimethylformamide.
[2] In chloroform.

The merocyanines, in which X represents sulfur, may be prepared by the usual processes, for example by condensation of a quaternary salt of a 2-alkylthiothiazole base with a ketomethylene compound or its ethylidene compound in pyridine or in alcohol with the addition of a base such as triethylamine.

The sensitizers in which X contains a heterocyclic ring may easily be prepared by quaternization of the dyes in which X represents sulfur, followed by condensation with ketomethylene compounds or 2-methyl quaternary salts of heterocyclic bases.

The preparations of dyes 1, 19, 30 and 32 are de-

scribed in detail below as examples of the preparative methods used.

Dye 1

2.2 g of 2-methylthio-4-methylthiazole acrylic acid-5 and 1.2 ml of dimethyl sulfate are heated together to 110° C in an oil bath of 20 minutes. The quaternary salt which crystallizes on cooling is dissolved without isolation in 20 ml of alcohol together with 1.4 g of N-ethyl-oxazolidone thione and 2 ml of triethylamine, and the mixture is heated on a stream bath for 10 minutes. The dye which precipitates on cooling is isolated by suction filtration and recrystallized from glacial acetic acid. 2.5 g, m.p. 263°–264° C (decomposition).

Dye 19

12.0 g of ethyl 2-methylthio-4-methylthiazole acrylate-5 together with 6 ml of dimethyl sulfate are slowly heated to 85° C in an oil bath, the reaction temperature rising to 135° C. The quaternary salt which is obtained is heated together with 10.0 g of N-ethyl-5-isopropylidene-rhodanine in 100 ml of methanol and 8 ml of triethylamine for 30 minutes at 50° C without first being isolated. The reaction solution is cooled and the dye is separated by suction filtration and washed with methanol. 15.1 g, m.p. 276°–278° C.

Dye 30

4.0 g of the dye 19 together with 7 ml of dimethyl sulfate are heated in an oil bath to 110° C for 10 minutes and the resulting melt is triturated with ether when cold. The quaternary salt is heated on a steam bath for 30 minutes together with 4.2 g of 2-methyl-3-ethyl-4,5-diphenylthiazolium iodide in 30 ml of alcohol and 2 ml of triethylamine, and the resulting reaction solution is poured on to a solution of potassium iodide, and dye 30 is isolated by suction filtration and recrystallized from methanol. 4.9 g, m.p. 253°–254° C.

Dye 32

4.0 g of dye 19 are quaternized as in the preceding example and heated on a steam bath for 15 minutes together with 1.6 g of N-ethyl-rhodanine in 100 ml of alcohol with the addition of 2.5 ml of triethylamine. The solution of dye is cooled and the dye is isolated by suction filtration and recrystallized from a 1:1 mixture of chloroform and methanol. 2.7 g m.p. 292°–294° C.

2-Methylthio-5-β-carboxyvinyl-thiazole and esters thereof can be easily prepared by condensation of the corresponding thiazole aldehydes with malonic acid, cyanoacetic acid, etc., which aldehydes can in turn easily be obtained by formulation of the corresponding thiazoles by the method of Vilsmeyer according to German Auslegeschrift No. 1,147,584.

2-Methylthio-4-methyl-5-β-carboxyvinyl-thiazole

37.4 g of 2-methylthio-4-methyl-5-formyl-thiazole together with 30 g of malonic acid in 50 ml of pyridine and 1 ml of piperidine are heated to 110° C on an oil bath with stirring for 5 hours. The reaction mixture is poured on to 500 g of ice water and acidified with 2N hydrochloric acid and the product is isolated by suction filtration and is recrystallized from methanol. 27.2 g, m.p. 194°–195° C.

Ethyl ester of 2-methylthio-4-methyl-5-β-carboxyvinylthiazole

21.5 g of 2-methylthio-4-methyl-5-β-carboxyvinylthiazole are dissolved in 250 ml of absolute alcohol, hydrogen chloride is introduced, and the solution is boiled under reflux for 1½ hours. 22.1 g of the ethyl ester are obtained as the hydrochloride on cooling, m.p. 154°–155° C. The free base is easily obtained from the aqueous solution of the hydrochloride by the addition of sodium bicarbonate and extraction with ether, b.p.$_{12\ mm}$ 192°–196° C.

Preparation of photographic silver halide emulsions comprise substantially three stages:

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 invention may be used in any silver halide emulsions. Suitable silver halides include silver chloride, silver bromide or mixtures thereof, if desired with a small silver iodide content of up to 10 mols percent. Because the dyes according to the invention can be washed out so completely and can be used with a high degree of safety in the dark room, they are particularly suitable for use in emulsions on paper, especially silver chloride emulsions and silver chlorobromide emulsions. They may also be used in admixture with other sensitisers. The silver halides may be dispersed in the usual hydrophilic compounds such as carboxymethyl cellulose, polyvinyl alcohol, polyvinyl pyrrolidone, alginic acid and its salts, esters or amides or, preferably, in gelatin.

The sensitizing dyes for use 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 to the expert. The sensitizing dyes are generally incorporated with the emulsion in the form of solutions, e.g. in alcohol or alcohol/water mixtures. The solvents must, of course, be compatible with gelatin and must not have any adverse effect on the photographic properties of the emulsion. The solvents used are generally water, methanol or mixtures thereof. The quantity of sensitizing dye added may vary within wide limits, e.g. between 2 and 200 mg, preferably between 10 and 60 mg/kg of silver halide emulsion. The concentration of the dye may be adapted to the individual requirements according to the nature of the emulsion, the sensitizing effect which it is desired to achieve, etc. The most suitable concentration for any given emulsion can easily be determined by the usual tests used in photographic practice.

The emulsions may also be chemically sensitized, e.g. by the addition of sulfur-containing compounds in the chemical ripening, for example allyl isothiocyanate, allyl thiourea, sodium thiosulfate, and the like. The chemical sensitizer used may also be reducing agents, e.g. the tin compound described in Belgian Pat. Nos. 493,464 or 568,687, or polyamines such as diethylene triamine or aminomethyl sulfinic acid derivatives, e.g. according to British Pat. No. 789,823.

Noble metals and noble metal compounds such as 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 of molecular weight 1,000 to 20,000, or with condensation products of alkylene oxides and aliphatic alcohols, glycols, cyclic dehydration products of hexitols, alkyl-substituted phenols, aliphatic carboxylic acids, aliphatic amines, aliphatic diamines and amides. The condensation products have a molecular weight of at least 700, preferably above 1,000. These sensitizers may, of course, be combined in order to achieve special effects,

as described in Belgian Pat. No. 537,278 and in British Pat. No. 727,982.

The emulsions may in addition also contain other spectral sensitizers, e.g. the usual monomethine or polymethine dyes such as cyanines, hemicyanines, streptocyanines, merocyanines, oxonoles, hemioxonoles, styrene dyes or other methine dyes which can contain also three or more nuclei. Sensitizers of this type have been described by F. M. Hamer in the work "The Cyanine Dyes and Related Compounds" (1964), Interscience Publishers John Wiley and Sons.

The emulsions according to the invention may contain the usual stabilisers, e.g. homopolar or salt-type compounds of mercury having aromatic or heterocyclic rings, such as mercaptotriazoles, simple mercury salts, sulfonium mercury double salts and other mercury compounds. Azaindenes are are also suitable for use as stabilizers, especially tetra and pentaazaindenes, 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 include heterocyclic mercapto compounds, e.g. phenyl mercapto tetrazole, 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, such as mucobromic acid, diketones, methane sulfonic acid esters, dialdehydes and the like.

The emulsions according to the invention can be used for all sorts of different photographic processes, for example for materials used for taking original photographs, materials for copying, photographic films for the production of duplicates, X-ray films, materials which are suitable for the silver salt diffusion process, color photographic materials, photographic materials for the silver dye bleaching process, dye diffusion transfer process, etc.

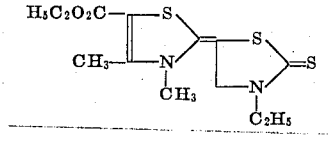
The sensitizers used according to the invention are also suitable for the spectral sensitization of electrophotographic layers, especially layers which contain photoconductive zinc oxide in an insulating binder.

EXAMPLE

30 mg of sensitizing dye are added to a conventional photographic silver chlorobromide gelatin emulsion. The emulsion is poured on to a baryta paper support in the usual manner and dried. The light-sensitive layer is exposed behind a step wedge ($\sqrt[3]{2}$ wedge) for 10 seconds and developed for 2 minutes in a developer of the following composition:

Water	1000 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 compounds is seen in the follwoing table. The compounds were used as indicated above the the steps visible after exposure and development were counted. The sensitizer of the following formula:



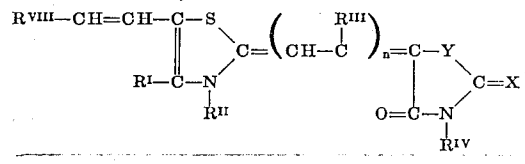
which is known to be a good sensitizer was used for comparison. It will also be seen from the table that the introduction of the acrylic acid group shifts the absorption maximum and sensitization maximum by about 25 to 30 nm into the longer wavelength region compared with the corresponding sensitizers used for comparison.

Table

Sensitizer	Absorption Maximum	Sensitization Maximum	Steps $\sqrt[3]{2}$
Comparison sensitizer	433 nm	480 nm	22
Dye 1	444	486	23
Dye 2	459	510	24
Dye 7	461	508	24
Dye 8	460	510	25
Dye 9	449	485	23
Dye 11	483	520	24

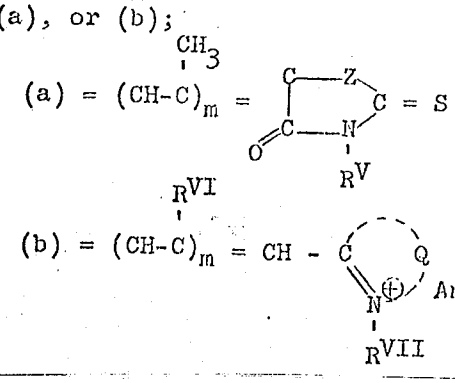
We claim:

1. A light-sensitive photographic material which comprises a silver halide and spectral sensitizer of the following formula:

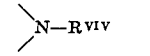


in which

X is a sulfur atom or is one of the following groups (a), or (b);



Y is an oxygen or sulfur atom or a group

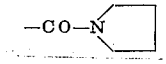


or —CO—NR^{V}—

Z is an oxygen or sulfur atom

wherein

R^{VIII} is COOH, —$COOC_2H_5$,



R^{I} is an alkyl, or aryl group;

R^{II} and R^{VII}, which may be the same or different, is an aliphatic group;

R^{III} is a hydrogen atom or an alkyl group;

R^{IV} is a saturated or olefinically unsaturated aliphatic or aryl group;

R^{V} is a saturated aliphatic group;

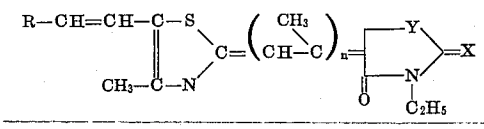
R^{VI} is an alkoxy group;
Q represents the ring members required to complete a thiazole or oxazole ring;
n is 0, and 1; and
m is 0, and 1; and Anion is any anion but may be absent if the dye molecule contains an acid group in anionic form.

2. A material as claimed in claim **1,** which contains the spectral sensitizer in a light-sensitive silver halide emulsion layer.

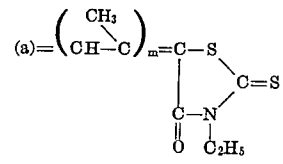
3. A material as claimed in claim **2** in which the content of sensitizer is 2 to 200 mg per kilogram of silver halide emulsion.

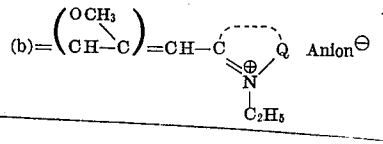
4. A material as claimed in claim **3** in which the content is 10 to 60 mg/kg.

5. A light-sensitive photographic material which comprises a silver halide and spectral sensitizer of the following formula:



in which
X is a sulfur atom or is one of the following groups (a), or (b);





Y is O and S
wherein
R is COOH and $COOC_2H_5$
Q is thiazole
n is 0 and 1; and
Anion is an anion or may represent an anion in the molecular structure.

* * * * *