United States Patent

[11] 3,630,748

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[31] **P 19 17 163.2**

[54] **SPECTRALLY SENSITIZED LIGHT-SENSITIVE SILVER HALIDE MATERIAL**
2 Claims, No Drawings

[52] **U.S. Cl.** **96/139,** 260/304
[51] **Int. Cl.** **G03c 1/08**
[50] **Field of Search** 96/139

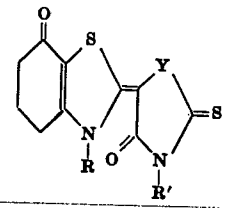
[56] **References Cited**

UNITED STATES PATENTS

2,157,351	5/1939	Schneider et al.	96/139
3,385,707	5/1968	Riester et al.	96/139

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

ABSTRACT: Light-sensitive photographic silver halide material is spectrally sensitized in the blue or blue-green range of the spectrum by new sensitizing dyes of the formula



wherein
Y stands for O,S,N-aryl or N-alkyl;
R stands for alkyl, and
R′ stands for alkyl, cycloalkyl, aryl or aralkyl which groups are preferably substituted with acid groups.

The new compounds exhibit no "Schwarzschild effect" and are useful sensitizers for color photographic silver halide emulsions.

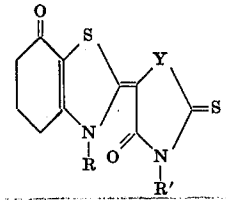
SPECTRALLY SENSITIZED LIGHT-SENSITIVE SILVER HALIDE MATERIAL

The present invention relates to light-sensitive photographic layers, especially silver halide emulsion layers, which have been spectrally sensitized with new types of sensitizing dyes.

It has been known for 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 layers. Numerous substances which mainly belong to the class of cyanine dyes have been described so for sensitizing silver halide emulsion layers. These known substances, however, often have disadvantages in that their sensitizing effect is inadequate or that 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 absorption 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, optical brightening agents, 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. Further there are wanted certain sensitizing properties, for example, in addition to a sufficient sensitizing intensity a decrease of sensitizing towards longer wavelengths, which is as steep as possible. For these reasons, there is considerable interest in finding new sensitizing dyes, which have not these above disadvantages.

It is among the objects of the present invention to provide sensitizing dyes for spectrally sensitizing light-sensitive layers, especially silver halide emulsion layers, that do not suffer the above-mentioned disadvantages.

It has not been found that light-sensitive materials, especially silver halide emulsion layers, can be spectrally sensitized in outstanding manner by means of O-methinmerocyanines of the following formula



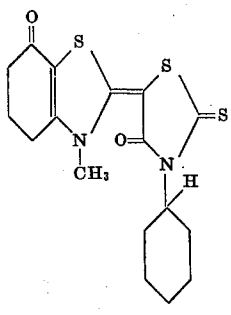
wherein:

Y stands for O, S, N-aryl or N-alkyl;

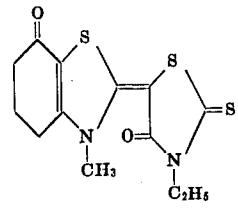
R stands for alkyl having up to four carbon atoms, which alkyl may be substituted, for example, with hydroxy, halogen, carboxyl or sulfo;

R' stands for a hydrocarbon group, for example aklyl having up to four carbon atoms, cycloalkyl such as cyclohexyl, aryl, such as phenyl, or aralkyl, such as benzyl, which hydrocarbon groups may be further substituted, for example with carboxyl or sulfo.

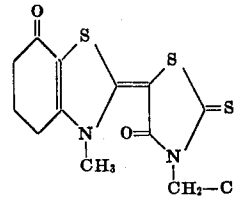
Compounds of the following formulas, for example are suitable sensitizers:



M.P.>335° C. (I)

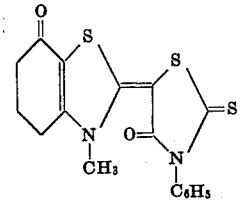


M.P. 310° C. (II)

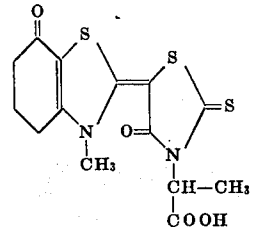


M.P. 290° C. (III)

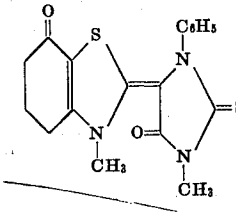
maximum of absorption: 331 nm (methanol)



M.P.>380° C. (IV)

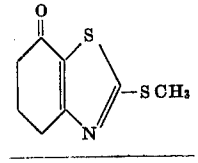


M.P. 265° C. (V)



M.P.>300° C. (VI)

The preparation of the sensitizing dyes according to the invention has become possible once having been prepared as a new intermediate product the base 2-methylthio-7-oxotetrahydrobenzothiazole of the following formula:



This compound has been prepared in the following way:

Cyclohexanedione (1,3) is brominated as described in Z. Chem. 7, (1967), page 422.

This bromination product (191 g.) is reacted with ammonium dithiocarbomate (138 g.) in 1,000 ml. of ethanol. The reaction is slightly exotherm and is completed by heating on a steam-bath for several hours whereas sulfur and ammoniumbromide are separated. After filtration the mixture is concentrated by evaporation until all ammoniumbromide has crystallized out. The solution is again filtered and the filtrate is poured into aqueous 2n solution of sodium hydroxide (500 ml.), again filtered and then mixed with dimethylsulfate (80 g.). The reaction product is extracted with ether. The residue remaining after the evaporation of the ether can be used immediately for the preparation of dyes. The distillation in

vacuum which however is accompanied with considerable decomposition is possible (boiling point 0.15 mm./140°–160° C.).

Analysis:

	C	H	O	N	S
calc.:	48,3%	4,5%	8,0%	7,0%	32,2%
found:	48,7%	5,2%	8,0%	7,0%	30,5%

The preparation of the sensitizing dyes according to the invention can be performed in principle following the usual methods which are known to an expert having ordinary skill in the chemistry of cyanine dyes. As an example the preparation of dye I is described in detail below.

DYE I

Twenty grams of 2-methylthio-7-oxotetrahydrobenzothiazole (crude product) and 13 g. of dimethylsulfate are heated on a steambath. The temperature of the reaction mixture arises to 105° to 110° C. The dark oil which is formed is mixed with a hot solution of 20 g. of n-cyclohexyrhodanine in 125 ml. of ethanol and with 10 ml. of triethylamine. After a short time the dye crystallizes out. The dye is separated and carefully washed with ethanol, ether and acetone.

Analysis:

	C	H	O	N	S
calc.:	53,7%	5,3%	8,4%	7,4%	25,3%
found:	53,7%	5,7%	8,4%	7,1%	25,5%

The other dyes can be prepared in an analogous manner. In the preparation of dye VI, however, the use of the pure base which has been distillized is preferred.

The new dyes according to the invention are excellent sensitizing dyes which sensitize silver halide emulsions in the blue and blue-green range of the spectrum with a steep decrease of sensitization towards longer wavelengths of the spectrum. The maximum of sensitization which is brought about from the dyes according to the present invention which are derived from 7-oxotetrahydrobenzothiazole is shifted but slightly bathochrome if compared with the sensitizing maximum effected by analogous dyes which are derived from benzothiazole. However, the dyes according to the invention are distinguished over those benzothiazole dyes by a considerably increase intensity of sensitization.

As another important advantage it has appeared that the silver halide emulsions which are sensitized according to the invention do not exhibit the "Schwarzschildeffekt." Under the term "Schwarzschildeffekt" is understood the deviation from the law of reciprocity which states that the product of intensity of light and time of exposure which product is necessary to bring about a definite density in a photographic silver halide emulsion layer is constant.

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 of up to 10 mols percent. The silver halides may be dispersed in the usually 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 before the chemical ripening or 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 an alcohol such as methanol or ethanol or acetone or mixtures these solvents with water. The solvents must, of course, be compatible with gelatin and must not have any adverse effects on the photographic properties of the emulsion. 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 salt, sulfonium mercury double salts and other mercury compounds. Other suitable stabilizers are azaindenes, especially tetra- or pentaazaiedenes, 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 sensitivity which is brought about by means of the sensitizing dyes according to the present invention is also maintained in the presence of color couplers it being immaterial whether the couplers have been added to the emulsion in form of an aqueous solution or in an emulsified form. This property as well as the behavior of reciprocity (no "Schwarzschildeffekt") enables the new sensitizers to be used advantageously in color photographic emulsions.

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 advantageous properties of the new sensitizing dye may be explained in the following examples:

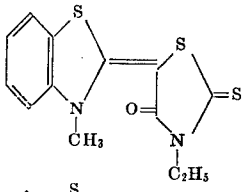
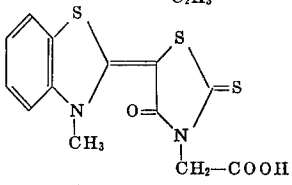
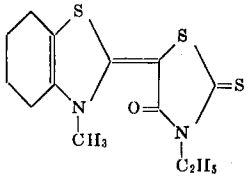
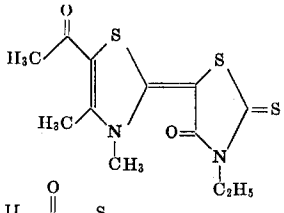
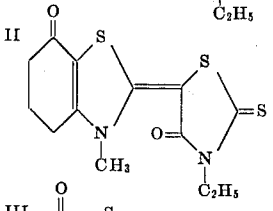
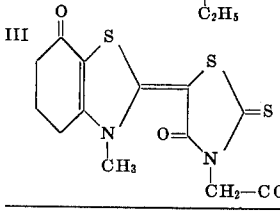
EXAMPLE 1

A silver chlorobromide emulsion as commonly used in photographic papers, which contains the usual additives such as formaldehyde as hardening agent and saponine as wetting agent, is divided in 6 parts. Each part is sensitized with one sensitizer of the following table and is subsequently cast on a layer support. After drying the materials are exposed to light in a sensitometer behind a grey step wedge having $\sqrt{2}$-steps and behind filters which are mentioned in the table. The development is carried out as usual.

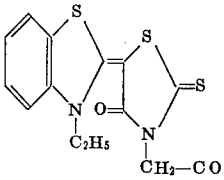
Dye V has proved to be a sensitizer just as useful as dye III. This dye after processing does not a least effect a discoloration of the layer, but brings about excellent white tones of paper.

EXAMPLE 2

A silver bromide emulsion as commonly used in color photographic papers, which contains per kg. 70 g. of gelatin, 0.4 moles of silver bromide, 15 g. of p-stearoylaminobenzoyl-(3,5-dicarboxy)-acetanilide as a yellow-forming coupler, and the usual additives as 0.35 g. of saponine, 3 ml. of a 5 percent aqueous methanolic solution of N,N',N''-trisacryloyl-hexahydro-1,3,5-triazine and 300 mg. of 1,3,7-triaza-4-hydroxy-6-methylindolizine, is divided in 4 parts. Three parts are sensitized with one dye of the following table. One part serves as a comparison test.

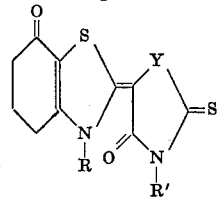
Compound	Sensitization maximum (nm)	Agfa-Gevaert-filter U 449 (blue)	Agfa-Gevaert-filter L 489 (spectrum minus blue)	
	480	17	11	Discoloration.
	480	17	13	Slight discoloration.
	480	18	17	Do.
	485	18	18	Do.
II 	485	18	19	Do.
III 	485	18	18	No discoloration.

After coating and drying the exposure and processing is performed as described in example 1. The results are shown in the following table:

	Sensitization maximum (nm)	Agfa-Gevaert-filter U 449 (blue)	Agfa-Gevaert-filter L 489 (spectrum minus blue)
Unsensitized emulsion		11	
	475	13	6
Dye II	485	13	10.5
Dye III	485	13	10

What is claimed is:

1. Light-sensitive photographic material comprising at least one silver halide emulsion layer, which material contains a sensitizing dye of the following formula



wherein:

Y stands for O,S, N-aryl or N-alkyl;

R stands for alkyl having up to four carbon atoms, and

R' stands for alkyl having up to four carbon atoms, cycloalkyl, aryl or aralkyl.

2. Material according to claim 1 wherein Y stands for S and R' stands for alkyl having up to four carbon atoms and being further substituted with carboxyl or sulfo.

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