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3,592,657

OPTICALLY SENSITIZED SILVER HALIDE LIGHT-SENSITIVE MATERIAL

Helmut Kampfer, Cologne-Stammheim, Germany, assignor to Agfa-Gevaert Aktiengesellschaft, Leverkusen, Germany

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U.S. Cl. 96—142 5 Claims

ABSTRACT OF THE DISCLOSURE

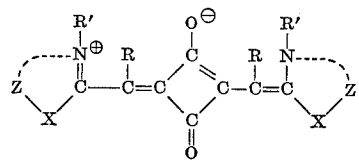
The present invention relates to light-sensitive photographic layers, especially silver halide emulsion layers, spectrally sensitized with pentamethine cyanine sensitizing dyes in which the methine chain contains a squaric acid ring.

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 layers. 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 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 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 have 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, that do not suffer the above-mentioned disadvantages.

I now have found that light-sensitive photographic materials, especially silver halide emulsion layers, can be spectrally sensitized with cyanine dyes, the methine chain of which contains a four-membered ring derived from squaric acid.

Sensitizing dyes of the following formula have proved to be particularly suitable:



wherein

Z represents the non-metallic 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, 4-ethoxy-benzothiazole, 5-ethoxy-benzothiazole, tetrahydrobenzothiazole, 5,6-dimethoxy-benzothiazole, 5,6-methylenedioxy-benzothiazole, 5-hydroxy-benzothiazole, 6-hydroxy-benzothiazole, etc.); those of the naphthothiazole series (e.g. α-naphthothiazole, β-naphthothiazole, 5-methoxy-β-naphthothiazole, 5-ethoxy-β-naphthothiazole, 7-methoxy-β-naphthothiazole, 8-methoxy-α-naphthothiazole); those of the selenazole series (e.g. 4-methylselenazole, 4-thienylselenazole); those of the benzoselenazole series (e.g. benzoselenazole, 5-chloro-benzoselenazole, 5-methoxy-benzoselenazole, 5-hydroxy-benzoselenazole, tetrahydro-benzoselenazole); those of the naphthoselenazole series (e.g. β-naphthoselenazole); those of the thiazoline series (e.g. thiazoline, 4-methylthiazoline); those of the quinoline series (e.g. quinoline, 3-methylquinoline, 5-methylquinoline, 7-methylquinoline, 6-chloroquinoline, 8-chloroquinoline, 6-methoxyquinoline, 6-ethoxyquinoline, 6-hydroxyquinoline, 8-hydroxyquinoline 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, 3,4-dimethylpyridine, 3,5-dimethylpyridine, 3,6-dimethylpyridine, 4,5-dimethylpyridine, 4-chloropyridine, 5-chloropyridine, 6-chloropyridine, 3-hydroxypyridine, 4-hydroxypyridine, 2-phenylpyridine, 4-phenylpyridine, 2-methylpyridine, 2,3-dimethylpyridine, 2-hydroxypyridine); those of the thiodiazole, imidazole or benzimidazole series or those of the pyrroline series;

R represents a hydrogen atom or an alkyl radical with preferably up to 6 carbon atoms;

R′ represents saturated or olefinically unsaturated aliphatic group, preferably with up to 5 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; R′ may also represent a cycloalkyl such as cyclohexyl, aralkyl such as benzyl or phenylethyl, or aryl such as phenyl;

X represents a sulfur selenium or nitrogen atom or the groupings

or —C(R″)$_2$—;

R″ represents hydrogen or a saturated or olefinically unsaturated aliphatic radical with preferably up to 5 carbon atoms, cycloalkyl such as cyclohexyl or aryl, in particular a radical of the phenyl series.

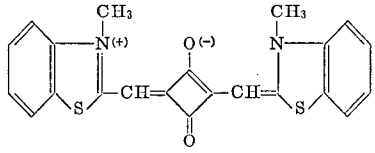
The sensitizing dyes to be used according to the present invention may be regarded chemically as pentamethine cyanine sensitizers. They have many advantages, in particular, in comparison with the known pentamethine cyanine dyes. The dyes of the invention, especially those of the benzothiazole and benzoselenazole series, possess very narrow spectral sensitization ranges owing to the resonance stabilization which is reinforced by the four-membered ring substituted with oxygen. The sensitization ranges obtained, in contrast to those of normal pentamethine cyanines, are characterized by a sharp decrease in sensitivity towards the shortwave length. This property makes the dye especially valuable for use in color photographic materials in which good separation of the color sensitivity of the three layers is important.

This applies especially to the dyes of the benzoselenazole series which sensitize to light of the long-wave red region. Another advantage of the dyes according to the invention over ordinary pentamethines is the excellent thermal stability of the emulsions containing these dyes.

The sensitivity of the emulsion remains constant on exposure at temperatures between normal room temperature and elevated temperature, (e.g. 50° C.). The new sensitizers are compatible with other additives such as hardeners, stabilizers and color couplers.

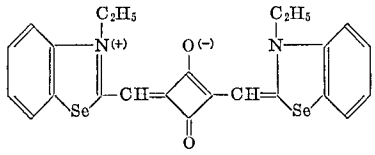
Examples of suitable dyes are the following (all absorptions are given in millimicrons):

Dye I:



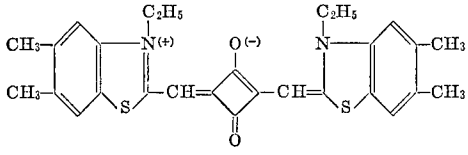
M.P. 289–291° C. with decomposition, absorption maximum 647

Dye II:



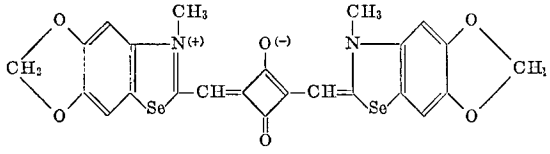
M.P. 307–309° C. with decomposition, absorption maximum 665

Dye III:



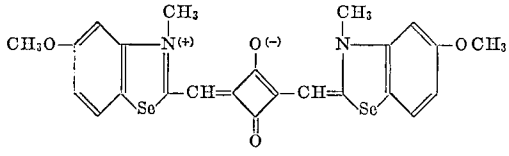
M.P. 328–332° C. with decomposition, absorption maximum 657

Dye IV:



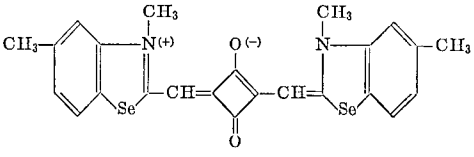
M.P. >360° C. absorption maximum 690

Dye V:



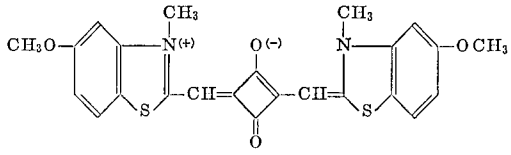
M.P. >360° C. absorption maximum 677

Dye VI:



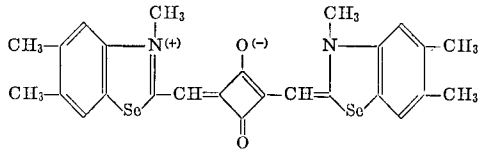
M.P. >360° C. absorption maximum 670

Dye VII:



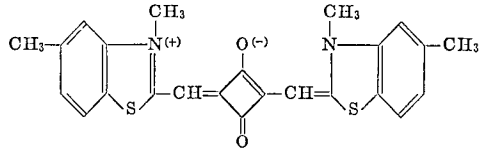
M.P. 310–315° C. with decomposition, absorption maximum 662

Dye VIII:



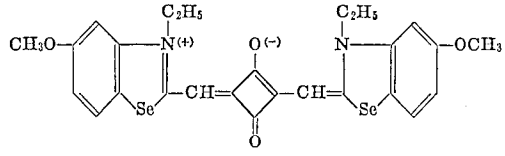
M.P. >360° C. absorption maximum 672

Dye IX



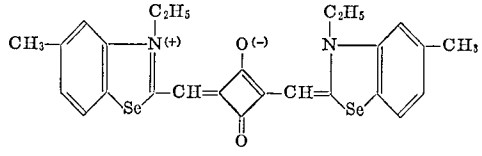
M.P. >321–323° C. absorption maximum 652

Dye X



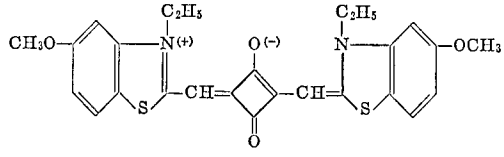
M.P. 307–310° C. with decomposition, absorption maximum 677

Dye XI



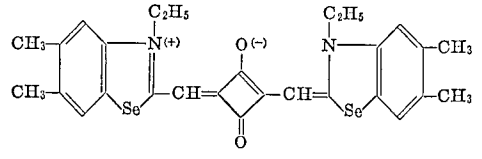
M.P. >311–314° C. absorption maximum 670

Dye XII



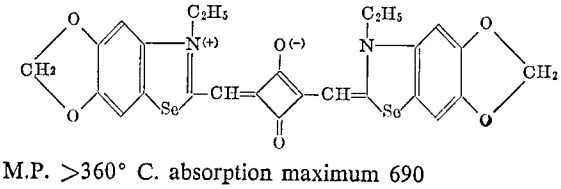
M.P. 249–254° C. with decomposition, absorption maximum 662

Dye XIII



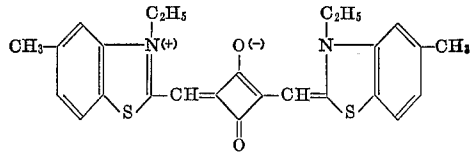
M.P. >360° C. absorption maximum 672

Dye XIV



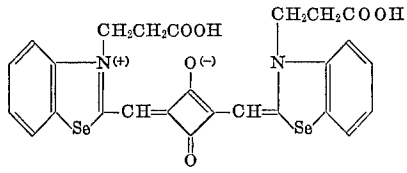
M.P. >360° C. absorption maximum 690

Dye XV



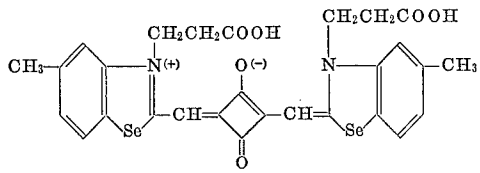
M.P. 318–320° C. with decomposition, absorption maximum 652

Dye XVI



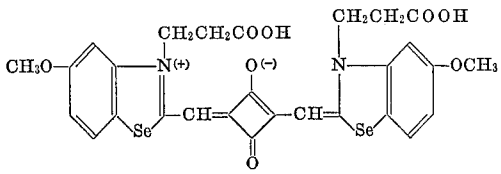
M.P. >360° C. absorption maximum 665

Dye XVII



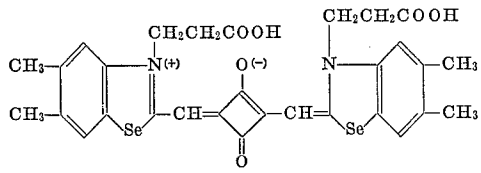
M.P. 286–294° C. with decomposition, absorption maximum 670

Dye XVIII



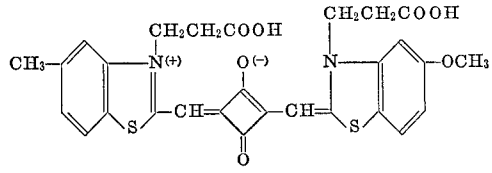
M.P. >360° C. absorption maximum 680

Dye XIX



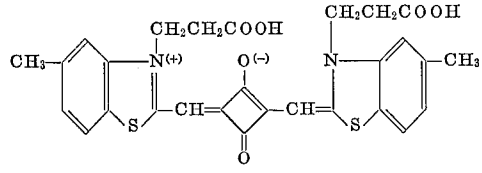
M.P. 282–290° C. with decomposition, absorption maximum 675

Dye XX



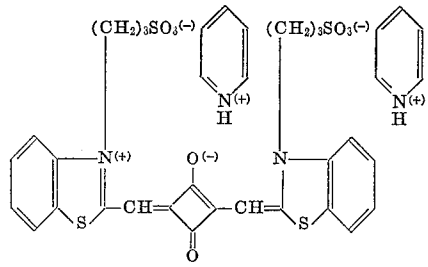
M.P. 289–295° C. with decomposition, absorption maximum 665

Dye XXI



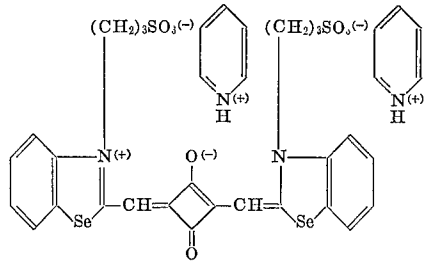
M.P. 292–299° C. with decomposition, absorption maximum 655

Dye XXII



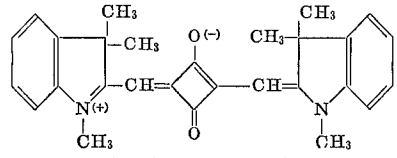
M.P. 244–246° C. with decomposition, absorption maximum 650

Dye XXIII



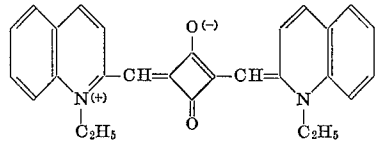
M.P. 242–246° C. with decomposition, absorption maximum 665

Dye XXIV



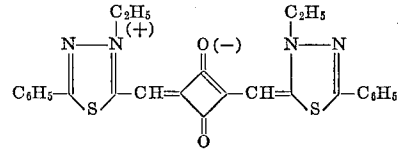
M.P. 316–317° C. with decomposition, absorption maximum 620

Dye XXV



M.P. 326–328° C. with decomposition, absorption maximum 700

Dye XXVI



M.P. 279–281° C. with decomposition, absorption maximum 650

The new dyes are generally prepared by condensation of the usual heterocyclic 2-methyl quaternary salts or 2-methylene bases with squaric acid or squaric acid derivatives such as squaric acid mono or di-alkyl esters, if desired in solvents such as butanol, hexanol or cyclohexanol, in the presence of an organic base such as pyridine. In cases where the quaternary salts are only soluble with difficulty, solvents for these salts may also be added, such as phenol or m-cresol. The preparation of squaric acid has been described in Angew. Chemie 78 (1966) 927.

Dye I: 3.3 of 2,3-dimethylbenzothiazolium-p-toluene sulfonate are boiled for 3 hours with 0.57 g. of squaric acid in 100 ml. of n-butanol with the addition of 3 ml. of pyridine, during which time the dye separates. It is washed

with alcohol and recrystallized from pyridine. Yield 1 g., M.P. 289–291° C. (decomposition).

Dye X: 3.3 g. of 2-methyl-3-ethyl-5-methoxybenzoselenazolium-p-toluenesulfonate are heated to boiling with 0.44 g. of squaric acid in 50 ml. of butanol. After the addition of 3 ml. of pyridine, the reaction mixture is boiled for 30 minutes, during which time the dye separates in the form of green needles. M.P. 307–310° C. (decomposition), yield 0.6 g.

Dye XI: 3.5 g. of 2,5-dimethyl-3-ethyl-benzoselenazolium-p-toluenesulfonate are boiled for one hour with 0.49 g. of squaric acid in 50 ml. of n-butanol with the addition of 3 ml. of pyridine. The dye, which separates in the pure state, is suction-filtered and washed with methanol. Yield 1 g., M.P. 311–314° C.

Dye XXII: 0.6 g. of squaric acid are dissolved in 50 ml. of boiling butanol, to which is added a solution of 2.7 g. of 2-methyl-3-sulfopropylbenzothiazolium betaine in 25 ml. of m-cresol, and boiled for 3 hours after the addition of 10 ml. of pyridine. The reaction solution is then concentrated by evaporation in vacuo and treated with a mixture of acetone and ether (1:1). The dye which separates is suction-filtered, washed with acetone and recrystallized in aqueous alcohol with the addition of acetone. Yield 1.2 g. M.P. 244–246° C. (decomposition).

Dye XXIV: 7 g. of 1,3,3-trimethyl-2-methylene-indoline are boiled for 2 hours with 2 g. of squaric acid in 50 ml. of n-butanol. The dye which crystallizes out during this process is suction-filtered and washed with methanol and ether. Yield 4.7 g., M.P. 316–317° C. (decomposition).

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 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 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 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 pentaazaindenes, 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.

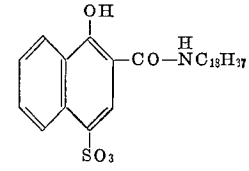
The emulsions according to the invention may be used for all sorts of different photographic processes, for example, for copying materials, for reproduction photography, for materials which are suitable for use in the silver salt diffusion process, for color photographic materials for the silver dye 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 photo-conductive zinc oxide distributed in an insulating binder.

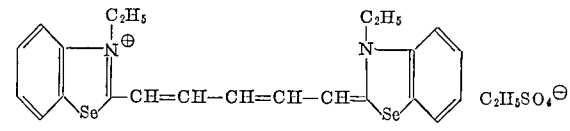
Another distinct advantage of the sensitizing dyes according to the present invention lies in the ease of their combination with suitable hypersensitizers. The sensitizing effect of the sensitizing dyes can thereby be considerably enhanced. Particularly suitable for this purpose are the compounds described in French Pat. No. 1,426,623.

EXAMPLE

A highly sensitive silver bromide gelatin emulsion which has a silver iodide content of 3 mols percent and which contains the blue-green coupler of the following formula



and in addition 50 ml. of a 5% aqueous solution of saponine as wetting agent 1.5 ml. of a 30% aqueous solution of formaldehyde as hardener and 2-mercapto-5-chloro-7-sulfobenzoxazole as stabilizer, is divided into two parts. To sample 1 are added 10 mg. of dye II per kg. of emulsion, and to sample 2 are added 10 mg. of the known pentamethine cyanine of the following formula:



per kg. of emulsion.

The two emulsion samples are then cast onto a baryta-coated paper support and dried in known manner.

The resulting layers are exposed in a sensitometer customarily employed behind a step wedge of slope

$$\sqrt[3]{2}$$

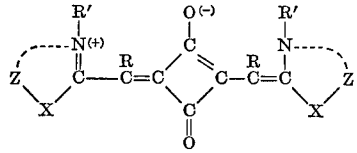
at 20° C. and 50° C. and behind a red filter. After the usual color-forming processing comprising development

in a color-forming developer and bleach fixing, the following relative sensitivities are obtained (in steps of wedge):

	Behind red filter	Relative sensitivity at— 20° C.	50° C.
Sample 1 (dye II)	22	14	14
Sample 2	18	10	12

I claim:

1. In a light-sensitive photographic material that contains at least one silver halide emulsion layer and is spectrally sensitized by a dye, the improvement according to which the sensitizing dye has the formula



wherein

X is sulfur, selenium, nitrogen,

or $-C(R'')_2-$,

Z represents non-metallic ring members that complete a 5- or 6-membered heterocyclic ring that may have a benzene or naphthalene ring fused thereto,

R represents hydrogen or alkyl,

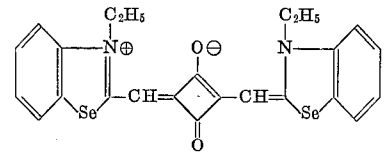
R′ represents a saturated or olefinically unsaturated aliphatic group which may be substituted by halogen, hydroxyl, alkoxy, sulfo, sulfonamide, carboxyl, carbamoyl or phosphoric acid, and

R″ represents hydrogen, a saturated or olefinically unsaturated aliphatic group, cycloalkyl, or a radical of the phenyl series.

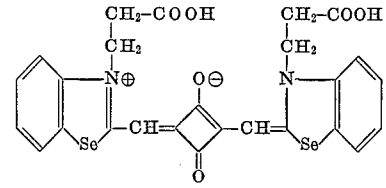
2. The combination of claim 1, wherein Z represents the ring members necessary for completing a benzthiazole or benzselenazole ring.

3. The combination of claim 1, wherein R represents hydrogen and R′ an alkyl group having up to 5 carbon atoms.

4. The combination of claim 1 in which the sensitizing dye has the following formula:



5. The combination of claim 1 in which the sensitizing dye has the following formula:



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J. TRAVIS BROWN, Primary Examiner

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