

sulfobutyl, δ -sulfobutyl, etc., a sulfatoalkyl group, e.g., β -sulfatoethyl, γ -sulfatopropyl, etc., or an acyloxyalkyl group, e.g., β -acetoxylethyl, γ -acetoxypentyl, γ -propoxypentyl, etc.

Q and Q₁ in combination represent the atoms necessary to complete a thiazolidinone nucleus such as a 4-thiazolidinone nucleus or a 5-thiazolidinone nucleus and may be substituted as known to one skilled in the art. Examples of substituents include substituted or unsubstituted alkyl group of 1 to 12 carbon atoms such as methyl, ethyl or propyl, an allyl group, a substituted or unsubstituted aralkyl group of 1 to 6 carbon atoms in the alkyl moiety thereof such as benzyl or p-carboxyphenylmethyl, an aryl group of 6 to 12 carbon atoms, e.g. a phenyl group or a p-carboxyphenyl, a hydroxyalkyl group, e.g. β -hydroxyethyl, a carboxyalkyl group, e.g. carboxymethyl, an alkoxyalkyl group, e.g. methoxycarbonylethyl, halogen (e.g. chloro, fluoro), hydroxy, alkoxy (e.g. methoxy, ethoxy) and other conventional dye substituents that would be apparent to one skilled in the art.

L₁, L₂ and L₃ each represents a methine group or a substituted methine group of the formula :

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wherein R₂ may be unsubstituted alkyl having 1 to 6 carbon atoms, such as methyl or ethyl or a substituted alkyl group having 1 to 6 carbon atoms substituted with, for example an alkoxy group, a carboxy group, an alkoxyalkyl group, or an aryl group and, more specifically, β -ethoxyethyl, β -carboxyethyl, β -methoxycarbonylethyl, benzyl or phenethyl, an unsubstituted aryl group or an aryl group substituted with an alkoxy group (e.g. having 1 to 6 carbon atoms), a halogen atom (e.g. fluorine, chlorine, bromine or iodine) or a carboxy group, for example phenyl, p-methoxyphenyl, p-chlorophenyl or o-carboxyphenyl.

The anion represented by X⁻, although not particularly restricted is, for example, a halogen ion (e.g., chloride, bromide, iodide), p-toluene sulfonate (PTS⁻), ethylsulfonate, perchlorate, or the like.

Each of m, n and p is 0 or 1, provided that p is 0 when the dye forms an intramolecular salt.

When the term "group" or "nucleus" is used in this invention to describe a chemical compound or substituent, the described chemical material includes the basic group or nucleus and that group or nucleus with conventional substitution. Where the term "moiety" is used to describe a chemical compound or substituent, only an unsubstituted chemical material is intended to be included. For example, "alkyl group" includes not only such alkyl moieties such as methyl, ethyl, octyl, stearyl, etc., but also such moieties bearing substituents groups such as halogen, cyano, hydroxyl, nitro, amine, carboxylate, etc. On the other hand, "alkyl moiety" or "alkyl" includes only methyl, ethyl, octyl, stearyl, cyclohexyl, etc.

Examples of the first sensitizing dyes according to this invention include the following. However, the scope of this invention is not limited to only these compounds.

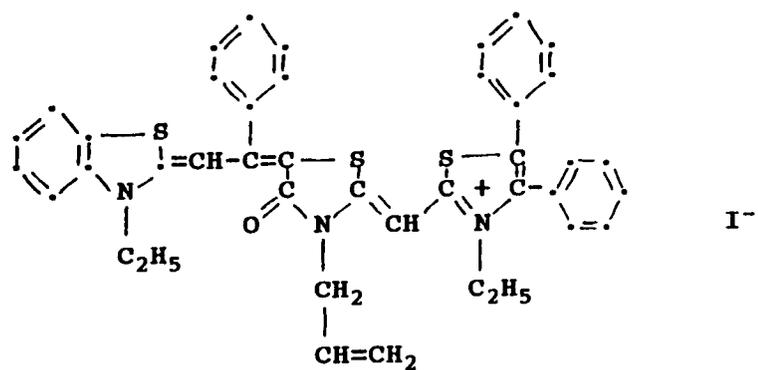
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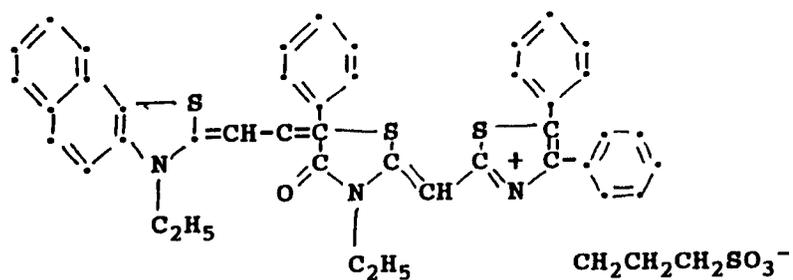
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(I.1)

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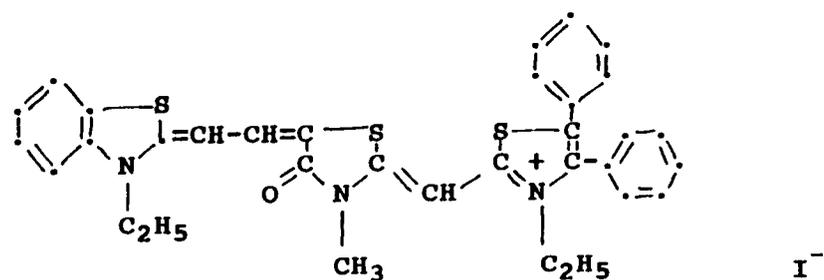


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(I.2)

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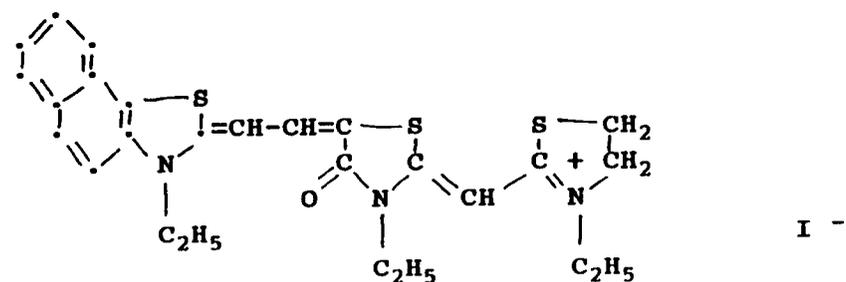
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(I.3)

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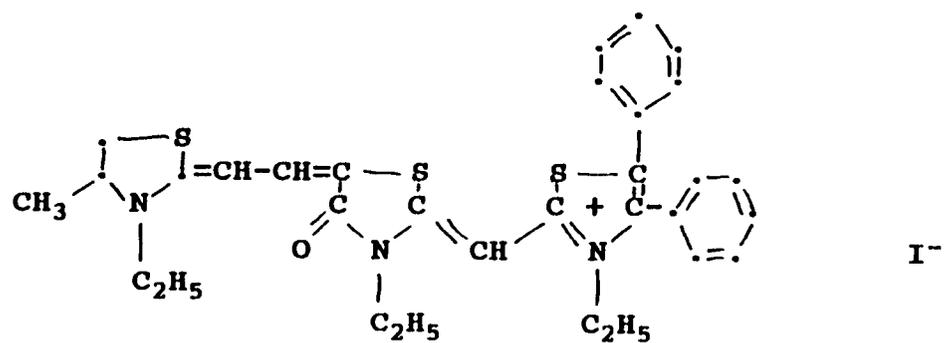
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(I.4)

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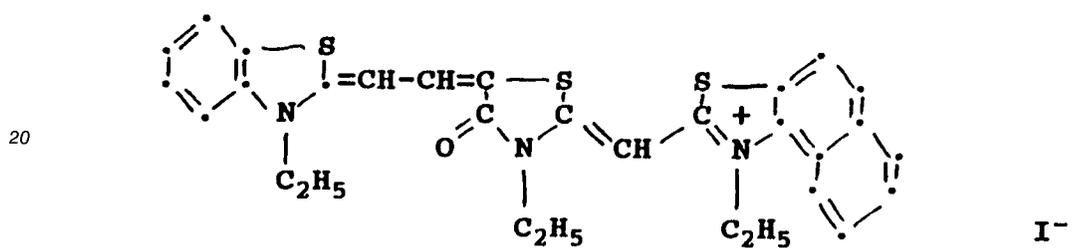
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(I.5)

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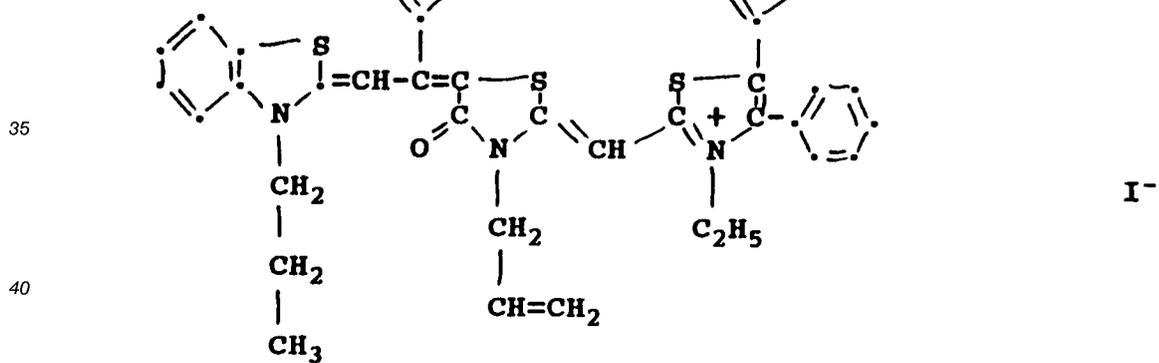


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(I.6)

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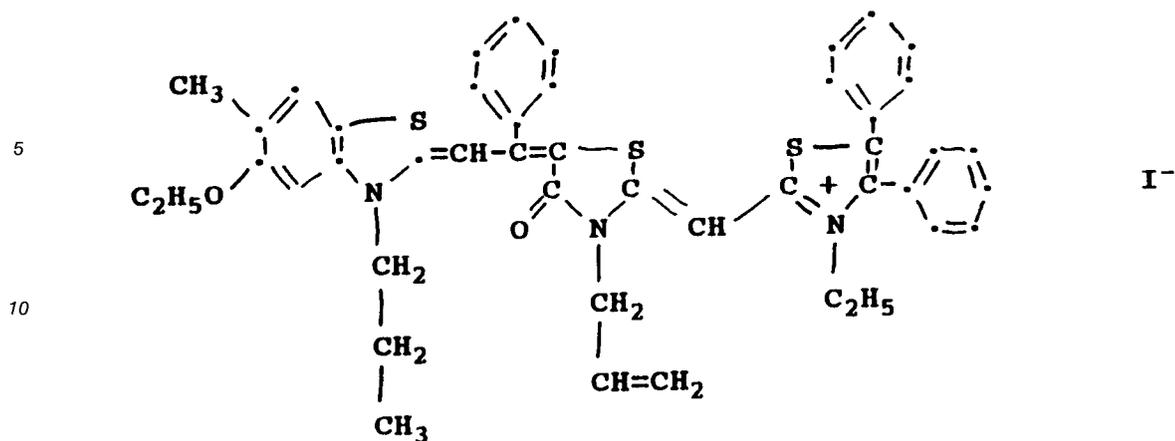
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(I.7)

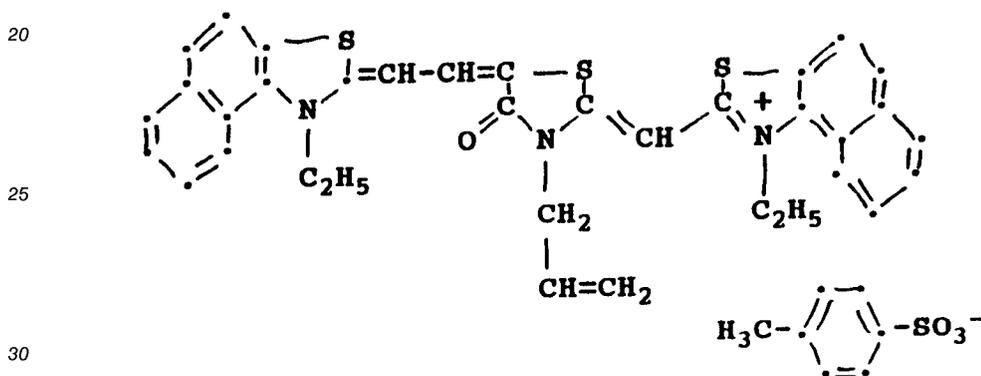
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(I.8)



(I.9)

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The sensitizing dyes (I.1) to (I.9) of the present invention can be easily sensitized by one skilled in the art by reference to M.Hamer, "The Cyanine Dye and Related Compounds", J.Wiley & Sons Ltd. (1964), German Patents Nos. 971,941 and 1,013,167 or US Patent Reissue No. 29,476.

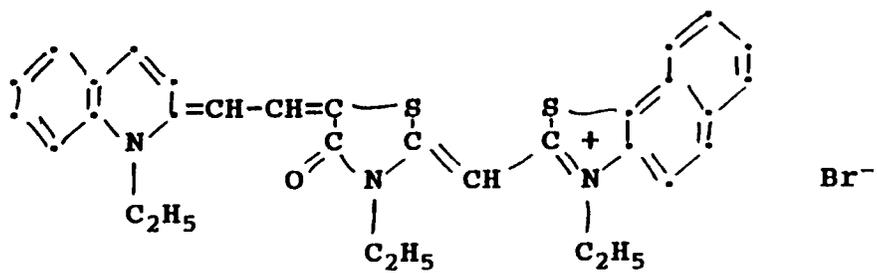
40 In the formula (II) of the present invention, Z₃ represents the atoms necessary to complete a substituted or unsubstituted 6-membered nitrogen-containing heterocyclic nucleus such as 2-quinoline group, 4-quinoline group and the like, optionally containing substituent(s) and/or fused ring(s). These nuclei may be substituted by any of a number of groups known to be substituents for such nuclei. These includes sulfo, halogen (e.g. chloro, fluoro), alkyl of 1 to 12 carbon atoms (preferably of about 1 to 4 carbon atoms, e.g. methyl, ethyl, butyl, which may themselves be substituted with known elements such as hydroxy, halogen or sulfo), alkoxy of 1 to 12 carbon atoms (preferably of about 1 to 4 carbon atoms, e.g. methoxy, ethoxy, butoxy), carboxy, carboxylate of from 1 to 4 carbon atom (e.g. methyl ester, ethyl ester), sulfonamido or carbonamido. Examples of useful nuclei for Z₃ include a 2-quinoline nucleus, e.g. quinoline, 3-methylquinoline, 5-methylquinoline, 6-chloroquinoline, a 4-quinoline nucleus, e.g. quinoline, 6-methoxyquinoline, 7-methylquinoline, 8-methylquinoline, and the like.

50 Z₄ represents heterocyclic rings which include all of those defined by the rings completed by Z₁ or Z₂ of the previous formula (I).

R₃ and R₄ each independently represents a hydrogen atom, an alkyl group of 1 to 18 carbon atoms (preferably of 1 to 12 carbon atoms such as methyl, ethyl, propyl, isopropyl, butyl, octyl, etc.) or a phenyl group (such as phenyl, carboxylphenyl).

55 Examples of the second sensitizing dyes according to this invention include the following exemplary compounds. However, the scope of this invention is not limited to only these compounds.

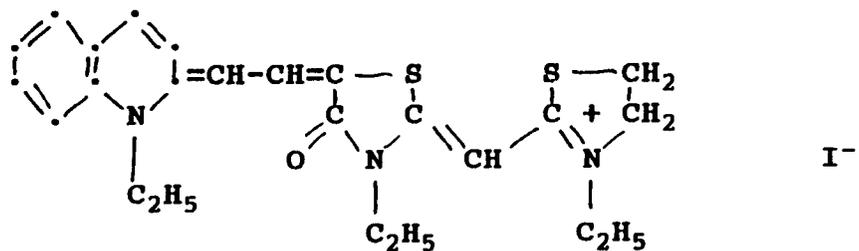
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(II.1)

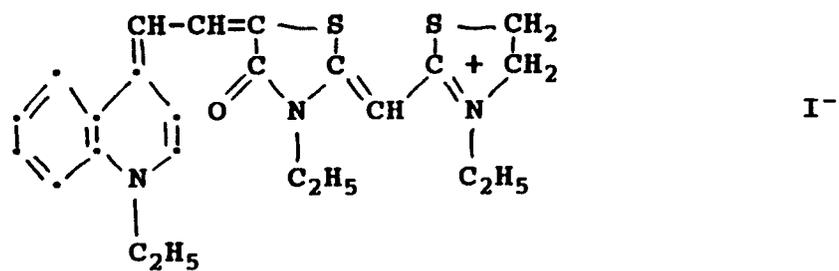
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(II.2)

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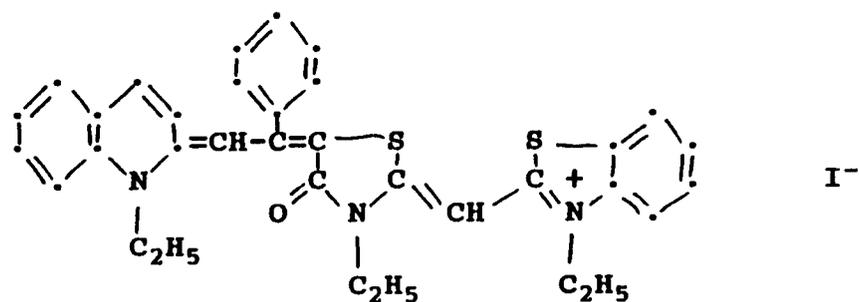


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(II.3)

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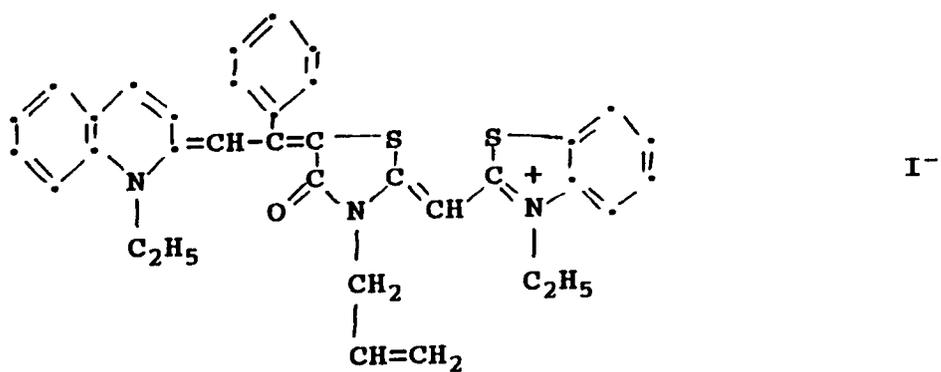
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(II.4)

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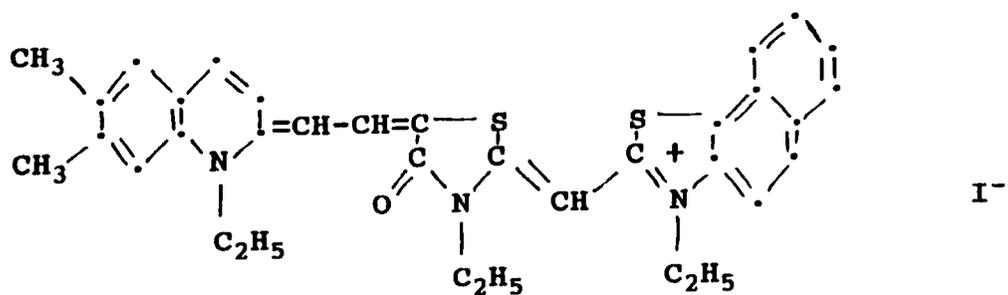


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(II.5)

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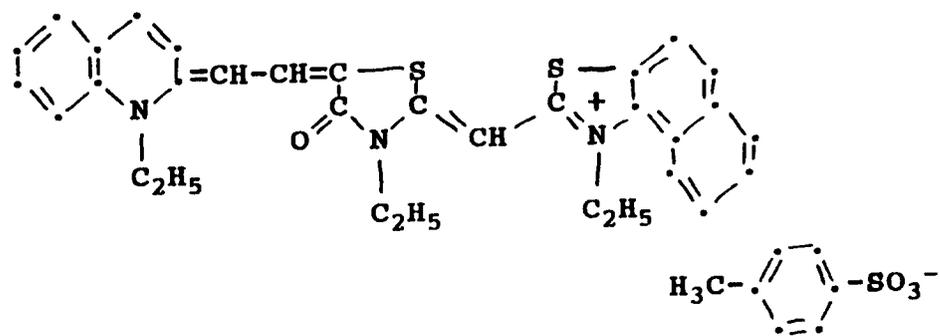


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(II.6)

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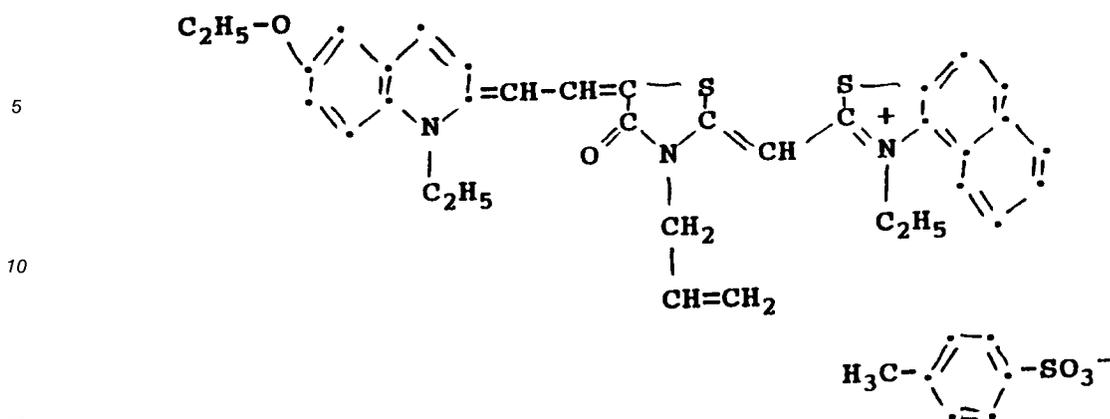
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(II.7)

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(II.8)

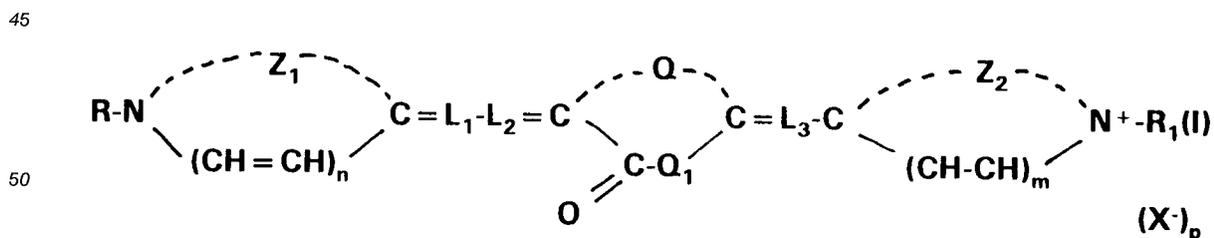
20 **Synthesis of compound (II.1)**

3.79 g of 5-(1-ethylquinolin-2-yl)ethylidene-2-ethylthio-3-ethyl rhodaninium tosylate (0.007 mole), 2.79 g of 2-methyl-3-ethyl-naphthothiazolium tosylate (0.007 mole), 60 ml of ethanol and 6 ml of triethylamine were refluxed with stirring for 20 minutes. 1.44 g of NaBr (0.014 mole) were then added and the mixture was refluxed for other 10 minutes. The precipitates were collected by filtration and washed with methanol. The product was then boiled in acetone, filtered, washed with water and dried under vacuum. The product structure was confirmed by NMR.

30 **Synthesis of compound (II.7)**

21.6 g of 5-(1-ethylquinolin-2-yl)ethylidene-2-ethylthio-3-ethyl rodaninium tosylate (0.039 mole), 16.0 g of 2-methyl-3-ethyl-naphthothiazolium tosylate (0.039 mole), 340 ml of ethanol and 34 ml of triethylamine were refluxed with stirring for 30 minutes. The mixture was left at room temperature overnight and then separated solid was filtered, then suspended in 500 ml of acetone, refluxed for 15 minutes, filtered and dried under vacuum. The product structure was confirmed by NMR.

The present invention also refers to a method for forming a silver image comprising image-wise exposing by means of a light source emitting light in the wavelength range of from 600 to 690 nm a photographic material containing a support having coated thereon at least a silver halide emulsion layer incorporating a first sensitizing dye and a second sensitizing dye spectrally sensitizing said emulsion for said wavelength range or for a substantial part of said wavelength range and wet-processing the exposed photographic material with aqueous developing or activating solutions and fixing solutions, thereby dissolving away said dyes from the resulting silver-image-containing material, wherein said first sensitizing dye is represented by the formula (I):



55 wherein Z₁ and Z₂ each independently represents the atoms necessary to complete a substituted or unsubstituted 5-membered nitrogen-containing heterocyclic group; R and R₁ each independently represents a substituted or unsubstituted alkyl group; Q and Q₁ in combination represent the atoms required to complete a thiazolidinone nucleus; L₁, L₂ and L₃ each represents a methine group or a substituted methine

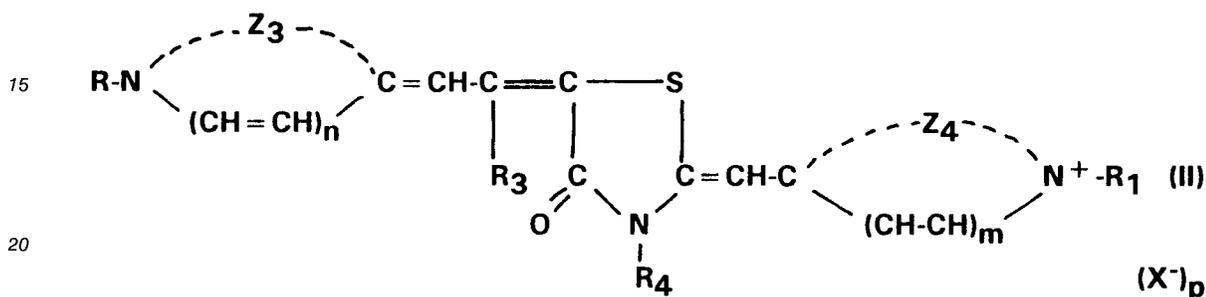
group of the formula



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wherein R₂ is an optionally substituted alkyl group having 1 to 6 carbon atoms or an optionally substituted aryl group having 6 to 10 carbon atoms; X⁻ is an anion and each of m, n and p is 0 or 1, provided that p is 0 when the dye forms an intramolecular salt;

10 and wherein second sensitizing dye is represented by formula (II):



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25 wherein Z₃ represents the atoms necessary to complete a substituted or unsubstituted 6-membered nitrogen-containing heterocyclic group optionally containing substituent(s) and/or fused ring(s); Z₄ represents the atoms necessary to complete a substituted or unsubstituted 5-membered nitrogen-containing heterocyclic group optionally containing substituent(s) and/or fused ring(s); R₃ and R₄ each represents a hydrogen atom, an alkyl group or a phenyl group; R, R₁, m, n, X and p have the same meaning of formula (I).

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The first and second spectral sensitizing dyes of the present invention can be prepared according to well-known procedures in the art, such those described in James, The Theory of Photographic Processes, MacMillan, 4th Edition, 1977.

35 The first and second spectral sensitizing dye of the present invention spectrally sensitize silver halide emulsions to radiation in the wavelength range of from 600 to 700 nm, especially from 620 to 680 nm, to provide photographic elements which are particularly suitable with a number of commercially available laser diodes. A further important advantage derived from the combined use of said first and said second spectral sensitizing dyes of the present invention is that the photographic material containing said sensitizing dyes exhibits an increased contrast and a reduced residual color stain after processing compared to the materials containing only one of the two spectral sensitizing dye.

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The first spectral sensitizing dyes of the present invention are incorporated in the silver halide photographic emulsion in a content of from 0.01 to 0.20 grams/mol of silver, preferably from 0.02 to 0.16 grams/mol of silver.

45 The second spectral sensitizing dyes of the present invention are incorporated in the silver halide photographic emulsion in a content of from 0.005 to 0.20 grams/mol of silver, preferably from 0.01 to 0.15 grams/mol of silver.

The spectral sensitizing dyes of the present invention can be directly dispersed in the emulsion. Alternatively, they may be first dissolved in a suitable solvent such as methyl alcohol, ethyl alcohol, methyl cellosolve, acetone, water, pyridine, or a mixture thereof to add them to the emulsion as a solution. Processes for adding the sensitizing dyes to the photographic emulsion are described, for example, in US Pat. Nos. 3,469,987, 3,676,147, 3,822,135, 4,199,360, and in US Pat. Nos. 2,912,343, 3,342,605, 2,996,287 and 3,429,835. The aforesaid sensitizing dyes may be uniformly dispersed in the silver halide emulsion before coating on a suitable support. Of course, this dispersing procedure may be conducted in any suitable step of preparing the silver halide emulsion.

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Any of the various types of photographic silver halide emulsions may be used in the practice of the present invention. Silver chloride, silver bromide, silver iodobromide, silver chlorobromide, silver chloriodobromide, and mixtures thereof may be used, for example, dispersed in a hydrophilic colloid or carrier. Any configuration of grains, cubic, orthorhombic, hexagonal, epitaxial, or tabular (high aspect ratio)

grains may be used. The colloid may be partially hardened or fully hardened by any of the variously known photographic hardeners. Such hardeners are free aldehydes, aldehyde releasing compounds, triazines and diazines, aziridines, vinylsulfones, carbodiimides, and the like may be used, as described, for example, in US Pat. Nos. 3,232,764, 2,870,013, 3,819,608, 3,325,287, 3,992,366, 3,271,175 and 3,490,911.

5 The silver halide emulsions may be chemically sensitized using the usual sensitizing agents. Sulfur containing compounds, gold and noble metal compounds, polyoxylakylene compounds are particularly suitable. Methods for chemically sensitizing silver halide emulsions are described, for example, in Research Disclosure 17643, Section III, 1978.

10 Other conventional photographic addenda such as coating aids, antistatic agents, acutance dyes, antihalation dyes and layers, antifoggants, latent image stabilizers, supersensitizers, antikinking agents, high intensity reciprocity failure reducers, plasticizers, matting agents, developing agents, color couplers, absorbing and scattering materials, which may be added to the silver halide emulsions are described in Research Disclosure 17643, 1978.

15 Gelatin is generally used as hydrophilic colloid for the silver halide photographic elements of the present invention. As hydrophilic colloids, gelatin derivatives, natural substances such as albumin, casein, agar-agar, alginic acid and the like, and hydrophilic polymers such as polyvinyl alcohol, polyvinylpyrrolidone, cellulose ethers, partially hydrolyzed polyvinyl acetate, and the like can be used in addition to or instead of gelatin. Further, gelatin can be partially substituted with polymer latexes obtained by emulsion polymerization of vinyl monomers, such as polyethylacrylate latexes, to improve the physical characteristics
20 of the photographic layers.

Support base used in the silver halide photographic materials of this invention can be any of the conventionally used support bases, such as glass, cloth, metal, film including for example cellulose acetate, cellulose acetate-butyrate, cellulose nitrate, polyester, polyamine, polystyrene, and the like, paper including baryta, coated paper, resin-coated paper, and the like.

25 The silver halide emulsions according to the present invention may be used as photosensitive emulsions for various photographic materials, such as high surface sensitivity or high internal sensitivity negative emulsions, surface-fogged or unfogged direct-positive emulsions, print-out emulsions, reversal emulsions, emulsions for black-and-white materials, for color materials, radiographic materials, transfer color materials, and the like.

30 The photographic materials according to this invention may be processed to form a visible image upon association of the silver halides with an alkaline aqueous medium in the presence of a developing agent contained in the medium or in the material, as known in the art. In the case of color photographic materials, the processing comprises at least a color developing bath and, optionally, a prehardening bath, a neutralizing bath, a first (black and white) developing bath, etc. These and other baths which complete the photographic processing (e. g., bleaching, fixing, bleach-fixing, intensifying, stabilizing and washing baths)
35 are well known in the art and are described for instance in Research Disclosure 17643, 1978.

The present invention is now illustrated by reference to the following example.

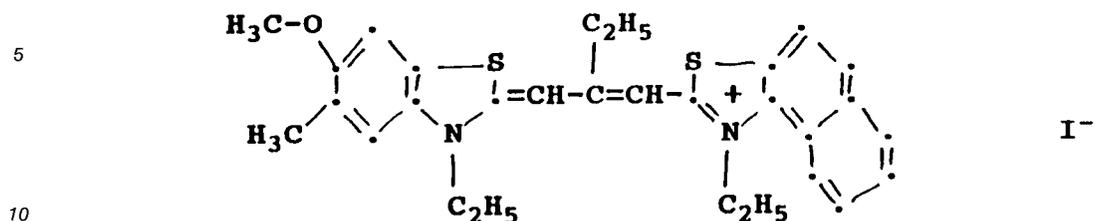
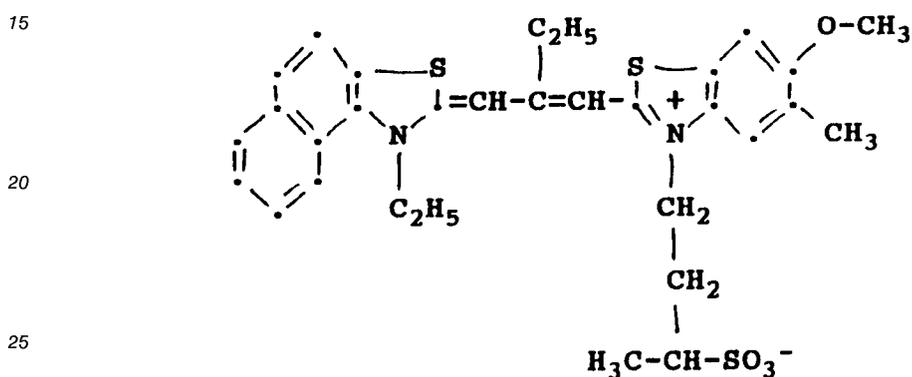
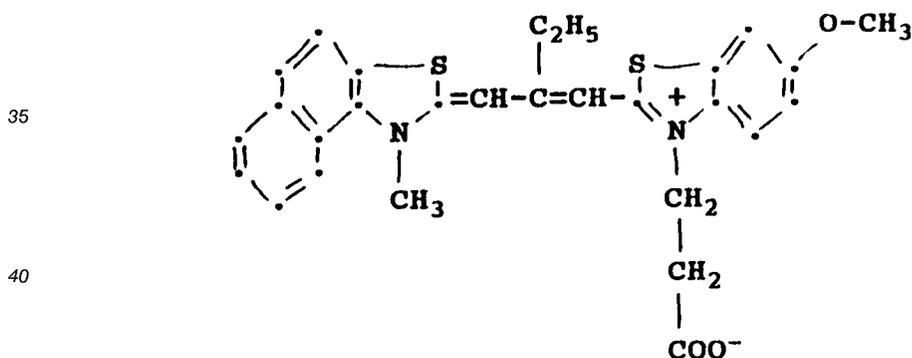
EXAMPLE

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A cubic monodispersed 0.32 μm silver chlorobromide (40 mole percent bromide) was prepared as in Example N. 2 of the European Patent application No. 423,538. The resulting emulsion was gold and sulfur sensitized, then split in several parts and each part was optical sensitized according to the following scheme :

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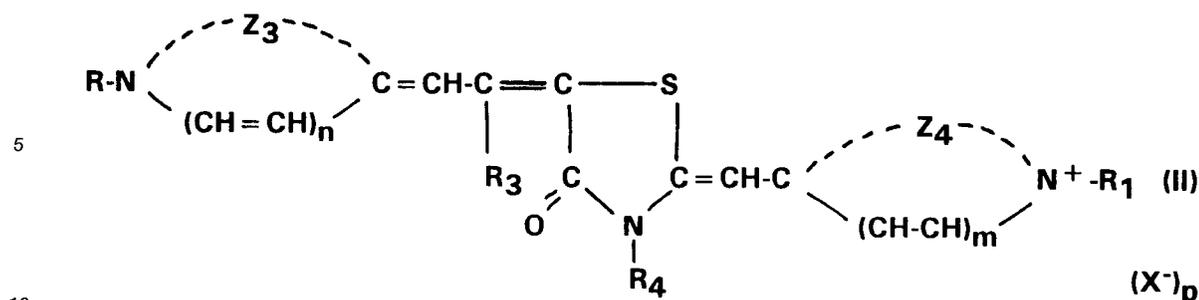
Emulsion Samples	First Optical Sensitizer	Second Optical Sensitizer
1 (comp.)	I.1	none
2 (inv.)	I.1	II.1
50 3 (inv.)	I.1	II.7
4 (inv.)	I.1	II.8
5 (comp.)	I.1	Compound A
6 (comp.)	I.1	Compound B
7 (comp.)	I.1	Compound C
55 8 (comp.)	none	II.1
9 (comp.)	none	II.8

Compound A**Compound B****Compound C**

45 The resulting emulsion samples were coated onto a poly(ethylene terephthalate) support in amount of 4.1 g/sqm as silver. The gelatin content in thus formed emulsion layer was 2.6 g/sqm. A protective layer of gelatin (0.7 g/sqm) was superposed over the emulsion layer. The samples were exposed, in a first case, at 60 Ergs/square centimeter with a laser diode Toshiba Told 9215 emitting a laser beam at 670 nm and, in a second case, to a Helium-neon laser source emitting a laser beam at 632.8 nm. The samples were then

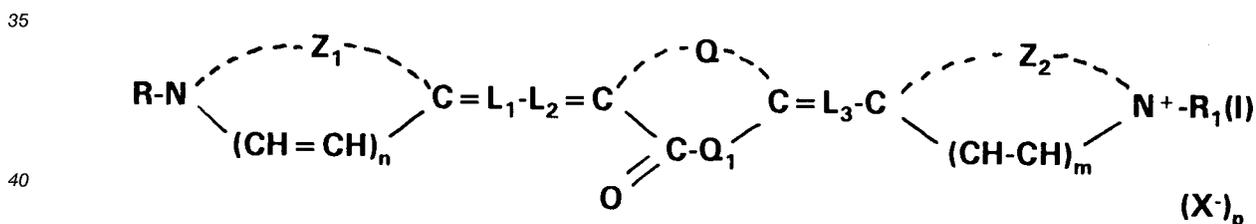
50 sensitometrically examined. The speed has been measured in Log E, wherein E is expressed in lux.seconds at a density of 1.0 above Dmin. The contrast corresponds to the absolute value of the sensitometric curve slope measured at the densities of 0.07 and 0.17 above Dmin. The results are shown in the following Table 1, wherein Speed1 and Contrast1 refers, respectively, to the speed and contrast values obtained when the samples were exposed at 670 nm, and Speed2 and Contrast2 refers, respectively, to the

55 speed and contrast values obtained when the samples were exposed at 632.8 nm.



15 wherein Z₃ represents the atoms necessary to complete a 6-membered nitrogen-containing heterocyclic group; Z₄ represents the atoms necessary to complete a 5-membered nitrogen-containing heterocyclic group; R₃ and R₄ each represents a hydrogen atom, an alkyl group or a phenyl group; R, R₁, m, n, X and p have the same meaning of formula (I).

- 20
2. Silver halide photographic material as described in claim 1 wherein Z₁ and Z₂ each independently represents a thiazole, a benzothiazole or a naphthothiazole nucleus.
- 25
3. Silver halide photographic material as described in claim 1 wherein Z₃ represents a quinoline group.
4. Silver halide photographic material as described in claim 1 wherein Z₄ represents a thiazole, a benzothiazole or a naphthothiazole nucleus.
- 30
5. Method for forming a silver image comprising image-wise exposing by means of a light source emitting light in the wavelength range of from 600 to 690 nm a photographic material containing a support having coated thereon at least a silver halide emulsion layer incorporating a first sensitizing dye and a second sensitizing dye spectrally sensitizing said emulsion for said wavelength range or for a substantial part of said wavelength range and wet-processing the exposed photographic material with aqueous developing or activating solutions and fixing solutions, thereby dissolving away said dyes from the resulting silver-image-containing material, wherein said first sensitizing dye is represented by the formula (I):

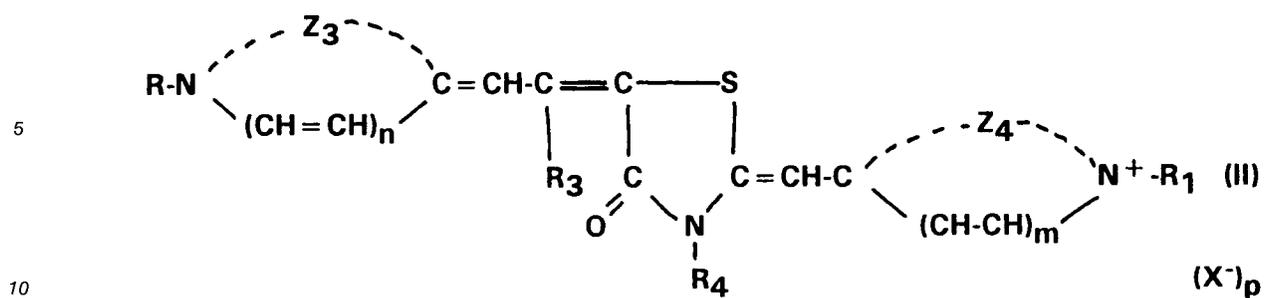


45 wherein Z₁ and Z₂ each independently represents the atoms necessary to complete a 5-membered nitrogen-containing heterocyclic group; R and R₁ each independently represents an alkyl group; Q and Q₁ in combination represent the atoms required to complete a thiazolidinone nucleus; L₁, L₂ and L₃ each represents a methine group or a substituted methine group of the formula:



55 wherein R₂ is an alkyl group having 1 to 6 carbon atoms or an aryl group having 6 to 10 carbon atoms; X⁻ is an anion and each of m, n and p is 0 or 1, provided that p is 0 when the dye forms an intramolecular salt;

and wherein second sensitizing dye is represented by formula (II):



wherein Z₃ represents the atoms necessary to complete a 6-membered nitrogen-containing heterocyclic group; Z₄ represents the atoms necessary to complete a 5-membered nitrogen-containing heterocyclic group; R₃ and R₄ each represents a hydrogen atom, an alkyl group or a phenyl group; R, R₁, m, n, X and p have the same meaning of formula (I).



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 93 10 0646

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	DE-A-2 401 368 (MITSUBISHI PAPER MILLS LTD.) * page 11, line 1 - line 8; claims 1-6 * ---	1-5	G03C1/29 G03C1/26
A	FR-A-1 598 987 (EASTMAN KODAK COMPANY) * claims 1-2 * ---	1-5	
A	PATENT ABSTRACTS OF JAPAN vol. 12, no. 147 (P-698)(2994) 7 May 1988 & JP-A-62 265 647 (KONISHIROKU PHOTO IND., CO., LTD.) 18 November 1987 * abstract * -----	1-5	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 27 SEPTEMBER 1993	Examiner HINDIAS E.
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

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