

1

2

3,702,767
SPECTRALLY SENSITIZED LIGHT SENSITIVE MATERIAL

Hans Öhlschläger, Cologne, Oskar Riester, Leverkusen, and Heinz Meckl, Cologne, Germany, assignors to Agfa-Gevaert Aktiengesellschaft, Leverkusen, Germany
No Drawing. Filed Jan. 4, 1971, Ser. No. 103,798
Claims priority, application Germany, Jan. 15, 1970,
P 20 01 572.9

Int. Cl. G03c 1/40, 1/08

U.S. Cl. 96-127

7 Claims

ABSTRACT OF THE DISCLOSURE

Cyanine and merocyanine dyes which are derived from 5-oxo-5,6,7,8-tetrahydroquinoline are good spectral sensitizers for silver halide emulsion layers and layers containing photoconductive zinc oxide in an insulating binder.

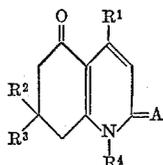
The invention relates to light sensitive layers, in particular to silver halide emulsion layers, which are spectrally sensitized with new types of sensitizing dyes.

The increase in the sensitivity of light sensitive layers, in particular of silver halide emulsion layers, by the addition of substances which increase the spectral sensitivity range of the light sensitive substances has been known for a long time. Numerous substances, mostly belonging to the class of cyanine dyes, have been described for the sensitization of silver halide emulsion layers. These known substances, however, often have disadvantages, e.g. in that their sensitizing effect is unsatisfactory, in that they impart an interfering colour to the layer or in that they adversely influence the photographic process itself. This applies particularly to special photographic materials. The adsorption on the silver halide should be so strong that the sensitizing effect is disturbed as little as possible by other necessary additives such as wetting agents and emulsifiers, stabilizers, colour couplers, dyes which can be bleached, white toners, etc. The sensitization must also be ensured under extreme conditions such as elevated temperature and high humidity. Moreover, the sensitizing dyes must not increase the basic fog present, as occasionally occurs with basic cyanine dyes. The sensitizing dyes must, in addition, have certain sensitizing properties which, apart from a sufficient intensity of sensitization in the sensitization range, include above all a steep decrease in sensitization at the transition to longer wavelengths of light. For the reasons mentioned above, there is considerable interest in finding new sensitizing dyes which do not have the disadvantages mentioned.

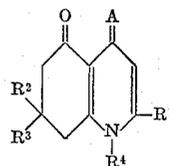
It is the object of the invention to find sensitizing dyes for sensitizing light sensitive layers, in particular silver halide emulsion layers, which do not have the disadvantages mentioned above.

A photographic material comprising at least one spectrally sensitized silver halide emulsion layer has now been found which contains, as sensitizing dyes, a dye of the following Formula I or II:

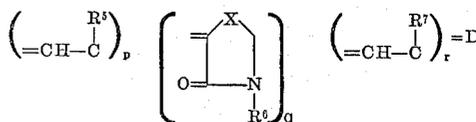
(I)



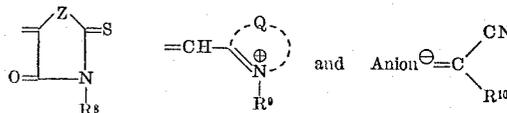
(II)



in which the symbols have the following meanings:
A=the radical



D=one of the radicals



R¹, R² and R³ are the same or different radicals and are hydrogen, alkyl preferably containing up to 6 carbon atoms such as methyl, ethyl, propyl, isopropyl or butyl, cycloalkyl such as cyclohexyl, aralkyl such as benzyl or aryl such as phenyl;

R⁴ and R⁹ are the same or different radicals and are (1) saturated or unsaturated aliphatic groups which preferably contain up to 6 carbon atoms and which may be substituted, e.g. with phenyl, hydroxy, amino, carboxyl, sulpho, sulphonylamino, sulphamyl, carbon-amido, carbamyl, carbalkoxy, sulphato or thiosulphato, (2) cycloalkyl such as cyclohexyl or (3) aryl, in particular phenyl;

R⁵ and R⁷ are the same or different radicals, and are hydrogen, saturated or olefinically unsaturated aliphatic groups containing up to 3 carbon atoms, alkoxy preferably having up to 3 carbon atoms, such as methoxy or ethoxy, alkylthio having preferably up to 3 carbon atoms, such as methylthio or ethylthio, or aryl, for example phenyl;

R⁶, R⁸ and R¹¹ are the same or different radicals and are (1) hydrogen, (2) saturated or olefinically unsaturated aliphatic groups which may be substituted, e.g. with phenyl, hydroxy or carboxyl, or (3) aryl such, for example, as phenyl or naphthyl;

R¹⁰=cyano, carbalkoxy or thiocarbamido;

X and Z are the same or different and represent —O—, —S—, —NR¹¹— or —CO—NR¹¹—;

p, q and r anion[⊖] are the same or different and represent 0 or 1; any photographically inert, e.g. halide such as chloride, bromide or iodide, perchlorate, sulphate, methylsulphate, p-toluenesulphonate and the like; the anion is absent if R⁹ contains an acid group in anionic form so that a betaine is present;

Q=a radical required to complete a heterocyclic group comprising a 5-membered or 6-membered hetero ring; the heterocyclic group may also comprise a condensed benzene or naphthalene ring and may contain further substituents; the heterocyclic groups may be any of

70

the usual groups found in cyanine chemistry, for example

those of the thiazole series series (e.g.

thiazole,
4-methylthiazole,
5-methylthiazole,
4,5-dimethylthiazole,
4-phenylthiazole,
5-phenylthiazole,
4,5-diphenylthiazole,
benzothiazole,
4-chlorobenzothiazole,
5-chlorobenzothiazole,
6-chlorobenzothiazole,
7-chlorobenzothiazole,
6-bromobenzothiazole,
5-iodobenzothiazole,
6-iodobenzothiazole,
4-methylbenzothiazole,
5-methylbenzothiazole,
6-methylbenzothiazole,
5,6-dimethylbenzothiazole,
4-phenylbenzothiazole,
5-phenylbenzothiazole,
6-phenylbenzothiazole,
5-hydroxybenzothiazole,
6-hydroxybenzothiazole,
4-methoxybenzothiazole,
5-methoxybenzothiazole,
6-methoxybenzothiazole,
5-ethoxybenzothiazole,
6-ethoxybenzothiazole,
5,6-dimethoxybenzothiazole,
5,6-methylenedihydroxybenzothiazole,
5-diethylaminobenzothiazole,
6-diethylaminobenzothiazole,
5-carboxybenzothiazole,
5-sulphobenzothiazole,
tetrahydrobenzothiazole,
7-oxotetrahydrobenzothiazole,
naphtho[1,2-d]-thiazole,
naphtho[2,1-d]-thiazole,
5-methoxynaphtho[2,1-d]-thiazole,
5-ethoxynaphtho[2,1-d]-thiazole,
7-methoxynaphtho-[2,1-d]-thiazole,
8-methoxynaphtho[1,2-d]-thiazole, etc.),

those of the selenazole series (e.g.

4-methylselenazole or 4-phenylselenazole,
benzoselenazole,
5-chlorobenzoselenazole,
5,6-dimethyl-benzoselenazole,
5-hydroxybenzoselenazole,
5-methoxybenzoselenazole,
tetrahydrobenzoselenazole,
naphtho[1,2-d]selenazole or
naphtho[2,1-d]selenazole),

those of the oxazole series (e.g.

oxazole,
4-methyloxazole,
4-phenyloxazole,
4,5-diphenyloxazole,
benzoxazole,
5-chlorobenzoxazole,
6-chlorobenzoxazole,
5,6-dimethylbenzoxazole,
5-phenylbenzoxazole,
5-hydroxybenzoxazole,
5-methoxybenzoxazole,
5-ethoxybenzoxazole,
6-dialkylaminobenzoxazole,
5-carboxybenzoxazole,
5-sulphobenzoxazole,
5-sulphonamidobenzoxazole,

5- β -carboxyvinylbenzoxazole,
naphtho[1,2-d]oxazole,
naphtho[2,1-d]oxazole or
naphtho[2,3-d]oxazole),

5 those of the imidazole series (e.g.

1-methyl-imidazole,
1-ethyl-4-phenylimidazole,
1-butyl-4,5-dimethylimidazole,
10 1-methylbenzimidazole,
1-butyl-4-methylbenzimidazole,
1-ethyl-5,6-dichlorobenzimidazole,
1-ethyl-5-trifluoromethylbenzimidazole,
1-methylnaphtho[1,2-d]imidazole or
15 1-ethylnaphtho[2,3-d]imidazole),

those of the 3,3-dialkylindolenine series (e.g.

3,3-dimethylindolenine,
3,3,5-trimethylenine,
3,3-dimethyl-5-methoxyindolenine, etc.),

20 pyridine,
3-methylpyridine,
4-methylpyridine,
5-methylpyridine,
6-methylpyridine,
25 3,4-dimethylpyridine,
3,5-dimethylpyridine,
3,6-dimethylpyridine,
4,5-dimethylpyridine,
4,6-dimethylpyridine,

30 4-chloropyridine,
5-chloropyridine,
6-chloropyridine,
3-hydroxypyridine,
4-hydroxypyridine,
35 5-hydroxypyridine,
6-hydroxypyridine,
3-phenylpyridine,
4-phenylpyridine,
40 6-phenylpyridine, etc.),

those of the 4-pyridine series (e.g.

2-methylpyridine,
3-methylpyridine,
2,3-dimethylpyridine,
45 2,5-dimethylpyridine,
2,6-dimethylpyridine,
2-chloropyridine,
3-chloropyridine,
2-hydroxypyridine,
50 3-hydroxypyridine, etc.),

those of the 2-quinoline series (e.g.

quinoline,
3-methylquinoline,
55 5-methylquinoline,
7-methylquinoline,
8-methylquinoline,
6-chloroquinoline,
8-chloroquinoline,
60 6-methoxyquinoline,
6-ethoxyquinoline,
6-hydroxyquinoline,
8-hydroxyquinoline,
5-oxo-5,6,7,8-tetrahydroquinoline, etc.),

65 those of 4-quinoline series (e.g. quinoline, 6-methoxy-
quinoline, 7-methylquinoline, 8-methylquinoline, etc.),
those of the isoquinoline series (e.g. isoquinoline or 3,4-
dihydroisoquinoline), those of the thiazoline series (e.g.
70 thiazoline, 4-methylthiazoline, etc.), and those of the
pyrroline, tetrahydropyridine, thiadiazole, oxadiazole,
pyrimidine, triazine or benzothiazine series.

The heterocyclic groups may in addition carry any
other substituents, e.g. additional alkyl groups prefer-
75 ably containing up to 3 carbon atoms, such as methyl

5

or ethyl, halogen such as chlorine or bromine, hydroxyl, alkoxy preferably with up to 3 carbon atoms, such as methoxy or ethoxy, hydroxyalkyl, alkylthio, aryl such as phenyl or aralkyl such as benzyl, amino, substituted amino and the like.

6

The following compounds, for example, are suitable. The absorption maxima have been determined in methanolic solution unless otherwise indicated. In the following table, DMF denotes dimethylformamide, DMSO dimethylsulphoxide.

No.	Dye	Absorption maximum (nm.)	Sensitization maximum (nm.)
1.....		560 DMF	620
2.....		579 DMF	631
3.....		558	618
4.....		560 DMF	620
5.....		580 DMF	637
6.....		531	590
7.....		556	608

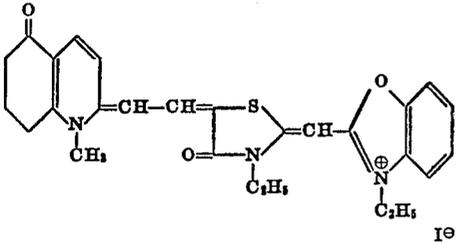
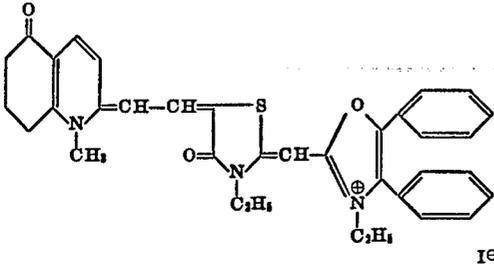
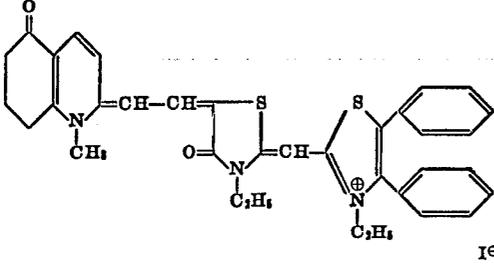
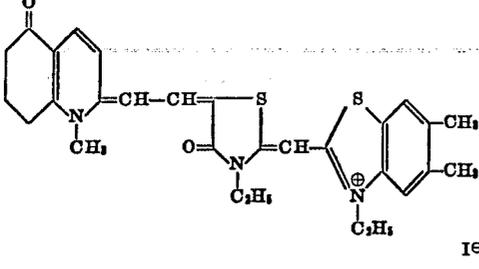
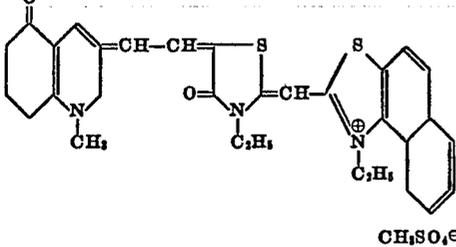
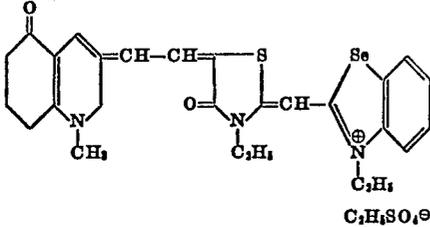
TABLE—Continued

No.	Dye	Absorption maximum (nm.)	Sensitization maximum (nm.)
8.....		519 DMSO	538
1.....		602	675
10.....		601 DMF	670
11.....		627 DMF	693
12.....		624 DMF	692
13.....		591 CHCl3	666
4.....		603	672

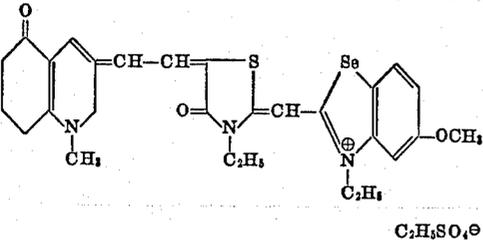
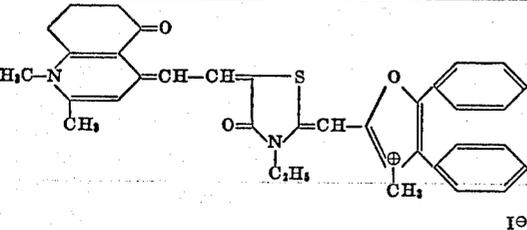
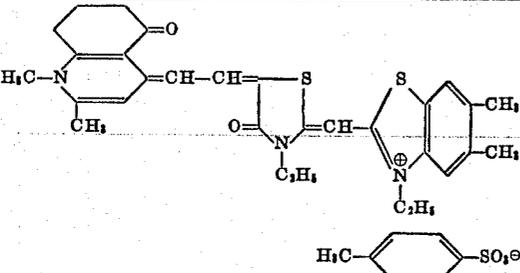
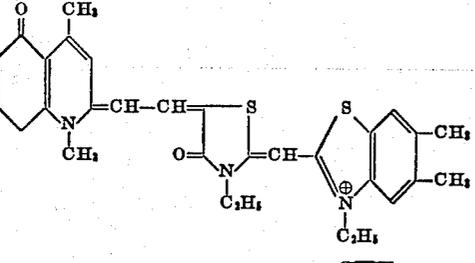
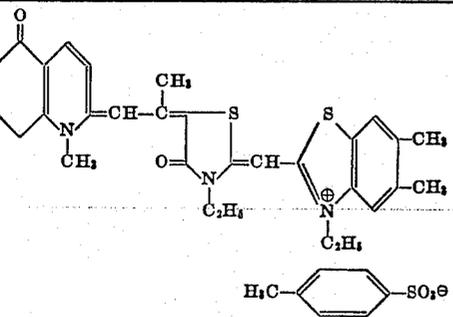
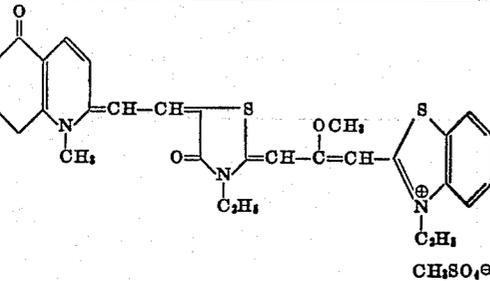
TABLE—Continued

No.	Dye	Absorption maximum (nm.)	Sensitization maximum (nm.)
15.....		597 CHCl ₃	672
16.....		580 CHCl ₃	657
17.....		595 CHCl ₃	670
18.....		631 CHCl ₃	676
19.....		525 CHCl ₃	555
20.....		628	660

TABLE—Continued

No.	Dye	Absorption maximum (nm.)	Sensitization maximum (nm.)
21.....		612	650
22.....		601	638
23.....		617	650
24.....		623	662
25.....		630	668
26.....		629	670

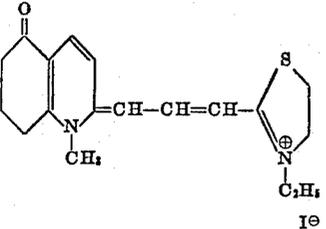
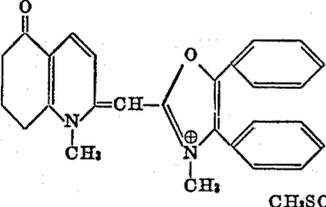
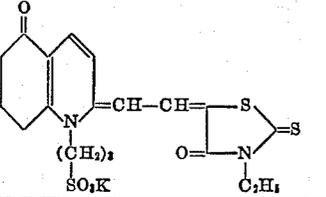
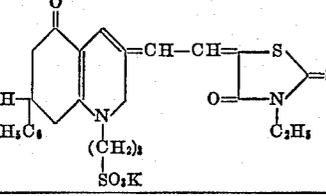
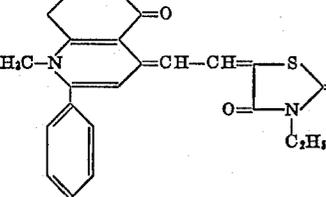
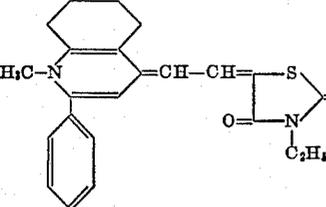
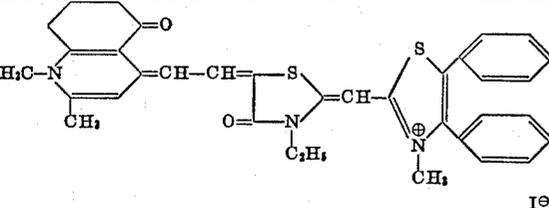
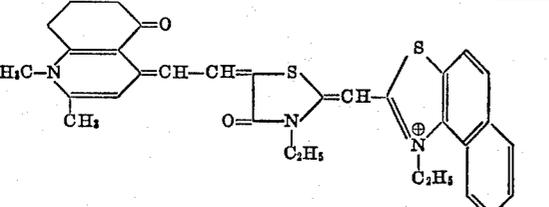
TABLE—Continued

No.	Dye	Absorption maximum (nm.)	Sensitization maximum (nm.)
27.....		627	665
$C_2H_5SO_3^-$			
28.....		626	660
I^-			
29.....		645	678
$H_3C-C_6H_4-SO_3^-$			
30.....		624	660
$H_3C-C_6H_4-SO_3^-$			
31.....		645 DMF	680
$H_3C-C_6H_4-SO_3^-$			
32.....		660	705
$CH_3SO_3^-$			

TABLE—Continued

No.	Dye	Absorption maximum (nm.)	Sensitization maximum (nm.)
23.....		605	658
24.....		654	700
25.....		612 DMF	645
26.....		602 DMF	642
27.....		580	623
28.....		544	580
29.....		484	515
40.....		608	654

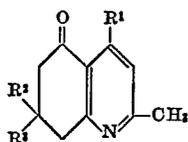
TABLE—Continued

No.	Dye	Absorption maximum (nm.)	Sensitization maximum (nm.)
41.....	 <p style="text-align: center;">I[⊖]</p>	525	570
42.....	 <p style="text-align: center;">CH₃SO₄e⁻</p>	440	487
43.....	 <p style="text-align: center;">(CH₃)₂ SO₃K</p>	563	620
44.....	 <p style="text-align: center;">(CH₃)₂ SO₃K</p>	566	624
45.....		585 DMF	634
46.....		627 DMF	695
47.....	 <p style="text-align: center;">I[⊖]</p>	641 DMF	670
48.....	 <p style="text-align: center;">I[⊖]</p>	650 DMF	680

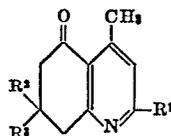
TABLE—Continued

No.	Dye	Absorption maximum (nm.)	Sensitization maximum (nm.)
49		647 DMF	682

The compounds used as starting material for the preparation of the dyes according to the invention are 5-oxo-5,6,7,8-tetrahydroquinolines of the following formulae:



or



in which R¹, R² and R³ have the meanings already given.

Oxo-5,6,7,8-tetrahydroquinolines are heterocyclic bases which can easily be prepared by condensation of dihydroresorcinols with 1,3-dicarbonyl compounds or their derivatives in the presence of ammonia or ammonium acetate.

2-methyl-5-oxo-5,6,7,8-tetrahydroquinoline

A mixture of 140 g. of acetylacetaldehyde dimethylacetal, 132 g. of dihydroresorcinol and 100 g. of ammonium acetate is heated to 120° C. on an oil bath for one hour and then distilled in vacuo. After a fore run, 109 g. of oxoquinoline, B.P. 14 mm., 142–144° C. are obtained. 2,4-dimethyl-5-oxo-5,6,7,8-tetrahydroquinoline, B.P. 14 mm., 144–148° C. is obtained in a similar manner from dihydroresorcinol and acetyl acetone; 2,7,7-trimethyl-5-oxo-5,6,7,8-tetrahydroquinoline, B.P. 13 mm., 142–146° C. from 5,5-dimethylcyclohexane-1,3-dione, and acetylacetaldehyde-dimethylacetal; 2-phenyl-4-methyl-5-oxo-5,6,7,8-tetrahydroquinoline, M.P. 109–110° C., from dihydroresorcinol and acetylacetophenone; and 2-methyl-7-phenyl-5-oxo-5,6,7,8-tetrahydroquinoline, B.P. 0.6 mm.: 174–178° C. from 5-phenylcyclohexane-1,3-dione and acetylacetaldehyde-dimethylacetal.

The merocyanines are obtained e.g. by condensation of a quaternary salt of a 2-methyl- (or 4-methyl-) 5-oxo-5,6,7,8-tetrahydroquinoline base with an alkoxyalkylidene derivative of a cyclic ketomethylene compound, for example N-alkyl-5-ethoxymethylenerrhodanine or by condensation of a 2-anilidovinylquaternary salt of a 5-oxo-5,6,7,8-tetrahydroquinoline with ketomethylene compounds, e.g. with rhodanines, oxazolidone thiones,

thiohydantoin or pyrazolones. If a quaternary salt of 2,4-dimethyl-5-oxo-tetrahydroquinoline is used, condensation occurs either at the methyl group in the 4-position or at the methyl group in the 2-position, depending on the condensation conditions and the solvent. When condensing 1,2,4-trimethyl-5-oxo-tetrahydroquinolinium methyl sulphate with N-ethyl-5-ethoxymethylene rhodanine in pyridine, for example, Dye 3 is obtained whereas when alcohol is used as solvent, Dye 2 is obtained.

If the merocyanines contain thione groups, additional dyes can be prepared by known methods, for example by further quaternisation and renewed condensation, e.g. with keto methylene compounds or with 2-methylquaternary salts of heterocyclic bases. Thus, for example on further condensation of merocyanines obtained from rhodanine, rhodacyanines are obtained.

Mono- and tri-methine dyes may also be prepared by the usual processes, for example starting from 2- (or 4-) methyl-5-oxo-5,6,7,8-tetrahydroquinolinium quaternary salts by condensation with suitably substituted derivatives of any heterocyclic bases, e.g. 2-alkylthio- or 2-anilidovinyl-quaternary salts, or conversely by condensation of 2-anilidovinyl-5-oxo-5,6,7,8-tetrahydroquinoline quaternary salts with 2-methylquaternary salts of heterocyclic bases.

The preparation of a few dyes is described in detail below.

Dye 1

1.6 g. of 2-methyl-5-oxo-5,6,7,8-tetrahydroquinoline and 1.1 ml. of dimethylsulphate are heated to 80° C. on an oil bath, the reaction temperature rising to 120° C. Without isolating the resulting quaternary salt, it is heated on a steam bath for 5 minutes together with 2.1 g. of 3-ethyl-5-ethoxymethylene rhodanine in 10 ml. of alcohol with the addition of 2 ml. of triethylamine, the dye partly precipitating. After cooling the mixture, it is filtered under suction and recrystallised from chloroform/methanol. 2.7 g., M.P.: 275–277° C. (decomposition).

Dye 2

1.7 g. of 2,4-dimethyl-5-oxo-5,6,7,8-tetrahydroquinoline and 1.1 ml. of dimethylsulphate are heated on an oil bath to 60° C., the reaction temperature rising to 90° C. The mixture is heated for another 10 minutes at 100° C. and then heated on a steam bath for 15 minutes together with 2.1 g. of N-ethyl-5-ethoxymethylenerrhodanine and 2 ml. of triethylamine in 20 ml. of alcohol. Dye 2 precipitates. After cooling, it is isolated by suction filtration and recrystallised from chloroform/methanol. 1.7 g., M.P.: 241° C. (decomposition).

1.7 g. of Dye 1 and 2.5 ml. of dimethylsulphate are heated to 110° C. on an oil bath for 15 minutes. The quaternary salt obtained is triturated with acetone to remove excess dimethylsulphate and then heated on a steam bath for 10 minutes together with 0.8 g. of N-ethylrhodanine in 50 ml. of alcohol with the addition of 2 ml. of triethylamine. The mixture is cooled and Dye 9 is isolated by suction filtration, washed with methanol and recrystallised from chloroform/methanol. 0.8 g., M.P.: 273-276° C.

Dye 24

3.4 g. of Dye 1 are quaternised as described in the previous example and the quaternary salt is heated on a steam bath for 15 minutes together with 3.3 g. of 2,5,6-trimethyl-3-ethyl-benzothiazolium iodide in 20 ml. of alcohol and 2 ml. of triethylamine. The dye which crystallises on cooling is removed by suction filtration and recrystallised from methanol. 1.7 g. of Dye 24 is obtained, M.P. 273-275° C. (decomposition).

Dye 34

4.2 g. of 1-methyl-2-anilidovinyl-5-oxo-5,6,7,8-tetrahydroquinolinium tosylate and 3.2 g. of N-methyl-lepidinium tosylate in 30 ml. of acetonitrile are heated together on a steam bath for 10 minutes with the addition of 2 ml. of triethylamine and 1.5 ml. of acetic acid anhydride. After cooling, suction filtration and recrystallisation from methanol, 2.3 g. of Dye 34 of M.P. 215° C. are obtained.

The absorption maxima and sensitization maxima of the dyes according to the invention are shifted towards longer wavelengths by 15 to 20 nm. compared with comparable dyes derived from α - or γ -picoline (absorption maximum of 3-ethyl-5-[(1-ethyl-2(1H)pyridylidene)-ethylene]-rhodanine: 540 nm.; Brooker et al., J. Am. Chem. Soc. 73, 5336).

The dyes according to the invention produce sensitizations of high intensity on silver halide emulsions and in contrast to the corresponding quinoline dyes they show a spectrally narrower sensitization curve.

In addition, the sensitizations obtained are completely resistant to the influence of the usual additives such as wetting agents, emulsifiers, stabilizers and colour couplers or dyes which can be bleached, even at elevated temperature and high humidity. It has also been found to be an advantage that the dyes can be easily washed out so that photographic layers which have been sensitized with these dyes have no interfering colour after processing. The dyes are therefore valuable sensitizers especially for colour photographic materials.

The sensitizing dyes according to the invention may be used in any silver halide emulsions. Suitable silver halides are silver chloride, silver bromide or mixtures thereof, if desired with a small silver iodide content of up to 10 mol percent.

The silver halides may be dispersed in the usual hydrophilic compounds, for example in carboxymethylcellulose, polyvinyl alcohol, polyvinylpyrrolidone, alginic acid and its salts, esters or amides or, preferably, in gelatine.

The sensitizing dyes for use according to the present invention are advantageously added to the photographic emulsions after chemical ripening and before casting. The methods used for this are generally known in the art. The sensitizing dyes are generally incorporated with 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 gelatine and must not exert any adverse influence 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 10 and 100 mg. per mol of silver halide, preferably between 30 and 300 mg. per mol of silver halide. The concentration of the dye can be adapted to the given requirements, depending on the nature of the emulsion, the desired sensitization effect, etc. The most suitable concentration for any given emulsion can easily be determined by the usual tests employed in photographic practice.

The emulsions may also be chemically sensitized, e.g. by the addition of compounds which contain sulphur during chemical ripening, for example allyl isothiocyanate, allyl thiourea, sodium thiosulphate and the like. Reducing agents, e.g. the tin compounds described in Belgian patent specifications Nos. 493,464 or 568,687, polyamines such as diethylenetriamine or aminomethylsulphonic acid derivatives, e.g. according to British patent specification No. 789,823, may also be used as chemical sensitizers.

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

The emulsions may also be sensitized with polyalkylene oxide derivatives, e.g. with polyethylene oxide having a molecular weight of between 1,000 and 20,000, or with condensation products of alkylene oxide 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 and preferably more than 1,000. These sensitizers may, of course, be combined in order to obtain special effects, as described in Belgian patent specification No. 537,278 and in British patent specification No. 727,982.

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

The mono- and tri-methinecyanines of the present invention may advantageously be combined with compounds which contain a mercapto group and a sulphonic acid group such as those mentioned in French patent specification No. 1,426,623; a supersensitizing effect is then observed.

The emulsions according to the invention may contain the usual stabilizers, e.g. homopolar or salt-containing compounds of mercury with aromatic or heterocyclic rings, such as mercaptotriazoles, simple mercury salts, sulphonium mercury double salts and other mercury compounds. Other suitable stabilizers include azaindenes, 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. phenylmercapto tetrazole, quaternary benzothiazole derivatives, benzotriazole and the like.

The emulsions may be hardened in the usual manner, for example with formaldehyde or halo-substituted aldehydes which contain a carboxyl group, such as mucobromic acid, diketones, methanesulphonic acid esters, dialdehydes and the like.

The emulsions according to the invention may be used for various photographic processes, for example for materials used for producing original photographs, for copying materials, for reprotechnical films, for X-ray films, for materials which are suitable for the silver salt diffusion process, for colour photographic materials, for photographic materials for the silver dye bleaching process, etc.

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

EXAMPLE 1

To 1 kg. of a conventional silver chlorobromide emulsion are added 10 g. of sodium salt of the cyan-forming coupler 1-hydroxy-4-sulfo-N-n-octadecyl-2-naphthamide as a 5% aqueous solution and are further added 10 mg. of a dye of the following Table 1. The emulsion is cast on a baryta-coated paper and dried. The various samples are exposed behind a step-wedge

$$(\sqrt[3]{2} - \text{steps})$$

and filters which are transparent only for red or green light, respectively. The samples are then developed in a color-forming developer bath, followed by fixing and rinsing.

The outstanding sensitizing intensity of the dyes according to the invention is shown in the following Table 1 from the number of visible steps which is used as a measure for the relative sensitivity of the sensitized emulsions. The known red sensitizer of the following formula is used as comparison.

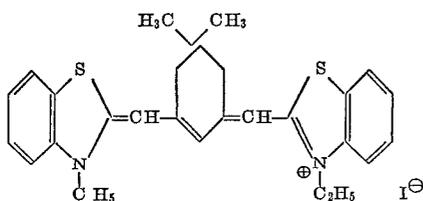


TABLE 1

Dye No.	Steps $\sqrt[3]{2}$		Sensitization maximum (nm.)
	Green light	Red light	
Comparison dye.....	6	25	700
9.....	14	30	675
10.....	11	27	670
12.....	11	28	692
13.....	13	27	670
14.....	12	27	670
16.....	11	27	657
17.....	11	27	670
22.....	15	27	640
23.....	14	28	655
24.....	13	28	662
25.....	11	27	668
27.....	9	26	670
29.....	9	27	678
30.....	14	30	660

EXAMPLE 2

In this example is shown the sensitization of an electrophotographic zinc oxide layer using the dyes according to the present invention.

To a mixture of 20 g. of photoconductive zinc oxide, 20 ml. of toluene, 11 ml. of ethyl acetate, 0.66 ml. of a 10% solution of tetrachlorophthalic anhydride in ethanol and 45 g. of a 50% solution of a copolymer consisting of 87 parts by weight of vinyl acetate, 12 parts of ethyl acrylate and 1 part of acrylic acid in a composition of 1 part by volume of toluene, 1 part of 1,2-dichloroethane and 4 parts ethyl acetate are added 100 mg. of a dye of the following Table 2 as a 0.1% solution in dimethyl formamide. This mixture is cast on a baryta-coated paper (25 g. of zinc oxide per m.²) and dried. The samples are charged and then exposed for 15 seconds behind a step wedge (increase of density 0.1) using an incandescent lamp of 450 watt and an intensity of 2280 lux. The development is performed according to a common developing method employing a powder developer. The sensitivity is shown by the number of steps at which no toner

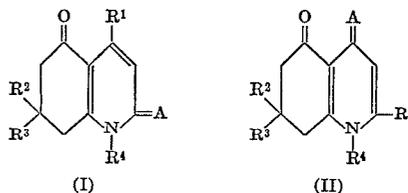
aparticles are deposited a ndwhich maintain the original density. The more steps, the greater is the sensitivity.

TABLE 2

Dye No.	Steps	Sensitization maximum (nm.)
1.....	9	570
3.....	25	570
6.....	19	540
7.....	23	540
8.....	19	555
9.....	28	525
16.....	27	600
21.....	25	585
22.....	31	620
23.....	29	610
24.....	31	625
25.....	32	630
27.....	30	640
29.....	32	640
34.....	32	660
35.....	32	670
36.....	32	620
37.....	31	610
39.....	31	590
40.....	20	490
41.....	32	610
42.....	26	530
47.....	18	440
48.....	29	660
49.....	29	665
49.....	29	660

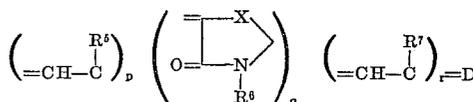
What we claim is:

1. A light sensitive photographic material which comprises a sensitising dye selected from the group consisting of the Formulae I or II:



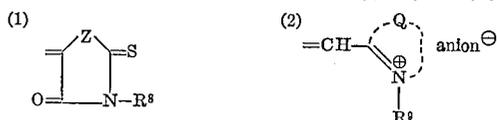
in which

A represents the radical



p, q and r, which may be the same or different are 0 or 1

D is one of the following radicals (1), (2) or (3)



X and Z, which may be the same or different each represent



R¹, R² and R³, which may be the same or different, each represent

- (1) a hydrogen atom
- (2) an alkyl group containing up to 6 carbon atoms
- (3) a cycloalkyl group
- (4) an aryl group

R⁴ and R⁹, which may be the same or different, each represent

- (1) a substituted or unsubstituted saturated or unsaturated aliphatic group containing up to 6 carbon atoms,
- (2) a cycloalkyl group
- (3) an aryl group

25

R⁵ and R⁷, which may be the same or different, each represent

- (1) a hydrogen atom
- (2) a saturated or unsaturated aliphatic group containing up to 3 carbon atoms
- (3) an alkoxy group containing up to 3 carbon atoms
- (4) an alkylthio group containing up to 3 carbon atoms, or
- (5) an aryl group

R⁶, R⁸ and R¹¹, which may be the same or different, each represent

- (1) a hydrogen atom,
- (2) a saturated or olefinically unsaturated substituted or unsubstituted aliphatic group
- (3) a cycloalkyl group, or
- (4) an aryl group

R¹⁰ represents a cyano, carbalkoxy or thiocarbamido group

anion[⊖] is an anion, and is absent if R⁹ contains an acid group

Q is a divalent radical necessary to complete a heterocyclic 5- or 6-membered ring.

2. A silver halide emulsion containing material as claimed in claim 1 which comprises 10 to 1000 mg. of the said dye per mol of silver halide.

26

3. A material as claimed in claim 1 which comprises 30 to 300 mg. of dye per mole of silver halide.

4. A material as claimed in claim 2 which also comprises one or more colour couplers.

5. The material of claim 1 in which said dye is selected from the group consisting of Formula 1 through Formula 49 as illustrated in the specification.

6. A silver halide emulsion containing material as claimed in claim 5 which comprises 10 to 1000 mg. of the said dye per mole of silver halide.

7. A material as claimed in claim 3 which also comprises one or more couplers.

References Cited

UNITED STATES PATENTS

3,511,664	5/1970	Nakazawa et al.	96—127
3,534,028	10/1970	Holtzclaw et al.	96—127
3,558,614	1/1971	Jenkins	96—127

J. TRAVIS BROWN, Primary Examiner

E. C. KIMLIN, Assistant Examiner

U.S. Cl. X.R.

25 96—1.7, 140, 131, 135, 132 100; 260—240.6