United States Patent Office 3,629,274 Patented Dec. 21, 1971

3,629,274

MEROCYANINE DYES AND PHOTOGRAPHIC MATERIALS PREPARED THEREWITH

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No Drawing. Original application July 22, 1966, Ser. No. 567,070, now Patent No. 3,486,897, dated Dec. 30, 1969. Divided and this application June 11, 1969, Ser. No. 832,415

Int. Cl. C09b 23/10

U.S. Cl. 260—304 11 Claims

ABSTRACT OF THE DISCLOSURE

Certain merocyanine dyes derived from cyanomethyl sulfones are useful as filter dyes and as spectral sensitizers in light-sensitive photographic silver halide emulsions. 2 - (3 - cyano-3-dodecylsulfonylallylidene)-3-ethylthiazolidine and 2 - (3 - cyano-3-dodecylsulfonylallylidene)-3-(3-sulfopropyl)thiazolidine, potassium salt are illustrative of the new merocyanine dyes.

This application is a division of my copending application Ser. No. 567,070, filed July 22, 1966, now U.S. Patent 3,486,897.

This invention relates to novel and improved photographic materials, and more particularly to light-sensitive photographic silver halide emulsions containing certain merocyanine dyes derived from cyanomethyl sulfones as filter and sensitizing dyes therein, to novel merocyanine dyes of the above kind, and to the preparation of these materials and dyes.

It is known to employ light-screening substances in photographic elements for antihalation purposes and for protecting a light-sensitive emulsion or emulsions from the action of light which it is not desired to record. For example, light-screening substances are often required (a) in backing layers on either side of the support to reduce halation, (b) in overcoats on photographic elements to protect the light-sensitive emulsion or emulsions from the effects of ultraviolet light, particularly in the case of color photographic elements, and (c) in interlayers between differentially color-sensitized emulsions to protect an underlying emulsion layer or layers from unwanted action of certain wavelengths of light. However, many of the light-screening substances that have been employed for the purposes indicated above are not resistant to diffusion and wander from their desired position or positions in the photographic element. Furthermore, many of them do not have sufficiently sharp absorption maxima and high extinction coefficients in the desired regions of the spectrum.

I have now made the important discovery that certain merocyanine dyes derived from cyanomethyl sulfones are especially useful as filter dyes and sensitizers in light-sensitive photographic silver halide emulsions. These dyes not only have desirably sharp absorption maxima and high extinction coefficients, but also show very high resistance to diffusion and remain firmly fixed in the applied positions in the photographic element. They are further characterized by providing photographic filter layers which absorb to appreciably shorter wavelengths in the ultraviolet region of the spectrum as compared with similar layers prepared with any of the previously known related dimethine type of dyes. This is of particular advantage in certain photographic applications. The dyes are further useful for the preparation of non-light sensitive photographic elements such as diffusion transfer sheets (or color and black-and-white), etc.

It is, accordingly, an object of this invention to provide

novel and improved photographic materials, and more particularly light-sensitive photographic silver halide emulsions containing at least one of the merocyanine dyes of the invention.

Another object of this invention is to provide novel and improved light-sensitive photographic elements comprising a support material having thereon at least one layer of the above novel emulsions of the invention.

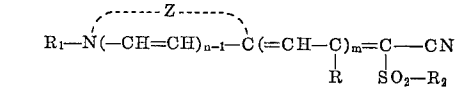
Another object of this invention is to provide novel and improved light-sensitive photographic elements comprising a support material having thereon at least one light-sensitive silver halide emulsion layer and at least one light-absorbing filter layer comprising a merocyanine dye of the invention.

Another object of this invention is to provide novel merocyanine dyes derived from cyanomethyl sulfones which absorb in the ultraviolet region of the spectrum, which have sharp absorption maxima and high extinction coefficients, and which have low diffusibility in the photographic layers of the invention.

Other objects will become apparent from the following description and examples.

The novel merocyanine dyes which are suitable for accomplishing the above objects of my invention include those represented by the following general formula:

I.

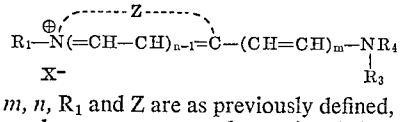


wherein each of n and m represents a positive integer of from 1 to 2; R represents a hydrogen atom, an alkyl group (including substituted alkyl) and preferably containing about from 1 to 8 carbon atoms, e.g., methyl, ethyl, propyl, isopropyl, butyl, hexyl, octyl, etc., an aryl group, e.g., phenyl, chlorophenyl, tolyl, etc., or an aralkyl group, e.g., benzyl, phenylethyl, etc.; R_1 represents an alcohol radical, e.g., an alkyl substituent (including substituted alkyl) and preferably containing from 1 to 12 carbon atoms, e.g., methyl, sulfoethyl, carboxyethyl, hydroxypropyl, sulfobutyl, carboxybutyl, hexyl, octyl, dodecyl, etc., or an aryl group, e.g., phenyl, sulfophenyl, carboxyphenyl, tolyl, etc.; R_2 represents an alkyl group (including substituted alkyl) and preferably containing from 1 to 12 carbon atoms, e.g., methyl, ethyl, propyl, isopropyl, butyl, hexyl, octyl, dodecyl, etc., an aryl group, e.g., phenyl, tolyl, naphthyl, etc., an aralkyl group, e.g., benzyl, phenylethyl, etc., or a nitrogen heterocyclic group attached to the sulfonyl group through a nuclear carbon atom such as an oxazolyl group a benzoxazolyl group, a pyridyl group, a quinolyl group, an imidazolyl group and a benzimidazolyl group, and Z represents the nonmetallic atoms required to complete a 5- to 6- membered heterocyclic nucleus such as those selected from the class consisting of a thiazole nucleus (e.g., thiazole, 4-methylthiazole, 4-phenylthiazole, 5-methylthiazole, 5-phenylthiazole, 4,5-dimethylthiazole, 4,5-diphenylthiazole, 4-(2-thienylthiazole, etc.), a benzothiazole nucleus (e.g., benzothiazole, 4-chlorobenzothiazole, 5-chlorobenzothiazole, 6-chlorobenzothiazole, 7-chlorobenzothiazole, 4-methylbenzothiazole, 5-methylbenzothiazole, 6 - methylbenzothiazole, 5 - bromobenzothiazole, 6 - bromobenzothiazole, 4-phenylbenzothiazole, 5-phenylbenzothiazole, 4-methoxybenzothiazole, 5-methoxybenzothiazole, 6 - methoxybenzothiazole, 5 - iodobenzothiazole, 6 - iodobenzothiazole, 4 - ethoxybenzothiazole, 5 - ethoxybenzothiazole, tetrahydrobenzothiazole, 5,6 - dimethoxybenzothiazole, 5,6 - dioxymethylenebenzothiazole, 5 - hydroxybenzothiazole, 6 - hydroxybenzothiazole, etc.), a naphthothiazole nucleus, (e.g., α-naphthothiazole, β-naphthothiazole, 5-methoxy-β,β-naphthothiazole, 5-ethoxy-β-naphthothiazole, 8 - methoxy - α-naphthothiazole, 7-methoxy-α-naphthothiazole, etc.), a thionaphtheno-7',6',4,5-

thiazole nucleus (e.g., 4'-methoxythianaphtheno-7',6',4,5-thiazole, etc.), an oxazole nucleus (e.g., 4-methyloxazole, 5-methyloxazole, 4-phenyloxazole, 4,5-diphenyloxazole, 4-ethyloxazole, 4,5-dimethyloxazole, 5-phenyloxazole, etc.), a benzoxazole nucleus (e.g., benzoxazole, 5-chlorobenzoxazole, 5-methylbenzoxazole, 5-phenylbenzoxazole, 6-methylbenzoxazole, 5,6-dimethylbenzoxazole, 4,6-dimethylbenzoxazole, 5-methoxybenzoxazole, 5-ethoxybenzoxazole, 5-chlorobenzoxazole, 6-methoxybenzoxazole, 5-hydroxybenzoxazole, 6-hydroxybenzoxazole, etc.) a naphthoxazole nucleus (e.g., α-naphthoxazole, β-naphthoxazole, etc.), a selenazole nucleus (e.g., 4-methylselenazole, 4-phenylselenazole, etc.), a benzoselenazole nucleus (e.g., benzoselenazole, 5-chlorobenzoselenazole, 5-methoxybenzoselenazole, 5-hydroxybenzoselenazole, tetrahydrobenzoselenazole, etc.), a naphthoselenazole nucleus (e.g., α-naphthoselenazole, β-naphthoselenazole, etc.), a thiazoline nucleus (e.g., thiazoline, 4-methylthiazoline, etc.), a thiazolidine nucleus, a 2-pyridine nucleus (e.g., 2-pyridine, 5-methyl-2-pyridine, etc.), a 4-pyridine nucleus (e.g., 4-pyridine, 3-methyl-4-pyridine, etc.), a 2-quinoline nucleus (e.g., 2-quinoline, 3-methyl-2-quinoline, 5-ethyl-2-quinoline, 6-chloro-2-quinoline, 8-chloro-2-quinoline, 6-methoxy-2-quinoline, 8-ethoxy-2-quinoline, 8-hydroxy-2-quinoline, etc.), a 4-quinoline nucleus (e.g., 4-quinoline, 6-methoxy-4-quinoline, 7-methyl-4-quinoline, 8-chloro-4-quinoline, etc.), a 1-isoquinoline nucleus (e.g., 1-isoquinoline, 3,4-dihydro-1-isoquinoline, etc.), a 3-isoquinoline nucleus (e.g., 3-isoquinoline, etc.), 3,3-dialkylindolenine nucleus, an imidazole nucleus (e.g., imidazole, 1-alkylimidazole, 1-alkyl-4-phenylimidazole, 1-alkyl-4,5-dimethylimidazole, etc.), a benzimidazole nucleus (e.g., benzimidazole, 1-alkylbenzimidazole, 1-aryl-5,6-dichlorobenzimidazole, etc.), a naphthimidazole nucleus (e.g., 1-alkyl-α-naphthimidazole, 1-aryl-β-naphthimidazole, 1-alkyl-5-methoxy-α-naphthimidazole, etc.), etc.

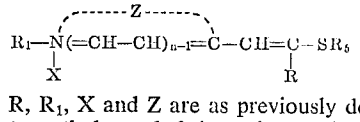
The above defined merocyanine dyes of the invention can conveniently be prepared, for example, by condensing a cyanomethyl sulfone corresponding to the formula $R_2—SO_2—CH_2—CN$, wherein R_2 is as previously defined, (prepared, for example, by the general method of Dijkstra and Backer, Rec. Trav. Chim., 73, 569 (1954)) with (1) derivatives of heterocyclic bases such as those represented by the general formula:

II.



wherein *m*, *n*, R_1 and Z are as previously defined, R_3 represents an acyl group, e.g., acetyl, propionyl, benzoyl, etc., R_4 represents an aryl group, e.g., phenyl or tolyl, and X represents an acid anion, e.g., chloride, bromide, iodide, p-toluenesulfonate, sulfamate, methyl sulfate, ethyl sulfate, perchlorate, etc., or (2) compounds represented by the general formula:

III.



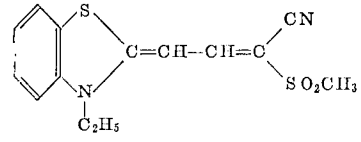
wherein *n*, R, R_1, X and Z are as previously defined, and R_5 represents methyl or ethyl, in an inert solvent medium e.g., alkanol such as methanol, butanol, etc., acetone, 1,4-dioxane, pyridine, dimethylformamide, dimethylacetamide, quinoline, and the like, at elevated temperatures and preferably at refluxing temperatures of the reaction mixture, in the presence of a basic condensing agent such as a trialkylamine, e.g., triethylamine, tri-n-propylamine, tri-n-butylamine, etc., N-methylpiperidine, N-ethylpiperidine, N,N-dimethylaniline, etc. The dye compounds are then separated from the reaction mixtures by chilling and dilution with nonsolvents such as water, alkanols such as methanol, ethanol, etc. and purified by one or more recrystallizations from suitable solvents such as above and mixtures of solvents, for example, pyridine and methanol.

The intermediate heterocyclic compounds represented by Formulas II and III above are all well known substances, and methods for preparing these compounds are well known to the art. For example, many of them are described in Brooker et al., U.S. Reissue Patent No. 24,292, issued Mar. 19, 1957, and Heseltine et al., U.S. Patent No. 3,140,182, issued July 7, 1964.

The following examples further illustrate this invention.

EXAMPLE 1

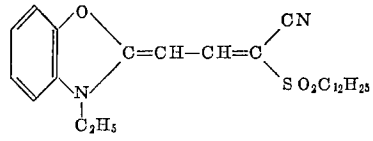
2-(3-cyano-3-methylsulfonylallylidine)-3-ethylbenzothiazoline



A mixture of 2-β-acetanilidovinyl-3-ethylbenzothiazolium iodide (3.15 g., 7 m. mole), methylsulfonylacetonitrile (0.38 g., 7 m. mole) and pyridine (10 ml.) as warmed almost to the solution point and triethylamine (1.5 ml., 10.5 m. mole) was then added. The resulting mixture was refluxed gently for 5 minutes, cooled and treated with ice and water to precipitate the dye as an oil which after solidification was collected on a filter and dried (1.62 g., 76%). Recrystallization twice from pyridine and methanol afforded the pure dye, M.P. 218–219° C., in 63% yield.

EXAMPLE 2

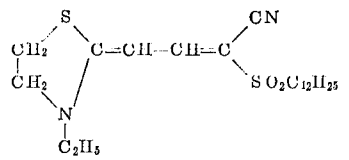
2-(3-cyano-3-dodecylsulfonylallylidene)-3-ethylbenzoxazoline



A mixture of 2-β-acetanilidovinyl-3-ethylbenzoxazolium iodide (4.34 g., 10 m. mole), dodecylsulfonylacetonitrile (2.73 g., 10 m. mole), acetic anhydride (0.9 ml.), pyridine (15 ml.) and triethylamine (2.8 mg., 20 m. mole) was boiled under reflux for 5 minutes, cooled and diluted with water. The aqueous suspension of oil was extracted twice with ether, the extracts were combined and the ether was removed by evaporation. The residue was taken up in a minimum of warm ethanol, the solution was cooled and the crystalline product collected (2.48 g., 52%). Recrystallization twice from methanol afforded the pure dye, M.P. 84–85.5° C., in 39% yield.

EXAMPLE 3

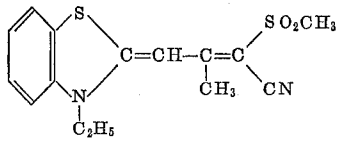
2-(3-cyano-3-dodecylsulfonylallylidene)-3-ethylthiazolidine



2-β-anilinovinyl-3-ethyl-2-thiazolinium iodide (3.62 g., 10 m. mole), dodecylsulfonylacetonitrile (2.73 g., 10 m. mole), pyridine (15 ml.), acetic anhydride (1.9 ml., 20 m. mole), and triethylamine (2.8 ml., 20 m. mole) were refluxed for 8 minutes and then cooled. The crystals which separated on addition of ice and water were collected on a filter, washed with methanol, and dried (3.52 g., 86%). Recrystallization twice from methanol afforded a 58% yield of the pure dye, M.P. 113–115° C.

EXAMPLE 4

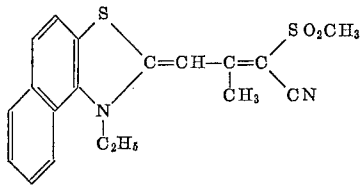
2-(3-cyano-2-methyl-3-methylsulfonylallylidene)-3-ethylbenzothiazoline



3-ethyl-2-thioacetonylidenebenzothiazoline (3.52 g., 15 m. mole) and methyl-p-toluenesulfonate (2.79 g., 15 m. mole) were heated on a steam bath with dimethylacetamide (5 ml.) for 10 minutes, whereupon the melt solidified. The resulting mixture was diluted with dimethylacetamide (10 ml.), methylsulfonylacetonitrile (1.79 g., 15 m. mole) was added, and the mixture was heated on a steam bath to dissolve the reactants. Triethylamine (3.2 ml., 22.5 m. mole) was then added and heating was continued for 10 minutes. The mixture was then rapidly brought to a boil to expel methyl mercaptan and allowed to cool. Dilution with ice and water precipitated an oil which crystallized on cooling (3.31 g., 69%). Recrystallization twice from pyridine and methanol afforded the pure dye, M.P. 226–227° C., in 26% yield.

EXAMPLE 5

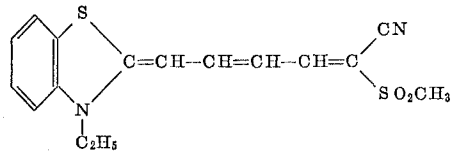
2-(3-cyano-2-methyl-3-methylsulfonylallylidene)-3-ethyl-naphtho[1,2-d]thiazoline



This dye was prepared from 1-ethyl-2-thioacetonylidenenaphtho[1,2-d]thiazoline and methylsulfonylacetonitrile by the method of Example 4. The pure dye, M.P. 252–253° C. from pyridine and methanol, was obtained in 25% yield.

EXAMPLE 6

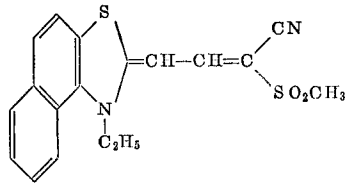
2-(5-cyano-5-methylsulfonyl-2,4-pentadienylidene)-3-ethylbenzothiazoline



2-(4-acetanilido - 1,3 - butadienyl - 3 - ethylbenzothiazolium iodide (2.38 g., 5 m. mole), methylsulfonylacetonitrile (1.19 g., 10 m. mole), 1,4-diazabicyclo[2,2,2]octane (1.12 g., 10 m. mole) and dimethylacetamide (10 ml.) were refluxed for 4 minutes. The resulting mixture was allowed to cool and was then diluted with methanol (30 ml.), chilled, and filtered. The crude dye obtained (1.14 g., 69%) was recrystallized twice from pyridine-methanol to obtain the pure dye, M.P. 205–206° C., in 56% yield.

EXAMPLE 7

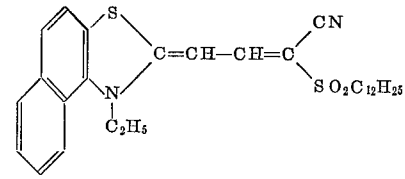
2-(3-cyano-3-methylsulfonylallylidene)-1-ethylnaphtho[1,2-d]thiazoline



A mixture of 2-anilinovinyl-1-ethylnaphthol[1,2-d]thiazolium iodide (3.52 g., 7 m. mole), methylsulfonylacetonitrile (0.84 g., 7 m. mole), acetic anhydride (1.32 ml., 14 m. mole) and dimethylacetamide (15 ml.) was heated; triethylamine (1.96 ml., 14 m. mole) was added; and the mixture was refluxed for 2 minutes. The resulting solution was cooled, diluted with 40 ml. of methanol, chilled, and the crude dye collected on a filter (2.45 g., 98%). Recrystallization of the crude dye from pyridine and methanol afforded the pure dye, M.P. 268–269° C., in 67% yield.

EXAMPLE 8

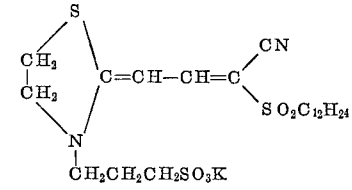
2-(3-cyano-3-dodecylsulfonylallylidene)-1-ethylnaphtho[1,2-d]thiazoline



This dye was prepared from 2-anilinovinyl-1-ethylnaphtho[1,2-d]thiazolium iodide and dodecylsulfonylacetonitrile by the method of Example 7. The pure dye, M.P. 155–156° C. from methanol, was obtained in 69% yield.

EXAMPLE 9

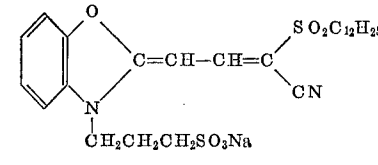
2-(3-cyano-3-dodecylsulfonylallylidene)-3-(3-sulfopropyl)thiazolidine, potassium salt



Anhydro-2-anilinovinyl - 3 - sulfopropyl-2-thiazolinium hydroxide (3.26 g., 10 m. mole), dodecylsulfonylacetonitrile (2.73 g., 10 m. mole), acetic anhydride (1.9 ml., 20 m. mole), dimethylacetamide (15 ml.) and triethylamine (2.8 ml., 20 m. mole) were heated slowly from 100 to 170° C. over about 5 minutes to obtain a clear, dark solution. The solution was cooled and diluted with ether to precipitate the crude dye which was washed several times with ether. The crude dye was dissolved in ethanol and treated with an ethanolic solution of potassium acetate (1.07 g., 11 m. mole) to precipitate the potassium salt of the dye. The resulting suspension was heated to boiling, treated with ethanol until solution was almost complete, and chilled. The crude product (3.48 g., 64%) was then collected on a filter and recrystallized twice from ethanol containing 15–20% water to obtain the pure dye salt, M.P. 218–220° C., in 39% yield.

EXAMPLE 10

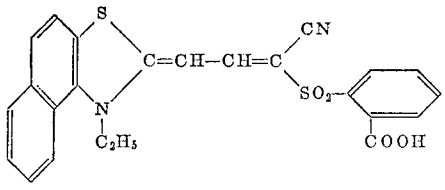
2-(3-cyano-3-dodecylsulfonylallylidene)-3-(3-sulfopropyl)benzoxazoline, sodium salt



This dye was prepared by a procedure similar to that employed in Example 9. The pure dye salt, M.P. 251–253° C., was obtained in 41% yield.

EXAMPLE 11

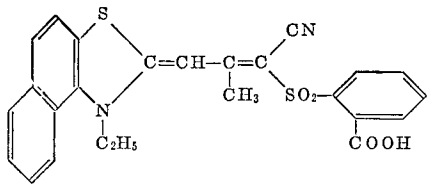
2-(3-o-carboxyphenylsulfonyl-3-cyanoallylidene)-1-ethyl naphtho[1,2-d]thiazoline



2 - anilinovinyl-1-ethylnaphtho[1,2-d]thiazolium iodide (3.52 g., 7 m. mol.), o-carboxyphenylsulfonylacetonitrile (2.26 g. 10.5 m. mol.), acetic anhydride (1.32 ml., 14 m. mol.), triethylamine (3.4 ml. 24 m. mole) and dimethylacetamide (10 ml.) were refluxed for two minutes and chilled. Ice, dilute hydrochloric acid, and water were added giving a gum which crystallized on boiling with methanol. The methanol solution was chilled and filtered. The dried precipitate weighed 2.30 g., a 71% yield. On recrystallization from mixtures of dimethylacetamide and acetic acid and dimethylacetamide and methanol, the pure dye, M.P. 234–235° C., was obtained in 49% yield.

EXAMPLE 12

2-(3-o-carboxyphenylsulfonyl-3-cyano-2-methylallylidene)-1-ethylnaphtho[1,2-d]thiazoline



3-ethyl-2-thioacetonylidenebenzothiazoline (7.13 g., 25 m. mol.) and methyl p-toluene sulfonate (5.12 g., 27.5 m. mol.) were heated with dimethylacetamide (15 ml.) on the steam bath until the mixture solidified. Then o-carboxyphenylsulfonylacetonitrile (30 m. mol.), triethylamine (8.7 ml., 60 m. mol.) and pyridine (30 ml.) were added and the mixture refluxed for five minutes. The addition of ice and water gave a gummy solid which was taken up in methanol acidified with conc. hydrochloric acid. The dye crystallized when this mixture was boiled and subsequently cooled. The yield was 3.91 g., 33%. It was twice recrystallized from dimethylacetamide from which the dye was thrown out with methanol. The yield of pure dye, M.P. 236–237° C., was 13%.

Among the especially preferred dyes of this invention are those corresponding to above Formula I wherein $n=1$, R_1 represents an alkyl group of from 1–4 carbon atoms bearing a substituent such as a carboxylic acid or sulfonic acid salt group which confers water solubility on the dye, and R_2 represents a group having a molecular weight sufficiently high to prevent diffusion of the dye in the photographic element. The dye of above Example 9 is particularly efficacious and is preferred.

The dyes of this invention have light-absorbing characteristics that make them valuable for use in light-absorbing filter layers in photographic elements. These characteristics are illustrated in the following Table 1 and in Example 13.

TABLE I
Absorption in Methanol

Dye of Example	Maximum (mμ	Coefficient of extinction E×10⁻⁴
1	433	7.9
2	398	9.0
3	381	6.1
4	432	8.3
5	451	9.3
6	526	13.1
7	453	7.9
8	455	7.8
9	382	6.2
10	398	7.2
11	460	8.4
12	459	7.8

EXAMPLE 13

A composition comprising gelatin, coating aids, hardeners, and the ultraviolet light-absorbing dye of Example 9, 2 - (3-cyano-3-dodecylsulfonylallylidene)-3-(3-sulfopropyl)-thiazolidine, potassium salt, was coated above the blue sensitive layer of a multilayer reversal color film of the type described in Mannes et al. U.S. Patent No. 2,252,718, issued Aug. 19, 1941. The resultant element (*a*) had 90 mg./ft.² of gelatin and 30 mg./ft.² of the above dye in the overcoat. A similar element without the light-absorbing overcoat was used as a control. Testing of these coatings by the methods recited in U.S. Patent 2,252,718, cited above, gave the following representative sensitometric results:

	Maximum density (Fresh test)			Maximum density change on incubation*		
Element	Red	Green	Blue	Red	Green	Blue
Control	3.78	3.42	3.78	0	0	−0.10
A	3.78	3.40	3.86	0	−0.08	−0.10

* Seven days at 120° F./50% relative humidity, relative to the corresponding fresh coating.

Other sensitometric tests of properties such as minimum density; speed, and metol-hydroquinone developer fog gave results which showed similar agreement between fresh and incubated coatings.

Spectrophotometric exposures demonstrated a significant decrease in ultraviolet sensitivity of the overcoated element A relative to the control element. Practical picture tests confirmed this protection. Pictures obtained with element A gave a color balance similar to those obtained with the control element when the control element was exposed through a Kodak 2A Wratten filter.

Various tests of physical properties which are customarily made on coatings of this type such as vertical swell, fold, wedge brittleness, ferrotyping, gate friction, and the like gave results which indicated that the control element and the overcoated element had essentially equal physical properties.

In the perparation of filter layers for photographic elements such as that illustrated in above Example 13; filter layers between differentially sensitized emulsion layers; filter layers on diffusion transfer receiving sheets such as those described in Land U.S. Patent 2,543,181, issued Feb. 27, 1951; filter layers in or upon color print materials such as those described in VanCampen U.S. Patent 2,956,879, issued Oct. 18, 1960; filter layers in or upon color transfer materials such as those described in British Patent 890,861, dated Mar. 7, 1962, Belgian Patent 636,371, and Rogers U.S. Patents 3,087,817, issued Apr. 30, 1963 and 2,983,606, issued May 9, 1961; and the like; the dyes of this invention are preferably incorporated in colloid layers which are permeable to aqueous processing solutions, said dyes being employed in concentrations which may vary considerably depending upon the particular product concerned and the effect desired. Methods for selecting the particular colloid to be employed, and for determining the amount of dye to be included, are well known in the art and need not be enumerated here. Representative colloids which may be employed include natural materials such as gelatin, protein derivatives, albumin, agar-

agar, gum arabic, alginic acid and the like; and synthetic resins such as polyvinyl alcohol, polyvinyl pyrrolidone, polyacrylamide, cellulose ethers and carboxylated derivatives of cellulose ethers, partially hydrolyzed cellulose esters, copolymers of acrylic and methacrylic acids, polymeric latexes or hydrosols, mixtures of these, and the like. Gelatin is the preferred colloid.

In the preparation of photographic silver halide emulsions comprising one or more of the above mentioned colloids, the new dyes of this invention are advantageously incorporated in the washed, finished, silver halide emulsion and should be uniformly distributed throughout the emulsion. Methods of incorporating dyes in emulsions are relatively simple and well known to those familiar with the art of emulsion making. For example, the dyes may be added from solutions in appropriate solvents which are free from deleterious effects on the ultimate light-sensitive materials. Methanol, isopropanol, and pyridine, alone or in admixture, have proven satisfactory as solvents for incorporating the majority of the dyes of this invention into emulsions.

The types of silver halide emulsions that can be sensitized with the new dyes of this invention include any of the conventional emulsions prepared with light-sensitive silver salts including silver chloride, silver bromide, silver iodide, silver chlorobromide, silver bromoiodide, silver chlorobromoiodide, etc. The concentration of the new dyes in the emulsion can vary widely, e.g., from about 5 to about 100 mg. per liter of flowable emulsion. The specific concentration will vary according to the type of light-sensitive material in the emulsion and the effects desired. The suitable and most economical concentration for a given emulsion will be apparent to those skilled in the art upon making the tests and observations customarily used in the art of emulsion making.

To prepare a gelatin-silver halide emulsion sensitized with one of the dyes of this invention, the following procedure is satisfactory. A quantity of the dye is dissolved in a suitable solvent and a volume of this solution containing from 5 to 100 mg. of dye is slowly added to about one liter of a gelatin-silver halide emulsion. With most of the dyes, 10 to 20 mg. of dye per liter of emulsion suffices to produce the maximum sensitizing effect with the ordinary gelatin-silver bromide (including bromoiodide and chlorobromide) emulsions. With fine grain emulsions, which include most of the ordinarily employed gelatin-silver chloride emulsions, somewhat larger concentrations of dye may be necessary to obtain the optimum sensitizing effect. While this procedure has dealt with emulsions comprising gelatin, it will be understood that these remarks apply generally to any emulsions wherein part or all of the gelatin is substituted by another suitable hydrophilic colloid, such as previously mentioned. It will also be understood that the above description is intended to be illustrative and should not be construed as limiting my invention in any sense since it is apparent that the new dyes can be incorporated by other methods in many of the photographic silver halide emulsions and hydrophilic colloid layers customarily employed in the art. For instance, the dyes can be incorporated by bathing a plate or film bearing an emulsion layer in a solution of one of the dyes in an appropriate solvent. Bathing methods, however, are not normally preferred.

The following example illustrates photographic elements prepared with the novel silver halide emulsions of the invention.

EXAMPLE 14

The sensitizing effects in photographic elements of the new dyes of the invention were determined as follows:

The dyes dissolved in suitable solvents, were added to separate portions of either a silver chloride emulsion or a silver chlorobromide (60:40) emulsion as indicated in Table 2 below, and at the indicated concentrations. After digestion at 50° C. for 10 minutes, the emulsions in each case were coated at a coverage of 432 mg. of silver per square foot and 1190 mg. of gelatin per square foot on a cellulose acetate film support. A sample of each coating was exposed on an Eastman 1B sensitometer and to a wedge spectograph, processed in a developer of the composition:

	G.
N-methyl-p-aminophenol sulfate	2.0
Sodium sulfite (anhydrous)	90.0
Hydroquinone	8.0
Sodium carbonate (monohydrate)	52.5
Potassium bromide	5.0

Water to make 1.0 liter.

and then fixed, washed, and dried. The sensitizing results are shown in the following table.

TABLE 2.—SENSITIZING DATA

Dye of Example	Emulsion type	Dye concentration, grams/mole silver	Sensitizing range (mμ) to—	Sensitizing maximum (mμ)
1	Chloride	0.13	490	455
2	do	0.13	490	430
4	do	0.13	490	450
5	do	0.13	530	470
5	Chlorobromide	0.16	510	470
6	Chloride	0.13	640	560
6	Chlorobromide	0.08	640	550
7	Chloride	0.13	530	480
7	Chlorobromide	0.16	530	470
10	Chloride	0.13	450	410
11	Chlorobromide	0.13	530	485
12	do	0.13	52	470

Photographic silver halide emulsions containing the sensitizing dyes of this invention can also contain other addenda such as chemical sensitizers, e.g., sulfur sensitizers (e.g., allyl thiocarbamide, thiourea, allylisothiocyanate, cystine, etc.), selenium and tellurium sensitizers, various gold compounds (e.g., potassium chloroaurate, auric trichloride, etc.) (see U.S. Patents to W. D. Baldsiefen, No. 2,540,085, issued Feb. 6, 1951; Re. E. Damschroder, No. 2,597,856, issued May 27, 1952; and H. C. Yutzy et al., U.S. Patent No. 2,597,915, issued May 27, 1952), various palladium compounds, such as palladium chloride (W. D. Baldsiefen, U.S. Patent No. 2,540,086, issued Feb. 6, 1951), potassium chloropalladate (R. E. Stauffer et al., U.S. Patent No. 2,598,079, issued May 27, 1952), etc., or mixtures of such sensitizers; antifoggants such as ammonium chloroplatinate (A. P. H. Trivelli et al. U.S. Patent No. 2,566,263, issued Aug. 28, 1951); benzotriazole, nitrobenzimidazole, 5-nitroindazole, benzidine, mercaptans, etc. (see Mees, "The Theory of the Photographic Process," MacMillan Pub., revised edition 1954, page 677), or mixtures thereof.

Photographic silver halide emulsion layers and other layers present in the photographic elements made according to the invention may contain developing agents such as hydroquinones, catechols, 1,3-pyrazolidones, aminophenols, etc.; and the layers can be hardened with any suitable hardeners such as aldehyde hardeners, aziridine hardeners, hardeners which are derivatives of dioxane, oxy polysaccharides such as oxy starch and oxy plant gums, mixtures of these, and the like. The layers present in photographic elements made according to the invention may also contain color couplers such as those described in I. F. Salminen et al. U.S. Pat. No. 2,423,730, issued July 8, 1947; Spence and Carroll U.S. Pat. No. 2,640,776, issued June 2, 1953, etc; or mixtures of such addenda. Dispersing agents for color couplers, such as those set forth in U.S. Patents to E. E. Jelley et al., U.S. Pat. No. 2,322,027, issued June 15, 1943, and L. D. Mannes et al., U.S. Pat. No. 2,304,940, issued Dec. 15, 1942; and non-ionic, anionic and amphoteric coating aids; can also be employed in the above described emulsions and colloid layers. The photographic emulsions can also contain additional additives, particularly those known to be beneficial in photographic emulsion, including, for example, stabilizers, particularly the water soluble inorganic acid salts

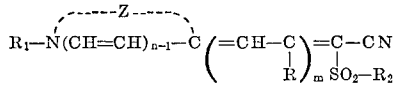
of cadmium, cobalt, manganese, and zinc, such as disclosed in Jones U.S. Pat. No. 2,839,405, issued June 17, 1958, and the substituted triazaindolizines such as disclosed in Heimbach et al. U.S. Pat. No. 2,444,605, issued July 6, 1948 and in Heimbach, U.S. Pat. No. 2,444,607; spectral sensitizers such as the cyanine, merocyanine, styryl, and hemicyanine dyes; speed increasing materials, such as polyalkylene glycols, onium salts, thioethers, etc.; plasticizers; absorbing dyes; mixtures of these additives; and the like.

Although the photographic element examples show coatings made on cellulose acetate supports, it will be understood that the photographic silver halide emulsions may be coated advantageously on any of the support materials commonly used in photographic elements, including glass, metals, paper, baryta coated paper, cellulose acetate, cellulose acetate butyrate, cellulose nitrate, etc., and synthetic film forming resinous materials such as polystyrenes, polyolefins, e.g., polyethylene, polypropylene, etc., such as polyethylene terephthalate, polyamides, e.g., nylon, etc., polycarbonates, polyvinyl acetals, etc. Supports such as papers which are partially acetylated or coated with an α-olefin polymer, particularly a polymer derived from an α-olefin containing 2–10 carbon atoms as exemplified by polyethylene and polypropylene, ethylene-butene copolymers, and the like, also give good results.

The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention as described hereinabove and as defined in the appended claims.

I claim:

1. A dye compound having the formula:



wherein n and m each represents a positive integer of from 1 to 2, R represents a member selected from the group consisting of a hydrogen atom, an alkyl group having 1 to 8 carbon atoms, phenyl, chlorophenyl, tolyl, benzyl and phenylethyl, R_1 represents a member selected from the group consisting of an alkyl group having 1 to 12 carbon atoms, a sulfoalkyl group having 2 to 4 carbon atoms, a carboxyalkyl group having 2 to 5 carbon atoms, a low carbon hydroxyalkyl group having more than 1 carbon atom, phenyl, sulfophenyl, carboxyphenyl and tolyl, R_2 represents a member selected from the group consisting of an alkyl group having 1 to 12 carbon atoms, phenyl, tolyl, carboxyphenyl, naphthyl, benzyl, phenylethyl, an oxazolyl group, a benzoxazolyl group, a pyridyl group, a quinolyl group, an imidazolyl group and a benzimidazolyl group, and wherein the heterocyclic groups just named are attached to the sulfonyl group through a nuclear carbon atom, and Z represents the nonmetallic atoms required to complete a 5- to 6-membered heterocyclic nucleus selected from the class consisting of a thiazole nucleus, a benzothiazole nucleus, a naphthothiazole nucleus, a thianaphtheno-7',6',4,5-thiazole nucleus, an oxazole nucleus, a benzoxazole nucleus, a naphthoxazole nucleus, a selenazole nucleus, a benzoselenazole nucleus, a naphthoselenazole nucleus, a thiazoline nucleus, a thiazolidine nucleus, a 2-pyridine nucleus, a 4-pyridine nucleus, a 2-quinoline nucleus, a 4-quinoline nucleus, a 1-isoquinoline nucleus, a 3-isoquinoline nucleus, a 3,3-dialkylindolenine nucleus, an imidazole nucleus, a benzimidazole nucleus, and a naphthimidazole nucleus.

2. A dye compound in accordance with claim **1** wherein R_2 is an alkyl group having 1 to 12 carbon atoms.

3. A dye compound in accordance with claim **1** wherein R_2 is a carboxyphenyl group.

4. A dye compound in accordance with claim **1** wherein n is 1, R is a hydrogen atom and R_1 and R_2 each represents an alkyl group having 1 to 12 carbon atoms.

5. A dye compound in accordance with claim **1** wherein the dye compound is 2-(3-cyano-3-dodecylsulfonylallylidene)-3-ethylthiazolidine.

6. A dye compound in accordance with claim **1** wherein the dye compound is 2-(3-cyano-3-methylsulfonylallylidene)-1-ethylnaphtho[1,2-d]thiazoline.

7. A dye compound in accordance with claim **1** wherein the dye compound is 2-(3-cyano-3-dodecylsulfonylallylidene)-1-ethylnaphtho[1,2-d]thiazoline.

8. A dye compound in accordance with claim **1** wherein the dye compound is a water soluble salt of the dye compound 2-(3-cyano-3-dodecylsulfonylallylidene)-3-(3-sulfopropyl)thiazolidine.

9. A dye compound in accordance with claim **1** wherein the dye compound is 2-(3-cyano-3-dodecylsulfonylallylidene)-3-(3-sulfopropyl)thiazolidine, potassium salt.

10. A dye compound in accordance with claim **1** wherein the dye compound is a water soluble salt of the dye compound 2-(3-cyano-3-dodecylsulfonylallylidene)-3-(3-sulfopropyl)benzoxazoline.

11. A dye compound in accordance with claim **1** wherein the dye compound is 2-(3-cyano-3-dodecylsulfonylallylidene)-3-(3-sulfopropyl)benzoxazoline, sodium salt.

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JOHN D. RANDOLPH, Primary Examiner

U.S. Cl. X.R.

96—84, 102; 260—240 R, 283 CN, 294.8 R, 298, 306.7, 309, 309.2, 326.11