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TRINUCLEAR DYES HAVING AN ACID NUCLEUS SUBSTITUTED WITH A SECONDARY AMINO SUBSTITUTED ALKYL GROUP USEFUL AS SPECTRAL SENSITIZERS FOR PHOTOGRAPHIC SILVER HALIDE EMULSIONS

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No Drawing. Original application May 4, 1964, Ser. No. 364,780, now Patent No. 3,335,010, dated Aug. 8, 1967. Divided and this application Mar. 8, 1967, Ser. No. 621,440

Int. Cl. C09b 23/10

U.S. Cl. 260—240.1 10 Claims

ABSTRACT OF THE DISCLOSURE

Novel trinuclear dyes having an acid nucleus which is substituted with a secondary amino substituted alkyl group are good spectral sensitizers for photographic silver halide emulsions. Their good solubility in aqueous media facilitates their incorporation in photographic emulsions and their removal from photographic elements containing them during photographic processing and reduces staining in the resulting photograph.

This application is a division of our copending application Ser. No. 364,780, filed May 4, 1964.

This application relates to photographic sensitizing dyes and more particularly to trinuclear sensitizing dyes having at least one acid nucleus substituted with at least one secondary amino substituted alkyl group, to photographic silver halide emulsions sensitized with said dyes, and to photographic elements containing said dyes.

It is known to use trinuclear dyes, such as complex cyanine dyes, complex merocyanine and holopolar dyes as optical sensitizers in photographic silver halide emulsion layers. Spectral sensitizing dyes are needed for extending (to longer wavelengths) the sensitivity of silver halide emulsions in various photographic materials including multicolor elements used for color photography. Sensitizing dyes must not only produce the desired sensitizing characteristics, but must be readily soluble, preferably in aqueous media for ease in sensitizing a photographic emulsion and also for ease in removal from the emulsion layers during the photographic processing so that a minimum of stain is produced in the resulting photograph. The requirement for minimum stain is particularly important in color photographic prints.

It is also known to use certain bleachable dyes in light-filtering hydrophilic colloid layers in light-sensitive photographic elements. Such light-filtering layers may be coated over the light-sensitive layer, between two differently sensitized light-sensitive layers, between a light-sensitive layer and the support or on the side of the support opposite to the side bearing a light-sensitive layer. Dyes useful for filter layers must not only absorb light of the desired wavelengths but must be readily bleachable and/or removable during the normal photographic processing operations.

Trinuclear dyes having desirable spectral sensitizing characteristics and good solubility in aqueous media are desired.

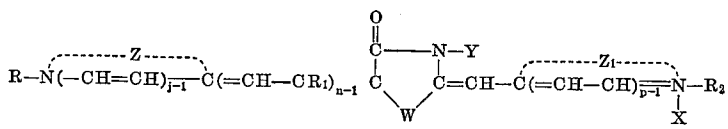
It is therefore an object of our invention to provide a new class of valuable trinuclear dyes including the complex cyanine dyes, complex merocyanine dyes and holopolar dyes that are good spectral sensitizers and which because of their high solubility in aqueous media leave less stain in photographic elements containing them than dyes known previously.

Another object is to provide improved photographic silver halide emulsions that are sensitized by our valuable trinuclear dyes which are distinguished from other dyes by having at least one secondary amino substituted alkyl group attached to at least one acidic nucleus in the dye.

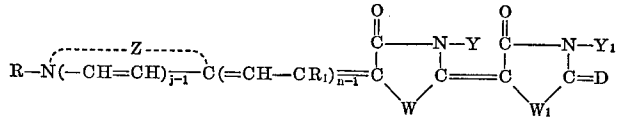
Still other objects will become apparent from the following specification and claims.

These and other objects are accomplished according to our invention by the synthesis and use in photographic elements of our trinuclear dyes which include those represented by the formulas:

(I)

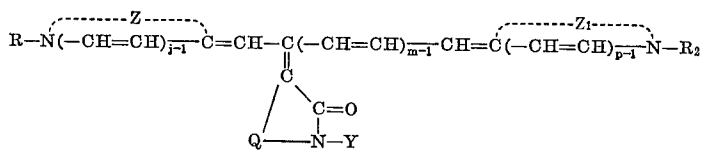


(II)



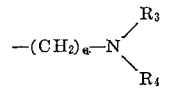
and

(III)

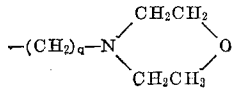


wherein R and R_2 each represent an alkyl group having from 1 to 8 carbon atoms, e.g., methyl, sulfoethyl, carboxyethyl, hydroxypropyl, sulfobutyl, carboxybutyl, hexyl, octyl, etc.; Z and Z_1 each represent the nonmetallic atoms required to complete a 5 to 6 membered heterocyclic nucleus such as those selected from the nuclei

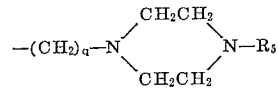
consisting of those of the thiazole series (e.g., thiazole, 4-methylthiazole, 4-phenylthiazole, 5-methylthiazole, 5-phenylthiazole, 4,5-dimethylthiazole, 4,5-diphenylthiazole, 4-(2-thienyl)thiazole, etc.), those of the benzothiazole series, (e.g. benzothiazole, 4-chlorobenzothiazole, 5-chlorobenzothiazole, 6-chlorobenzothiazole, 7-chlorobenzothiazole, 4-methylbenzothiazole, 5-methylbenzothiazole, 6-methylbenzothiazole, 5-bromobenzothiazole, 6-bromothiazole, 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.), those of the naphthothiazole series (e.g. α-naphthothiazole, β-naphthothiazole, 5-methoxy-β-naphthothiazole, 5-ethoxy-β-naphthothiazole, 8-methoxy-α-naphthothiazole, 7-methoxy-α-naphthothiazole, etc.) those of the thionaphtheno-7′,6′,4,5-thiazole series (e.g. 4′ - methoxythianaphtheno-7′,6′,4,5-thiazole, etc), those of the oxazole series (e.g. 4-methyloxazole, 5-methyloxazole, 4-phenyloxazole, 4,5-diphenyloxazole, 4-ethyloxazole, 4,5-dimethyloxazole, 5-phenyloxazole, etc.), those of the benzoxazole series (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.), those of the naphthoxazole series (e.g. α-naphthoxazole, β-naphthoxazole, etc.), those of the selenazole series, (e.g. 4-methylselenazole, 4-phenylselenazole, etc.), those of the benzoselenazole series (e.g. benzoselenazole, 5-chlorobenzoselenazole, 5-methoxybenzoselenazole, 5-hydroxybenzoselenazole, tetrahydrobenzoselenazole, etc.), those of the naphthoselenazole series (e.g. α-naphthoselenazole, β-naphthoselenazole, etc.) those of the thiazoline series (e.g. thiazoline, 4-methylthiazoline, etc.), those of the 2-pyridine series (e.g., 2-pyridine, 5-methyl-2-pyridine, etc.), those of the 4-pyridine series (e.g., 4-pyridine, 3-methyl-4-pyridine, etc.), those of the 2-quinoline series (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.), those of the 4-quinoline series (e.g., 4-quinoline, 6-methoxy-4-quinoline, 7-methyl-4-quinoline, 8-chloro-4-quinoline, etc.), those of the 1-isoquinoline series (e.g., 1-isoquinoline, 3,4-dihydro-1-isoquinoline, etc.), those of the 3-isoquinoline series (e.g., 3-isoquinoline, etc.), those of the 3,3-dialkylindolenine series (e.g., 3,3-dimethylindolenine, 3,3,5-trimethylindolenine, 3,3,7-trimethylindolenine, etc.), those of the imidazole series (e.g., imidazole, 1 - alkylimidazole, 1-alkyl-4-phenylimidazole, 1- alkyl-4,5-dimethylimidazole, etc.), those of the benzimidazole series (e.g., benzimidazole, 1-alkyl-benzimidazole, 1-alkyl-5,6- dichlorobenzimidazole, etc., those of the naphthimidazole series (e.g., 1-alkyl-α-naphthimidazole, 1-alkyl-β-naphthimidazole, 1-alkyl-5-methoxy-β-naphthimidazole, etc.), etc.; *j* represents an integer of from 1 to 2; R_1 represents the hydrogen atom, an alkyl group (e.g. methyl, ethyl, butyl, etc.) or an aryl group (e.g., phenyl, tolyl, etc.); *n* represents an integer of from 1 to 4; Y and Y_1 each represent a group such as, the hydrogen atom, an alkyl group (e.g., methyl, methoxyethyl, butyl, etc.), an aryl gruup (e.g., phenyl, tolyl, etc.), a



group, a



group, and a



group, such that at least one of the groups Y and Y_1 contains a group with a tertiary nitrogen atom; *q* represents an integer of from 2 to 4; R_3, R_4 and R_5 each represents an alkyl group (e.g., methyl, propyl, butyl, hexyl, etc.); W and W_1 each represent a group selected from the oxygen atom, the sulfur atom, the selenium atom, and a $>NR_6$ group wherein R_6 represents an alkyl group (e.g., methyl, ethyl, butyl, etc.), an aryl group (e.g., phenyl, tolyl, etc.), etc.; *p* represents an integer of from 1 to 2; X represents an acid group (e.g., chloride, bromide, iodide, perchlorate, sulfamate, thio cyanate, p-toluenesulfonate, benzenesulfonate, methylsulfate, etc.); D and D_1 each represent a group such as the sulfur atom, the selenium atom, or the oxygen atom; *m* represents an integer of from 1 to 2; Q represents a group, such as a

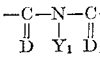


group, a

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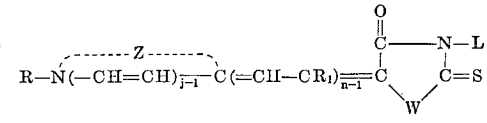


group; and R_7 represents a group, such as, any of the groups used on the 3-position of 2-pyrazolin-5-ones, e.g., hydrogen, alkyl (e.g., methyl, isopropyl, tertiary butyl, hexyl, etc.), aryl (e.g., phenyl, tolyl, halophenyl, etc.), amino (e.g., methylamino, diethylamino, phenylamino, etc.), carbonamido (e.g., ethylcarbonamido, phenylcarbonamido, etc.), sulfonamido (e.g., butylsulfonamido, phenylsulfonamido, etc.), sulfamoyl (e.g., propylsulfamoyl, phenylsulfamoyl, etc.), carbamoyl (e.g., ethylcarbamoyl, phenylcarbamoyl, etc.).

Our dyes are readily soluble in aqueous media, especially in the presence of one equivalent of acid, and are used to advantage to spectrally sensitize photographic hydrophilic silver halide emulsions. The dyes are valuable because of their sensitizing characteristics and their solubility which makes them easy to incorporate in photographic emulsions and also makes it easier to more completely remove the dyes during the processing operations.

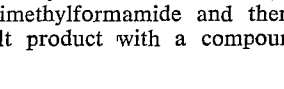
The dyes of Formula I are prepared to advantage by reacting a merocyanine dye having the formula:

(IV)



wherein R, Z, *j*, R_1, *n* and W are as defined previously and L represents a Y or a Y′ group, and when this group represents a substituted amino alkyl group, said group is advantageously a hydro salt of the amine, with dimethylsulfate and dimethylformamide and then reacting the quaternary salt product with a compound having the formula:

(V)

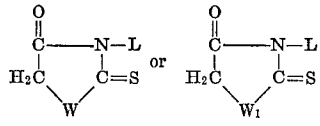


wherein Z_1, *p*, R_2 and *x* are as defined previously, preferably by heating in a suitable solvent in the presence of a basic condensing agent, e.g., the trialkylamines (e.g., tri-

ethylamine, tributylamine, etc.), the dialkylanilines (e.g., N,N-dimethylaniline, N,N-diethylaniline, etc.), heterocyclic tertiary amines (e.g., pyridine, quinoline, N-alkylpiperidines, etc.), alkali metal alcoholates (e.g., sodium ethylate, etc.).

The dyes of Formula II are prepared to advantage by reacting a compound of Formula IV with dimethyl sulfate and dimethylformamide, then condensing the quaternary salt product with a compound having the formula:

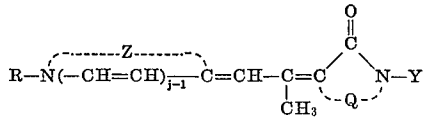
(VI)



wherein W, W_1 and L are as described previously. The condensation is carried out to advantage in an inert solvent in the presence of a basic condensing agent (described previously herein). Heating the reaction mixture to the reflux temperature is advantageous.

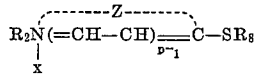
The dyes of Formula III are prepared to advantage by condensing a dye of formula:

(VII)



wherein R, Z, *j*, Y and Q are as defined previously, with a cyclammonium quaternary salt having the formula:

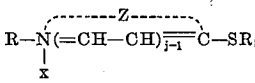
(VIII)



wherein R_2, *x*, Z_1, and *p* are as described previously and R_8 represents an alkyl group (e.g., methyl, ethyl, benzyl, etc.) or an aryl group (e.g., phenyl, tolyl, etc.). The reaction is conducted advantageously in an inert solvent in the presence of a basic condensing agent (described previously) and is aided by heating up to the reflex temperature of the reaction mixture.

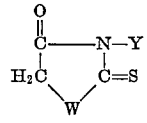
The dyes of Formula IV where *n* is 1 are prepared by condensing a cyclammonium quaternary salt having the formula:

(IX)



wherein R, *x*, Z, *j* and R_8 are as defined previously with an intermediate having the formula:

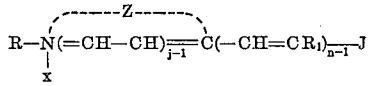
(X)



wherein W and Y are as defined previously, in an inert solvent, preferably in the presence of a basic condensing agent and preferably by heating.

The dyes of Formula IV in which *n* is from 2 to 4 are prepared to advantage by condensing a cyclammonium quaternary salt having the formula:

(XI)



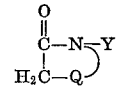
wherein R, *x*, Z, *j*, R_1 and *n* are as defined previously, J represents a



group, a —SR_{11} group or a halogen atom (e.g., chlorine, bromine, etc.); R_9 represents the hydrogen atom, an alkyl group, or the acyl group of a carboxylic acid, and R_{10} represents an aryl group or R_9 and R_{10} together represent the nonmetallic atoms necessary to complete a heterocyclic nucleus (e.g., a piperidino, a morpholino group, etc.) and R_{11} represents a lower alkyl group, with a compound of Formula X.

The dyes of Formula VII are prepared to advantage by condensing a compound of Formula XI in which R_1 is a methyl group and $n=2$, with a compound having the formula:

(XII)

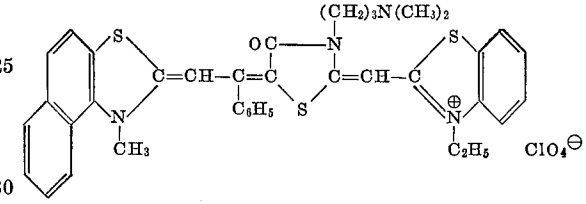


wherein Q and Y are as defined previously.

Included among the dyes of Formula I are the following typical examples:

DYE 1

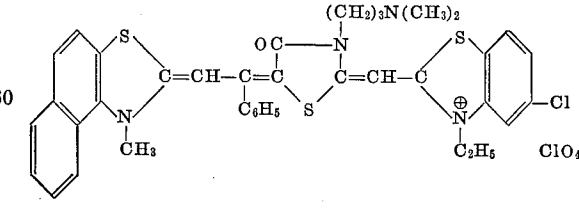
2-[(2-benzothiazolylethoperchlorate)methylene] - 3 - (3-dimethylaminopropyl) - 5 - [(1-methylnaphtho[1,2-d] thiazolin - 2 - ylidene) - 1 - phenylethylidene] - 4 - thiazolidinone



2.1 g. (1 mol.) of 3-(3-dimethylaminopropyl)-5-[(1-methylnaphtho[1,2-d]thiazolin - 2 - ylidene) - 1 - phenylethylidene]-rhodanine hydroperchlorate was added to 10 ml. of dimethylsulfate and 10 ml. of dimethylformamide, the mixture heated gently until solution was complete and allowed to stand at room temperature for 1 hour. The product was precipitated with ether and washed with ether. The oily residue was dissolved in 30 ml. of pyridine and treated with 2.0 g. (1 mol.+100%) of 3-ethyl-2-methylbenzothiazolium iodide and 5 ml. of triethylamine and the solution heated at reflux for 5 minutes. The reaction mixture was poured into 75 ml. of methanol, made basic with piperidine, chilled and the dye collected. The dye was twice recrystallized by dissolving in dimethylformamide and precipitating with methanol containing dissolved sodium perchlorate. The dye was obtained (yield 18%) as green crystals with coppery reflex of M.P. 283–284° with decomposition.

DYE 2

2-[(5-chloro - 2 - benzothiazolylethoperchlorate)methylene]-3-(3-dimethylaminopropyl) - 5 - [(1-methylnaphtho[1,2-d]thiazolin-2-ylidene) - 1 - phenylethylidene]-4-thiazolidinone

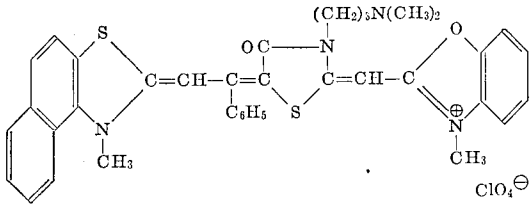


2.1 g. (1 mol.) of 3-(3-dimethylaminopropyl)-5-[(1-methylnaphtho[1,2 - d]thiazolin - 2 - ylidene) - 1 - phenylethylidene]rhodanine hydroperchlorate was added to 6 ml. of dimethylsulfate and 4 ml. of dimethylformamide and the solution heated gently over an open flame until a faint odor of methyl mercaptan was detected. The reaction mixture was cooled and 10 ml. of pyridine was added. After the exothermic reaction had subsided the solution was treated with 2.6 g. (1 mol.+100%) of 5-chloro-3-ethyl-2-methylbenzothiazolium p-toluenesulfo-

nate, 2 ml. of triethylamine and the solution warmed gently for 2 minutes. The mixture was poured into 40 ml. of methanol, made basic with piperidine and chilled. The dye was twice recrystallized by dissolving in dimethylformamide and precipitating with methanol containing dissolved sodium perchlorate. The dye was obtained (yield 36%) as green crystals of M.P. 262–264° with decomposition.

DYE 3

2 - [2 - benzoxazolylmethoperchlorate)methylene] - 3-(3 - dimethylaminopropyl) - 5 - [(1 - methylnaphtho [1,2 - d]thlazolin - 2 - ylidene) - 1 - phenylethylidene] 4-thiazolidinone

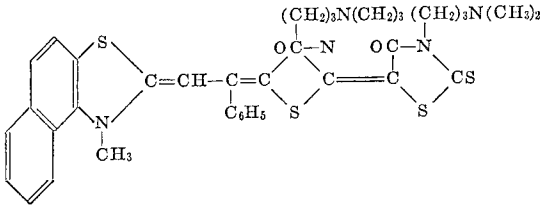


This dye was prepared by the method used to make dye 2 but by substituting an equivalent amount of 3-ethyl-2-methylbenzoxazolium iodide for the 5-chloro-3-ethyl-2-methylbenzothiazolium p-toluenesulfonate. The twice recrystallized dye was obtained (yield 36%) as green crystals of M.P. 262–265° C. with decomposition.

Included among the dyes of Formula II aer the following typical examples:

DYE 4

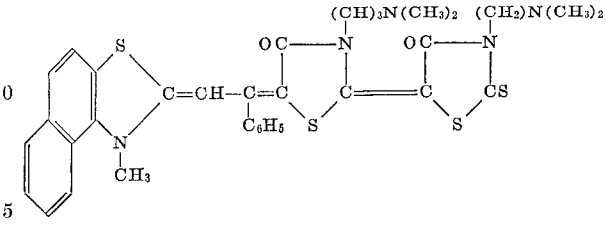
3 - (3 - dimethylaminopropyl) - 2 - [3 - (3 - dimethylaminopropyl) - 4 - oxo - 2 - thioxo - 5 - thiazolidinylidene] - 5 -[(1 - methylnaphtho[1,2 - d]thiazolin - 2-ylidene)-1-phenylethylidene]-4-thiazolidinone



1.03 g. (1 mol.) of 3-(3-dimethylaminopropyl)-5-[(1-methylnaphtho[1,2 - d]thiazolin - 2 - ylidene) - 1 -phenylethylidene]rhodanine hydroperchlorate was added to 5 ml. of dimetylsulfate and 2 ml. of dimethylformamide and the solution heated gently over a flame until a slight odor of methyl mercaptan was detected. The reaction mixture was then cooled and treated with 5 ml. of pyridine. After the exothermic reaction had subsided the mixture was treated with 1.0 g. (1 mol.+100%) of 3-(3 - dimethylaminopropyl)rhodanine hydroperchlorate and 2 ml. of triethylamine and warmed gently for approximately 2 minutes. The reaction mixture was poured into a solution containing 40 ml. of methanol and 5 ml. of piperidine and the solution chilled. The dye was collected on a filter and dried. The dye was twice recrystallized by dissolving in dimethylformamide and precipitating by the addition of methanol. The dye was obtained (yield 12%) as green crystals with gold reflex of M.P. 265–267° with decomposition.

DYE 5

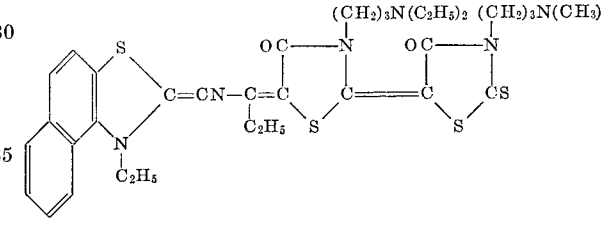
2 - [3 - (2 - dimethylaminoethyl) - 4 -oxo - 2 - thioxo-5 - thiazolidinylidene] - 3 - (3 - dimethylaminopropyl)-5 - [(1 - methylnaphtho[1,2 - d]thiazolin - 2 - ylidene)-1-phenylethylidene]-4-thiazolidinone



This dye was prepared by the method used for dye 4 but substituting an equivalent of 3-(2-dimethylaminoethyl)rhodanine hydroperchlorate for the rhodanine used to make dye 4. The recrystallized dye was obtained (yield 22%) as green crystals of coppery reflex of M.P. 273–275° C. with decomposition.

DYE 6

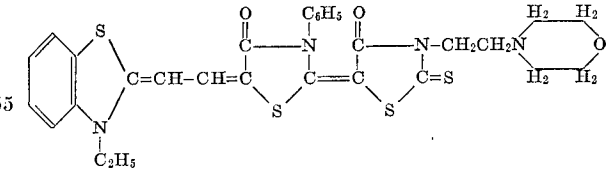
3 - (3 - diethylaminopropyl) - 2 - [3 - (3 - dimethylaminopropyl) - 4 - oxo - 2 - thioxo - 5 - thiazolidinylidene]-5 - [(1 - ethylnaphtho[1,2 - d]thiazolin - 2 -ylidene)-1-phenylethylidene]-4-thiazolidinone



This dye was prepared like dye 4 but substituting an equivalent amount of 3-(3-dietyhlaminopropyl)-5-[1-ethylnaphtho[1,2 - d]thiazolin - 2 - ylidene) - 1 -phenylethylidene]rhodanine hydroperchlorate as the parent dye. The recrystallized dye was obtained (yield 45%) as green crystals with gold reflex of M.P. 254–256° C. with decomposition.

DYE 7

5 - [3 - ethyl - 2 -benzothiazolinylidene)ethylidene] - 2-[3 - (2 - morpholinoethyl) - 4 - oxo - 2 - thioxo - 5-thiazolidinylidene]-3-phenyl-4-thiazolidinone



2.46 g. of (1 mol.) of 3-(2-morpholinoethyl)rhodanine, 5.82 g. (1 mol.) of 5-[3-ethyl-2-benzothiazolinylidene)ethylidene] - 2 - methylmercapto - 4 - oxo - 3-phenyl-2-thiazolinium p-toluenesulfonate and 3.08 ml. (2.2 mol.) of triethylamine were added to 25 ml. of acetic anhydride and heated under reflux with stirring for 5 minutes. The reaction mixture was cooled and poured with stirring into 300 ml. of ether. The dark green tar which separated was washed with ether and was then stirred with hot acetone. The acetone suspension of the dye was chilled, diluted with ether and filtered. The dye was recrystallized by dissolving in dimethylformamide and diluting with methanol. The dye was twice more recrystallized by dissolving in pyridine and diluting with methanol. The dye was obtained (4%) as dark green crystals of M.P.>310° C.

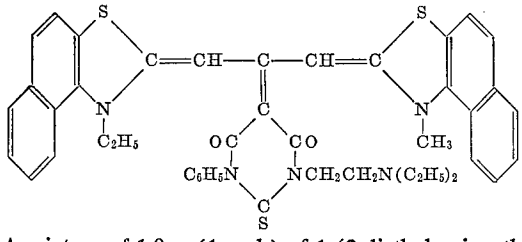
DYE 8

5-[(1-ethylnaphtho[1,2-d]thiazolin - 2 - ylidene)-1-phenylethylene] - 3 - (2-morpholinoethyl)-2-[3-(2-morpholinoethyl) - 4 - oxo - 2 - thioxo-5-thiazolidinylidene]-4-thiazolidinone

This dye was prepared as dye 7 but from a molar equivalent of quaternized 5-[(1-ethylnaphtho[1,2-d]thiazolin-2-ylidene)-1-phenylethylidene] - 3 - (2-morpholinoethyl) rhodanine. The solid dye product was washed with boiling benzene and with boiling toluene then recrystallized twice by dissolving in pyridine and diluting with benzene. The dye was obtained (13% yield) as purple crystals with a gold reflex of M.P. 245–247° C. with decomposition.

DYE 9

1-(2-diethylaminoethyl - 5 - [(1-ethylnaphtho[1,2-d]thiazolin-2-ylidene)-(1 - methylnaphtho[1,2-d]thiazolin-2-ylidene)isopropylidene]-3-phenyl - 2 - thiobarbituric acid



A mixture of 1.0 g. (1 mol.) of 1-(2-diethylaminoethyl-5-[(1-ethylnaphtho[1,2-d]thiazolin - 2 - ylidene)isopropylidene]-3-phenyl-2-thiobarbituric acid, 1.3 g. (1 mol. +100% excess) of 1-methyl-2-methylthionaphtho[1,2-d] thiazolium p-toluenesulfonate and .4 g. (1 mol.+100% excess) of triethylamine was heated at the refluxing temperature in 25 ml. of pyridine for ten minutes. The resulting solution was cooled and poured into ether and the precipitate was collected on a filter and the solid was washed with ether. The crude dye was dissolved in 600 ml. of hot pyridine, the solution was filtered hot, methanol was added and after chilling the dye was collected on a filter. The yield of dye after another like treatment was 14%. The shiny green crystals had a M.P. >300° C.

DYE 10

1-(2-diethylaminoethyl - 5 - [di(1-ethylnaphtho[1,2-d] thiazolin - 2 - ylidene isopropylidene]-3-phenyl-2-thiobarbituric acid

This dye was prepared as dye 9 but by substituting a molar equivalent of 1 - ethyl-2-ethylthionaphtho[1,2-d] thiazolium ethylsulfate for the intermediate used for dye 9. The twice recrystallized dye was obtained (8% yield) as shiny green crystals of M.P. 291–292° C. with decomposition.

DYE 11

1 - (2 - diethylaminoethyl) - 5-[(1 - ethylnaphthol[1,2-d] thiazolin - 2 - ylidene)-(1-methylnaphtho[1,2-d]thiazolin - 2 - ylidene)isopropylidene]-3-phenylbarbituric acid

The dye was prepared like dye 9 but using as the parent dye 1-(2-diethylaminoethyl) - 5 - [(1-ethylnaphtho[1,2-d] thiazolin-2-ylidene)isopropylidene] - 3 - phenylbarbituric acid in place of the corresponding thiabarbituric acid containing dye. The recrystallized dye was obtained (15% yield) as green crystals of M.P. 300–302° C. with decomposition.

DYE 12

1-(2-diethylaminoethyl) - 5 - [di(1-ethylnaphtho[1,2-d] thiazolin - 2 - ylidene)isopropylidene]-3-phenylbarbituric acid

This dye was prepared like dye 11 but by substituting 1-ethyl-2-ethylthionaphtho[1,2-d]thiazolium ethyl sulfate for the cylammonium quaternary salt used to make dye

11. The recrystallized dye was obtained (21% yield) as green crystals of M.P. 298–299° C. with decomposition.

The intermediates having Formulas V, VIII, IX and XI are well known in the art. The synthesis of intermediates having Formulas IV, VI, X and XII are illustrated with descriptions of representative intermediates used in preparing our dyes.

3-(3 - dimethylaminopropyl) - 5 - [(1-methylnaphtho [1,2-d]thiazolin - 2 - ylidene) - 1 - phenylethylidene] rhodanine hydroperchlorate

14.8 g. (1 mol.) of 2-(1-chlorostyryl)-1-methylnaphtho[1,2-d]thiazolium chloride and 12.8 g. (1 mol.) of 3-(3 - dimethylaminopropyl)rhodanine hydroperchlorate were dissolved in 80 ml. of dimethylformamide and the solution treated with 16.8 ml. of triethylamine and the solution heated at reflux for 5 minutes. The hot reaction mixture was filtered and the filtrate treated with a solution of 5.0 g. of sodium perchlorate in 100 ml. of ethanol, made acid with acetic acid and chilled. The dye was collected on a filter and recrystallized by dissolving in dimethylformamide and precipitating with ethanol containing dissolved sodium perchlorate. The dye was obtained (yield 59%) as green crystals of M.P. 236–238° with decomposition.

3-(3-diethylaminopropyl)rhodanine hydroperchlorate

22.6 g. (1 mol.) of bis(carboxymethyl)trithiocarbonate was suspended in 150 ml. of water and treated with 11.6 g. of sodium carbonate. The solution was then treated with 13.0 g. (1 mol.) of N,N-diethyl-1,3-propanediamine and heated on the steam bath for 1½ hours. The solution was then made strongly acid with concentrated hydrochloric acid and concentrated to a viscous oil on the rotary evaporator. The oil was dissolved in 70 ml. of water and treated with a solution of 18.3 g. of sodium perchlorate in 50 ml. of water and chilled. The product separated as a heavy oil which was washed once with a small portion of water containing dissolved sodium perchlorate and three times with isopropyl alcohol. After washing, the last traces of isopropyl alcohol were removed under vacuum. The product was then made crystalline by stirring with a small amount of methanol and obtained (yield 35%) as pinkish crystals of M.P. 102–104° with decomposition.

3-(2-dimethylaminoethyl)rhodanine hydroperchlorate

This was prepared by the same reaction used to prepare the preceding intermediate but by using N,N-dimethylethylenediamine.

3-(3-diethylaminopropyl) - 5 - [1-ethylnaphtho[1,2-d] thiazolin - 2 - ylidene)-1-phenylethylidene]rhodanine hydroperchlorate

15.0 g. (1 mol.) of 1-ethyl-2-(2-ethylthiostyryl)naphthio[1,2-d]thiazolium ethylsulfate and 10.2 g. (1 mol.) of 3 - (3 - diethylaminopropyl)rhodanine hydroperchlorate were dissolved in 50 ml. of dimethylformamide and 9 ml. of triethylamine and the solution heated on the steam bath for 1 hour. The reaction mixture was poured into a solution containing 100 ml. of methanol and 10 ml. of piperidine and chilled. The dye was collected on a filter and dried. The dye was recrystallized by dissolving in dimethylformamide and precipitating with methanol. The dye was obtained (yield 56%) as green crystals of M.P. 196–197° with composition.

1-(2-diethylaminoethyl) - 5 - [(1 - ethylnaphtho[1,2 - d] thiazolin-2-ylidene)isopropylidene] - 3 - phenyl-2-thiobarbituric acid

A mixture of 8.4 g. (1 mol.) of 1-(2-diethylaminoethyl)-3-phenyl - 2 - thiobarbituric acid hydroperchlorate, 8.0 g. (1 mol.) of 1-ethyl-2-methylnaphtho[1,2-d]thiazolium p-toluenesulfonate and 3.6 g. (1 mol.+100% excess) of ethyl orthoacetate was heated at the refluxing temperature in 50 ml. of pyridine for three minutes. The reaction mixture was poured into water, the resulting

precipitate was collected on a filter, washed with water and dried. The solid was dissolved in 300 ml. of hot pyridine, and 2.8 ml. of triethylamine and 300 ml. of methanol were added. After chilling, the dye was collected on a filter. After another such purification the yield of dye was 11%. The orange crystals had a M.P. of 260–261° C. with decomposition.

1-(2-diethylaminoethyl)-3-phenyl-2-thiobarbituric acid hydroperchlorate

A solution of 67.5 g. (1 mol.) of phenylisothiocyanate in 100 ml. of benzene was added dropwise with stirring to a solution of 58.5 g. (1 mol.) of N,N-diethylethylenediamine in 500 ml. of benzene. The reaction was exothermic. The whole was allowed to stir at room temperature for 2 hours and then 200 ml. of ethanolic HCl (90 g./l.) was added. The resulting solution was concentrated using a rotary evaporator. The residue was recrystallized from 600 ml. of ethanol. The yield of 1-(2-diethylaminoethyl)-3-phenyl - 2 - thiourea hydrochloride was 90%.

A solution of 28.2 (1 mol.) of malonyl dichloride in 100 ml. of chloroform was added dropwise with stirring to 57.4 g. (1 mol.) of 1-(2-diethylaminoethyl)-3-phenyl-2-thiourea hydrochloride in 200 ml. of chloroform. After the addition had been completed the whole was heated on a steam bath for one hour. The resulting mixture was concentrated using a rotary evaporator. To the residue dissolved in water, a water solution of 49 g. (1 mol+100% excess) of sodium perchlorate was added. The solid that precipitates was collected on a filter, washed with water and dried. The yield after one recrystallization from dimethylformamide-ethanol mixture was 64% and the colorless crystals had a M.P. of 224–225° C. with decomposition.

1-(2-diethylaminoethyl) - 5 - [(1 - ethylnaphtho[1,2 - d] thiazolin-2-ylidene)isopropylidene]-3 - phenylbarbituric acid

This was prepared like the corresponding dye containing the thiobarbituric acid nucleus by using 1-(2-diethylaminoethyl) - 3 - phenyl - barbituric acid hydroperchlorate. The purified dye was obtained (14% yield) as brownish crystals of M.P. 225–226° C. with decomposition.

1-(2-diethylaminoethyl)-3-phenylbarbituric acid hydroperchlorate

This was prepared like the corresponding thiobarbituric acid salt by using phenyl isocyanate in place of phenylisothiocyanate. The recrystallized intermediate was obtained (56% yield) as colorless crystals of M.P. 223–224° C. with decomposition.

Our dyes are used to advantage to optically sensitize silver halides, e.g., silver chloride, silver bromide, silver iodide, silver chlorobromide, silver bromoiodide, silver chlorobromoiodide, etc. dispersed in any of the hydrophilic colloids known to be satisfactory for making light-sensitive photographic emulsions. Useful hydrophilic colloids include natural materials, e.g., gelatin, albumin, agar-agar, gum arabic, alginic acid, etc., and synthetic materials, e.g., polyvinyl alcohol, polyvinyl pyrrolidone, cellulose ethers, partially hydrolyzed celluose acetate, etc.

The concentration of our dyes in the emulsions can vary widely, i.e., from about 5 to about 100 m. per liter of flowable emulsion. The specific concentration will depend upon the dye, the type of light-sensitive material in the emulsion and the particular effects desired. The most advantageous dye concentration for any given emulsion can be readily determined by making the concentration series and observations customarily used in the art of emulsion making.

As mentioned previously our dyes are readily soluble in water especially in the presence of one equivalent of acid. The hydrophilic colloid-silver halide emulsion is sensitized to advantage by adding the appropriate amount of dye in aqueous solution to the emulsion with intimate mixing to insure uniform distribution. Any of the other methods customarily used in the art can be used for incorporating our dyes. For example, the dyes can be incorporated by bathing a photographic element coated with the emulsion, in a solution of the dye. Photographic elements that have a silver halide film coating (deposited from the vapor state under vacuum) are also sensitized to advantage by bathing in a solution of our dye(s).

Photographic silver halide emulsions, such as those listed above, containing the sensitizing dyes of our invention can also contain such addenda as chemical sensitizers, e.g., sulfur sensitizers (e.g., allyl thiocarbamide, thiourea, allylisothiocyanate, cystine, etc.), various gold compounds (e.g., potassium chloroaurate, auric trichloride, etc.) (see U.S. Pats. 2,540,085; 2,597,856; and 2,597,915), various palladium compounds, such as palladium chloride (U.S. 2,540,086), potassium chloropalladate (U.S. 2,598,079), etc., or mixtures of such sensitizers; antifoggants, such as ammonium chloroplatinate (U.S. 2,566,245), ammonium chloroplatinite (U.S. 2,566,-263), benzotriazole, nitrobenzimidazole, 5-nitroindazole, benzidine, mercaptans, etc. (see Mees "The Theory of the Photographic Process," Macmillan Pub., page 460), or mixtures thereof; hardeners, such as formaldehyde (U.S. 1,763,533), chrome alum (U.S. 1,763,533), glyoxal (U.S. 1,870,354), dibromacrolein (Br. 406,750), etc.; color couplers, such as those described in U.S. Pat. 2,423,730, Spence and Carroll U.S. application 771,380, filed Aug. 29, 1947 (now U.S. Pat. 2,640,776), etc.; or mixtures of such addenda. Dispersing agents for color couplers, such as those set forth in U.S. Pats. 2,322,027 and 2,304,940, can also be employed in the above-described emulsions.

Our emulsions are coated to advantage on any of the materials used for photographic elements including, for example, paper, glass, cellulose acetate, cellulose nitrate, synthetic film forming resins, e.g., the polyesters, the polyamides, polystyrenes, etc.

The following examples will serve to further illustrate our invention by showing the sensitizing effects of representative dyes of our invention on silver halide emulsions.

EXAMPLE 1

Portions of a gelatino silver bromoiodide emulsion containing 0.77 mole percent iodide of the type described by Trivelli and Smith, Phot. Journal, 79, 330 (1939) were sensitized by adding a solution of the indicated dye in a suitable solvent. The sensitized emulsions were coated at a coverage of 432 mg. of silver per square foot on a cellulose acetate film support. A sample of each coating was exposed on an Eastman 1B Sensitometer (an intensity scale sensitometer), and on the wedge spectrograph, processed for three minutes in Kodak Developer D–19, fixed in a conventional sodium thiosulfate fix, washed and dried. Table 1 summarizes the spectral sensitization data obtained.

	Spectral sensitization	
	λMax., mμ	Range, mμ
Dye number:		
1	675	550–720
2	675	560–715
3	660	510–700

Similarly, it can be shown that these and other complex cyanine dyes of our invention are used to advantage to sensitize other hydrophilic colloid silver halide emulsion.

EXAMPLE 2

A portion of a silver bromoiodide emulsion as described in Example 1 and a portion of a silver chlorobromide emulsion containing 40 mole percent bromide were sensitized as specified in Table 2.

The dyes were added as solutions in a suitable solvent. The coatings were exposed, processed, and evaluated as in Example 1. The results are summarized in Table 2.

TABLE 2

	Emulsion	Spectral sensitization: λ Max., mμ	Spectral sensitization: Range, mμ
Dye number:			
7	Silver bromoiodide	645	520–700
8	Silver chlorobromide	680	550–730

EXAMPLE 3

Example 1 was repeated using dyes 9, 10, 11 and 12 in place of dyes 1, 2 and 3. The results are summarized in Table 3.

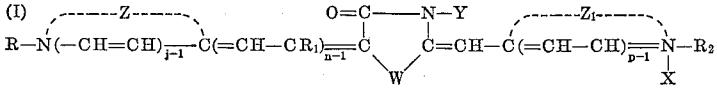
TABLE 3

	Spectral sensitization: Max., mμ	Spectral sensitization: Range, mμ
Dye number:		
9	675	530–705
10	670	530–700
11	685	–725
12	685	–725

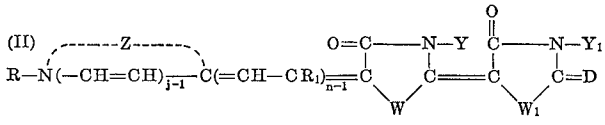
The invention has been described in detail with particular reference to preferred embodiments thereof but it will be understood that variations and modifications can be effected within the spirit and scope of the invention as described hereinabove and as defined in the appended claims.

We claim:

1. A dye selected from those having the formulas:



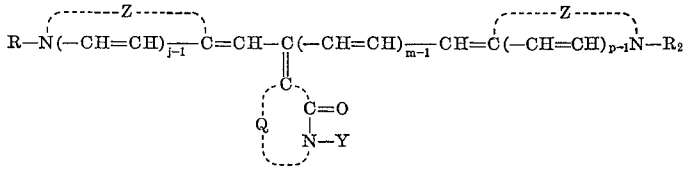
(I)



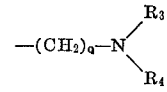
(II)

and

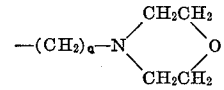
(III)



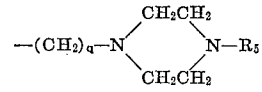
wherein R and R_2 each represents a member selected from the class consisting of an alkyl group having 1 to 8 carbon atoms, a sulfoalkyl group having 2 to 4 carbon atoms, a carboxy (alkyl of 2 to 4 carbons) group and a low carbon hydroxyalkyl group; Z and Z_1 each represent the nonmetallic atoms necessary to complete a 5 to 6 member 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 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-dimethylindolenine nucleus, an imizadole nucleus, a benzimidazole nucleus, and a naphthimidazole nucleus; *j* represents an integer of from 1 to 2; R_1 represents a member selected from the class consisting of the hydrogen atom, an alkyl group having 1 to 4 carbon atoms, phenyl and methylphenyl; *n* represents an integer of from 1 to 4; Y and Y_1 each represent a group selected from the class consisting of the hydrogen atom, an alkyl group having 1 to 4 carbon atoms, methoxyethyl, phenyl and methylphenyl; a



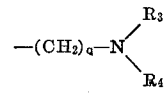
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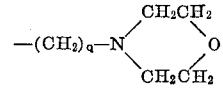
group, and a



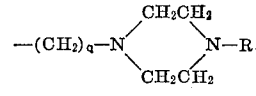
group, wherein Y of Formulas I and III and at least one of Y and Y_1 of Formula II is a



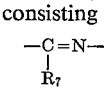
group, a



group or a



group; *q* represents an integer of from 2 to 4; R_3, R_4 and R_5 each represents an alkyl group having 1 to 6 carbon atoms, W and W_1 each represent a group selected from the class consisting of the oxygen atom, the sulfur atom, the selenium atom and a $>NR_6$ group wherein R_6 represents a group selected from the class consisting of an alkyl group having 1 to 4 carbon atoms, phenyl and methylphenyl; *p* represents an integer of from 1 to 2; X represents an acid group; D and D_1 each represent a group selected from the class consisting of the sulfur atom, the selenium atom and the oxygen atom; *m* represents an integer of from 1 to 2; Q represents a group selected from the class consisting of a



group, a



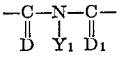
group, a



group, a



group and a



group; and R_7 represents a group selected from the class consisting of the hydrogen atom, an alkyl group having 1 to 6 carbon atoms, phenyl, methylphenyl, halophenyl, mono(low carbon alkyl)amino, di(low carbon alkyl)-amino, phenylamino, (low carbon alkyl)carbonamido, phenylcarbonamido, (low carbon alkyl)sulfonamido, phenylsulfonamido, (low carbon alkyl)sulfamyl, phenylsulfamyl, (low carbon alkyl)carbamyl and phenylcarbamyl.

2. A dye of claim **1** selected from those having Formula I.

3. A dye of claim **1** selected from those having Formula II.

4. A dye of claim **1** selected from those having Formula III.

5. A dye in accordance with claim **1** wherein said dye is 2 - [(2-benzothiazolylethoperchlorate)methylene]-3-(3-dimethylaminopropyl)-5-[(1 - methylnaphtho[1,2-d]-thiazolin-2-ylidene)-1-phenylethylidene]-4-thiazolidinone.

6. A dye in accordance with claim **1** wherein said dye is 2 - [(5-chloro-2-benzothiazolylethoperchlorate)-methylene]-3-(3-dimethylaminopropyl) - 5 - [(1-methylnaphtho-

[1,2-d]thiazolin-2-ylidene) - 1 - phenylethylidene]-4-thiazolidinone.

7. A dye in accordance with claim **1** wherein said dye is 1-(2-diethylaminoethyl)-5-(1-ethylnaphtho[1,2-d]thiazolin-2-ylidene) - (1-methylnaphthio[1,2 - d]thiazolin-2-ylidene)isopropylidene]-3-phenylbarbituric acid.

8. A dye in accordance with claim **1** wherein said dye is 1-(2-diethylaminoethyl)-5-(1-ethylnaphtho-[1,2-d]thiazolin-2-ylidene)isopropylidene-3-phenylbarbituric acid.

9. A dye in accordance with claim **1** wherein said dye is 3-(3-dimethylaminopropyl)-2-[3-(3-dimethylaminopropyl)-4-oxo-2-thioxo-5-thiazolidinylidene]-5-[(2 - methylnaphthio[1,2 - d]thiazolin-2-ylidene)-1-phenylethylidene]-4-thiazolidinone.

10. A dye in accordance with claim **1** wherein said dye is 5-[(1-ethylnaphtho[1,2-d]thiazolin-2-ylidene)-1-phenylethylene] - 3 - (2-morpholinoethyl)-2-[3-(2-morpholinoethyl)-4-oxo-2-thioxo - 5 - thiazolidinylidene]-4-thiazolidinone.

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JOHN D. RANDOLPH, Primary Examiner

U.S. Cl. X.R.

96—106; 260—240.4, 247.1, 552, 257, 260, 293.4, 295, 298, 302, 304, 305, 306, 306.7, 307, 309, 309.2, 326