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MEROCYANINE DYES FOR PHOTOGRAPHIC ELEMENTS CONTAINING AN EXTRACYCLIC TERTIARY AMINO GROUP

Robert C. Taber and Leslie G. S. Brooker, Rochester, N.Y., assignors to Eastman Kodak Company, Rochester, N.Y., a corporation of New Jersey
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ABSTRACT OF THE DISCLOSURE

A photographic silver halide emulsion containing incorporated color-forming coupler is advantageously spectrally sensitized with a merocyanine dye containing one basic heterocyclic nucleus and one acidic ketomethylene heterocyclic nucleus in which the ketomethylene nucleus has in its heterocyclic ring at least one nitrogen atom substituted with an extracyclic alkyl group terminating in a tertiary nitrogen atom (extracyclic) because of the ease with which the said dyes are incorporated in the emulsion, and the substantially lower stain left in the immediate emulsions after processing compared to emulsions spectrally sensitized with corresponding merocyanine dyes that do not contain the extracyclic tertiary amino group.

This application relates to photographic sensitizing dyes and more particularly to merocyanine dyes having an acid nucleus with at least one secondary amino substituted alkyl group attached thereto, to photographic silver halide elements sensitized with said dyes and to color photographic elements that contain couplers with said emulsions.

It is known to use merocyanine dyes as optical sensitizers in photographic silver halide emulsion layers. Such dyes are used to advantage in color photographic elements to differently sensitize the emulsion layers. Color photographic elements usually comprise a support coated with an emulsion that is sensitive to light in the green region of the spectrum, an emulsion that is sensitive to light in the red region of the spectrum and a third emulsion that is sensitive to light in the blue region of the spectrum. The layers may be arranged in various orders; however, one conventional arrangement is to have the red sensitive layer coated on the support with the green sensitive layer coated next, and the blue sensitive layer outermost, usually with a bleachable blue light-absorbing filter layer between the green sensitive and blue-sensitive layers. The color photographic elements are color developed after exposure during the photographic processing by developing exposed silver halide with an aqueous alkaline developer solution containing a p-phenylenediamine color developer in the presence of a color forming coupler(s). The couplers may be incorporated in the appropriate emulsion layers or be incorporated in the appropriate color developer solutions. For example, in the elements that contain the couplers, it is advantageous that the red-sensitive layer contain a cyan-forming coupler, the green-sensitive layer contain a magenta-forming coupler and the blue-sensitive layer contain a yellow-forming coupler.

Sensitizing dyes must not only have 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 great in color photographic prints.

Merocyanine type dyes having desirable optical sen-

sitizing characteristics and good solubility in aqueous media are desired.

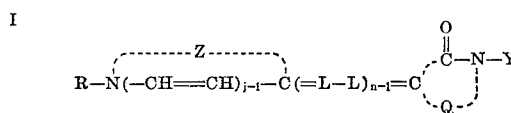
It is therefore an object of our invention to provide a new class of valuable merocyanine optical sensitizing dyes that have good solubility in aqueous media in the presence of one equivalent of acid and leave less stain when used in photographic processes than dyes known hitherto.

Another object is to provide improved photographic silver halide emulsions that are sensitized with our valuable merocyanine dyes that have an acid nucleus that has at least one secondary amino substituted alkyl group attached thereto.

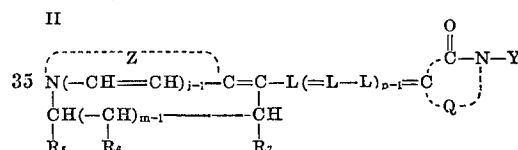
Another object is to provide improved photographic elements with incorporated color-forming couplers for color photography that contain at least one of our merocyanine dye sensitized emulsion layers and which have lower stain levels than photographic elements containing sensitizing dyes known heretofore.

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

These and other objects are accomplished according to our invention by the use of photographic silver halide emulsions containing at least one sensitizing dye represented by the formula:



and



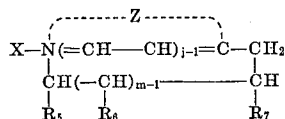
wherein R represents an alkyl group having from 1 to 8 carbon atoms, e.g., methyl, sulfoethyl, carboxyethyl, hydroxypropyl, sulfobutyl, carboxybutyl, hexyl, octyl, etc., or an aryl group, e.g., phenyl, sulfophenyl, carboxyphenyl, tolyl, etc.; Z represents the nonmetallic atoms required to complete a 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-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.), 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-methylloxazole, 5-methylloxazole, 4-phenylloxazole, 4,5-diphenylloxazole, 4-ethylloxazole, 4,5-dimethylloxazole, 5-phenylloxazole, etc.), those of the benzoxazole series (e.g., benzoxazole, 5-chlorobenzoxazole, 5-methylbenzoxazole, 5-phenylbenzoxazole, 6-methylbenzoxazole, 5,6-dimethylbenzoxa-

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the presence of a basic condensing agent, in an inert solvent and at an elevated temperature as described previously.

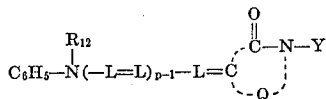
The dyes of Formula II are prepared to advantage by condensing a cyclammonium quaternary salt having the formula:

VI



wherein X, Z, j, R₅, R₆, R₇ and m are as defined previously with an intermediate having the formula:

VII



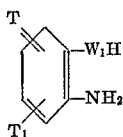
wherein L, p, Q and Y are as defined previously and R₁₂ represents the hydrogen atom or the



group. These condensations are carried out advantageously in the presence of a basic condensing agent, in an inert solvent and at a temperature between room temperature and the reflux temperature as described previously herein.

The compounds of Formula VI wherein Z represents the nonmetallic atoms necessary to complete a benzimidazole or a naphthalimidazole nucleus are prepared advantageously by the reaction of 1,2-diaminobenzene, 1,2-diaminonaphthalene or a 2,3-diaminonaphthalene compound with a lactone such as a γ -butyrolactone (e.g., γ -butyrolactone, β -ethyl- γ -butyrolactone, β -butyl- γ -butyrolactone, β -phenyl- γ -butyrolactone, β,γ -dimethyl- γ -butyrolactone, γ -methyl- γ -butyrolactone, β -phenyl- γ -butyrolactone, etc.), or a δ -valerolactone (e.g., δ -valerolactone, β -methyl- δ -valerolactone, β -propyl- δ -valerolactone, γ -ethyl- δ -valerolactone, δ -methyl- δ -valerolactone, γ -phenyl- δ -valerolactone, β,γ,δ -trimethyl- δ -valerolactone, etc.). The diaminobenzene or diaminonaphthalene compound used is provided with the appropriate substituents so they will be present on the base formed. Alternatively, these substituents can be substituted on the base after its formation. The cyclization reaction can be effected by heating the diaminobenzene or the diaminonaphthalene and lactone at atmospheric pressure or at an elevated pressure in an autoclave. In the presence of suitable solvents, such as, diphenyl ether, or chlorobenzene the reaction can be effected at lower temperatures. The base is quaternated by heating with the appropriate alkylating agent.

The compounds of Formula VI wherein Z represents the nonmetallic atoms required to complete a thiazole, an oxazole or a selenazole ring are produced to advantage by condensing a 2-mercaptoethylamine HCl, a 2-hydroxyethylamine HCl or a 2-selenylethamine HCl, respectively, with the appropriate δ -valerolactone or δ -butyrolactone (such as have been described in the preceding paragraph) by heating with an acid anion furnishing compound, e.g., phosphoryl chloride, hydrobromic acid, hydroiodic acid, hydrochloric acid, etc. The compounds of Formula VI wherein Z represents the nonmetallic atoms needed to complete the corresponding benzo or naphtho fused heterocyclic compounds are prepared to advantage by condensing a compound having the formula:



wherein W₁ represents the sulfur atom, the oxygen atom or the selenium atom, and T and T₁ each represent the

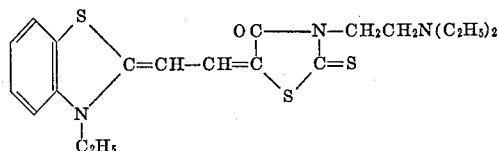
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hydrogen atom, an alkyl group (e.g., methyl, ethyl, butyl, etc.), an aryl group (e.g., phenyl, tolyl, etc.), a halogen atom (e.g., chlorine, bromine, etc.) or together T and T₁ contain the nonmetallic atoms necessary to complete a naphthalene compound, such as 1-amino-2-W₁H-naphthalene, 2-amino-3-W₁H-naphthalene or 2-amino-1-W₁H-naphthalene with the appropriate γ -butyrolactone or δ -valerolactone (typical examples of which have been listed in the preceding paragraph) in the presence of an acid anion furnishing compound, such as, phosphoryl chloride and the others listed previously.

Included among the dyes of Formulas I and II used according to our invention are the following typical examples.

DYE NO. 1

3-(2-diethylaminoethyl)-5-[(3-ethyl-2-benzothiazolylidene)-ethylidene]rhodanine



4.4 g. (1 mol.) of 3-(2-diethylaminoethyl)rhodanine and 8.2 g. (1 mol.) of 2- β -acetanilidovinyl-3-ethylbenzothiazolium iodide were added to 50 ml. of ethanol, 2.8 ml. (1 mol.) of triethylamine added, and the resulting solution heated under reflux for 40 minutes. The reaction mixture was chilled. Dye separated and was collected on a filter. The dye was twice recrystallized from ethanol (final yield 7%) and obtained as red needles M.P. 172-174° C. decomposition.

DYE NO. 2

3-(2-diethylaminoethyl)-5-[(3-ethyl-2-benzoxazolylidene)-ethylidene]rhodanine

4.4 g. (2 mol.) of 3-(2-diethylaminoethyl)rhodanine and 3.9 g. (1 mol.) of 2- β -acetanilidovinyl-3-ethylbenzoxazolium iodide were added to 50 ml. of ethanol, 2.8 ml. (2 mol.) of triethylamine added, and the resulting solution heated on the steam bath for 20 minutes and then chilled. Dye separated and was collected on a filter. The dye was twice recrystallized from ethanol (yield 16%) and obtained as reddish-orange needles M.P. 168-169° C. with decomposition.

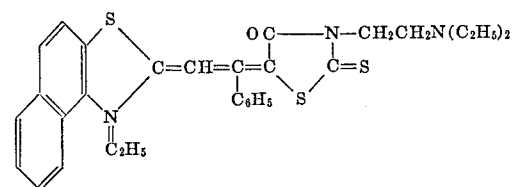
DYE NO. 3

3-(2-diethylaminoethyl)-5-[(3-methyl-2-thiazolidinylidene)-ethylidene]rhodanine

8.8 g. (2 mol.) of 3-(2-diethylaminoethyl)rhodanine and 7.8 g. (1 mol.) of 2- β -anilinoethyl-3-methyl-2-thiazolium iodide were added to 15 ml. of pyridine, 5 ml. of acetic anhydride added, and the solution heated on the steam bath for 15 minutes. The dye was precipitated as an oil by the addition of 100 ml. of water to the reaction mixture. On chilling, the oil gradually solidified and was collected on a filter. The dye was twice recrystallized from methanol and obtained (yield 9%) as light orange crystals M.P. 147-148° C. with decomposition.

DYE NO. 4

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

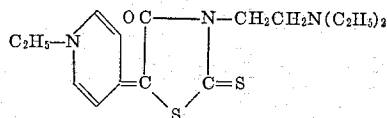


11.1 g. (2 mol.) of 3-(2-diethylaminoethyl)rhodanine and 12.6 g. (1 mol.) of 1-ethyl-2-(2-ethylthiostyryl)naph-

tho[1,2-d]thiazolium ethylsulfate were added to 100 ml. of ethanol, 7.0 ml. of triethylamine added, and the solution heated under reflux for 15 minutes. The dye separated on chilling and was twice recrystallized by dissolving in dimethylformamide and precipitating with methanol. The dye was obtained (56%) as green needles of M.P. 226–228° C. with decomposition.

DYE NO. 5

3-(2-diethylaminoethyl)-5-(1-ethyl-4(1H)pyridylidene)rhodanine



8.8 g. (2 mol.) of 3-(2-diethylaminoethyl)rhodanine and 6.8 g. (1 mol.) of 1-ethyl-4-phenylthiopyridinium iodide were added to 25 ml. of pyridine, 5.6 ml. of triethylamine added, and the solution heated under reflux for 10 minutes. The reaction mixture was treated with 50 ml. of benzene, chilled, filtered and the filtrate washed with 0.1 N aqueous sodium hydroxide. The benzene layer was separated and from it solid product was precipitated by addition of ligroin. The dye was twice recrystallized from ethanol and obtained (21%) as light orange platelets of M.P. 164–165° C. with decomposition.

DYE NO. 6

3-(2-diethylaminoethyl)-5-[(3-ethyl-2-benzothiazolylidene)-isopropylidene]rhodanine

This dye was prepared by the method used for Dye No. 1 but substituting one mole. of 3-ethyl-2-(2-ethylthiopropenyl)-benzothiazolium ethylsulfate for the benzothiazolium iodide used for No. 1. The dye was twice recrystallized to give purple crystals of M.P. 149–151° C. with decomposition.

DYE NO. 7

3-(2-diethylaminoethyl)-5-[(3-ethyl-2-benzothiazolylidene)-ethylidene]-2-thio-2,4-oxazolidinedione

16.8 g. (4 mol.) of 3-(2-diethylaminoethyl)-2-thio-2,4-oxazolidinedione and 9.0 g. (1 mol.) of 2-β-acetanilidovinyl-3-ethylbenzothiazolium iodide were added to 30 ml. of pyridine, 10 ml. of acetic anhydride added, and the solution heated under reflux for 15 minutes. The reaction mixture was diluted with 20 ml. of methanol, filtered, and the dye precipitated from the filtrate with water. The dye was suspended in a 50% water-methanol solution, dissolved by conversion to the hydroacetate on addition of acetic acid and reprecipitated by making the solution basic with piperidine. The dye was twice recrystallized in this fashion and obtained (11%) as dark red crystals of M.P. 172–175° C. with decomposition.

DYE NO. 8

3-(2-diethylaminoethyl)-5-[(3-ethylnaphtho[2,3-d]thiazolylidene)-ethylidene]-2-thio-2,4-oxazolidinedione

This dye was prepared by the method used to make Dye No. 7 but substituting one mol. of 2-β-acetanilidovinyl-3-ethylnaphtho[2,3-d]thiazolium iodide for the benzothiazolium iodide. The dye product was recrystallized twice to give dull reddish crystals of M.P. 228–230° C. with decomposition.

DYE NO. 9

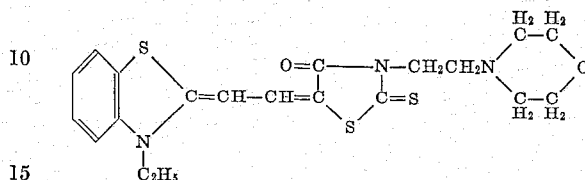
3-(2-diethylaminoethyl)-5-[(3-methyl-2-thiazolidinylidene)-ethylidene]-2-thio-2,4-oxazolidinedione

This dye was prepared by the method used to make Dye No. 7 but by using 2-β-anilinoethyl-3-methyl-2-thiazolium iodide for the benzothiazolium iodide. The

twice recrystallized dye was obtained as brownish-yellow crystals of M.P. 138–141° C. with decomposition.

DYE NO. 10

5-[(3-ethyl-2-benzothiazolylidene)ethylidene]-3-(2-morpholinoethyl)rhodanine



1.57 g. (1.73 mol.) of 3-(2-morpholinoethyl)rhodanine HCl, 1.66 g. (1 mol.) of 2-β-acetanilidovinyl-3-ethylbenzothiazolium iodide and 1.7 ml. (3.29 mol.) of triethylamine were added to 20 ml. of ethanol and heated under reflux for 20 minutes. The reaction mixture was chilled, the dye separated and was collected on a filter. The crude dye was dissolved in 125 ml. of ethanol containing glacial acetic acid. The solution was filtered, concentrated to 70 ml. neutralized with triethylamine and the dye collected on a filter. The dye was further purified by dissolving in a minimum of hot pyridine, filtering hot, diluting with methanol and chilling. It was obtained as purple crystals (18%) of M.P. 190–191.5° C. with decomposition.

DYE NO. 11

3-(2-morpholinoethyl)-5-[(1,3,3-trimethyl-2-indolylidene)-ethylidene]rhodanine

This dye was prepared by the method used for Dye No. 10 but substituting one mol. of 2-β-acetanilidovinyl-1,3,3-trimethyl-3H-indolium iodide for the benzothiazolium iodide. The twice recrystallized dye was obtained as reddish-orange crystals with a golden reflex of M.P. 163.5–164° C. with decomposition.

DYE NO. 12

5-[(1-ethylnaphtho[1,2-d]thiazolylidene)-ethylidene]-3-(2-morpholinoethyl)rhodanine

This dye was prepared by the method used for Dye No. 10 but substituting one mol. of 2-β-anilinoethyl-1-ethylnaphtho[1,2-d]thiazolium p-toluenesulfonate for the benzothiazolium iodide. The twice recrystallized dye was obtained as dark red crystals of M.P. 245.5–247.5° C. with decomposition.

DYE NO. 13

5-[(1-ethylnaphtho[1,2-d]thiazolylidene)-1-ethylidene]-3-(2-morpholinoethyl)rhodanine

This dye was prepared by the method used for Dye No. 10 but substituting one mol. of 1-ethyl-2-(2-methylthio-1-butenyl)-naphtho[1,2-d]thiazolium p-toluenesulfonate for the benzothiazolium iodide. The twice recrystallized dye was obtained as red crystals with a blue-gray reflex M.P. 193.5–195.5° C. with decomposition.

DYE NO. 14

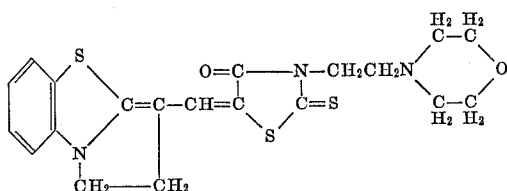
5-[(3-methyl-2-thiazolidinylidene)isopropylidene]-3-(2-morpholinoethyl)rhodanine

2.60 g. (1.05 mol.) of 3-(2-morpholinoethyl)rhodanine, 4.86 g. (2 mol.) of 2,3-dimethyl-2-thiazolinium iodide, 7.36 ml. (4 mol.) of ethylorthoacetate and 5.6 ml. (4 mol.) of triethylamine were added to 40 ml. of ethanol. The resulting solution was heated under reflux for one hour and chilled overnight. The dye was collected on a filter and washed with methanol. The dye was twice recrystallized by dissolving in pyridine, filtering and diluting with methanol. The dye was obtained (30%) as light red crystals of M.P. 198.5–199.5° C. with decomposition.

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DYE NO. 15

5-[(1,2-dihydropyrrolo[2,1-b]benzothiazol-3-yl)methylene]-3-(2-morpholinoethyl)rhodanine



1.97 g. (1 mol.) of 5-acetanilidomethylene-3-(2-morpholinoethyl)rhodanine, 1.28 g. (1 mol.) of 2,3-trimethylenbenzothiazolium bromide and 1.54 ml. (1.1 mol.) of triethylamine were added to 20 ml. of pyridine and the solution heated under reflux for 30 minutes. The reaction mixture was chilled, the dye collected on a filter and washed with methanol. The dye was obtained (31%) as reddish-brown crystals of M.P. 300–202° C. with decomposition.

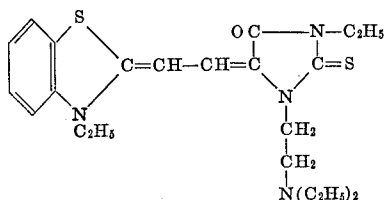
DYE NO. 16

5-[3-methylnaphtho[1,2-d]oxazolin-2-ylidene]-3-(2-morpholinoethyl)rhodanine

2.14 g. (1 mol.) of 2-methylmercaptanaphtho[1,2-d]oxazole and 1.69 ml. (1 mol.) of methyl p-toluenesulfonate were fused over an open flame until slight bubbling occurring. The resulting glassy melt was cooled to room temperature. 2.46 g. (1 mol.) of 3-(2-morpholinoethyl)rhodanine, 3.08 ml. (2.2 mol.) of triethylamine and 20 ml. of absolute ethanol were added and the resulting solution was heated under reflux for 5 minutes. The reaction mixture was chilled and the dye which separated was collected on a filter. The dye was twice recrystallized by dissolving in pyridine, filtering and diluting with methanol. The yellow crystals were obtained (34%) with melting point of 250–251° C. with decomposition.

DYE NO. 17

1-(2-diethylaminoethyl)-3-ethyl-5-[(3-ethyl-2-benzothiazolinyldene)ethylidene]-2-thiohydantoin



5.8 g. (2 mol.) of 1-(2-diethylaminoethyl)-3-ethyl-2-thiohydantoin hydrobromide and 4.5 g. of 2-β-acetanilidovinyl-3-ethylbenzothiazolium iodide were added to 50 ml. of ethanol, 4.2 ml. of triethylamine added and the solution heated under reflux for 5 minutes. The reaction mixture was filtered, an excess of piperidine added and the dye precipitated by the addition of water. The dye was recrystallized by dissolving in methanol and precipitating with water. The dye was further purified by recrystallization from ligroin (B.P. 100–115) and obtained (46%) as bluish-red crystals of M.P. 144–145° C. with decomposition.

DYE NO. 18

1-(2-diethylaminoethyl)-3-ethyl-5-[(3-ethyl-2-benzoxazolinyldene)ethylidene]-2-thiohydantoin

This dye was prepared by the method used for Dye No. 17 by substituting one mol. of 2-β-acetanilidovinyl-3-ethylbenzoxazolium iodide for the corresponding benzothiazolium iodide. The dye was recrystallized twice to give light orange crystals of M.P. 140–141° C.

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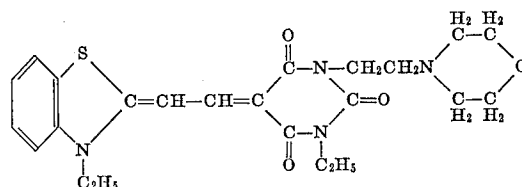
DYE NO. 19

1-(2-diethylaminoethyl)-5-[(3-ethylnaphtho[2,1-d]oxazolin-2-ylidene)ethylidene]-3-phenyl-2-thiohydantoin

This dye was prepared by the method used to make Dye No. 17 but using 1-(2-diethylaminoethyl)-3-phenyl-2-thiohydantoin hydrobromide and 2-β-acetanilidovinyl-3-ethylnaphtho[2,1-d]oxazolium iodide as the dye intermediates. The crude dye was recrystallized twice to give orange plates with metallic blue reflux of M.P. 236–238° C. with decomposition.

DYE NO. 20

1-ethyl-5-[(3-ethyl-2-benzothiazolinyldene)ethylidene]-3-(2-morpholinoethyl)barbituric acid



2.25 g. (1 mol.) of 2-β-acetanilidovinyl-3-ethylbenzothiazolium iodide, 2.70 g. (2 mol.) of 1-ethyl-3-(2-morpholinoethyl)barbituric acid and 1.54 ml. (2.2 mol.) of triethylamine were added to 25 ml. of absolute ethanol. The resulting solution was stirred at room temperature for 30 minutes. The reaction mixture was chilled and the dye which separated was collected on a filter, washed with methanol and finally with water. The dye was purified by dissolving in hot pyridine, filtering and diluting with methanol. Further purification was effected by recrystallizing the dye from a minimum of boiling methanol. The orange crystals obtained (13%) melted at 228.5–229.5° C. with decomposition.

DYE NO. 21

1-(2-diethylaminoethyl)-3-ethyl-5-[(3-ethyl-2-benzoxazolinyldene)ethylidene]barbituric acid

A mixture of 3.7 g. (4 mol.) of 1-(2-diethylaminoethyl)-3-ethylbarbituric acid, 2.17 g. (1 mol.) of 2-(2-acetanilidovinyl)-3-ethylbenzoxazolium iodide, 1.1 g. (1.10 mol.) of triethylamine and 25 ml. of ethanol was heated at the refluxing temperature for 15 minutes. The reaction mixture was chilled, the crude (1-(2-diethylaminoethyl)-3-ethyl-5-[(3-ethyl-2-benzoxazolinyldene)ethylidene]barbituric acid hydroiodide was collected on a filter and washed with water. The solid was suspended in water and the suspension was made basic with sodium carbonate and the solid was collected on a filter and washed with water. After two recrystallizations from methanol, the yield of yellow crystals was 23% and they had a M.P. 266–268° C.

DYE NO. 22

3-(3-dimethylaminopropyl)-5-[(3-ethyl-2-benzothiazolinyldene)ethylidene]rhodanine

This dye was prepared by the method used for Dye No. 1 but substituting one mol. of 3-(3-dimethylaminopropyl)-rhodanine hydroperchlorate for the 3-(2-diethylaminoethyl)rhodanine. The twice recrystallized dye was obtained as dark red crystals with a green reflux of M.P. 178–180° C. with decomposition.

DYE NO. 23

3-(3-dimethylaminopropyl)-5-[(3-ethyl-2-benzoxazolinyldene)ethylidene]rhodanine

1.1 g. (1 mol.) of 2-β-acetanilidovinyl-3-ethylbenzoxazolium iodide and 0.8 g. (1 mol.) of 3-(3-dimethylaminopropyl)rhodanine hydroperchlorate were added to

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20 ml. of ethanol and 2 ml. of triethylamine and the mixture heated at reflux for 3 minutes. The reaction mixture was filtered, the filtrate made basic with piperidine, chilled and the dye collected on a filter. The dye was twice recrystallized from ethanol and obtained (yield 64%) as reddish-orange plates of M.P. 159–160° C. with decomposition.

DYE NO. 24

3 - (3 - dimethylaminopropyl) - 5 - [(3-ethyl-2-benzothiazolinyldene)-ethylidene]-2-thio-2,4-oxazolidinedione

1.1 g. (1 mol.) of 2-β-acetanilidovinyl-3-ethylbenzothiazolium iodide and 2.6 g. (1 mol.+300%) 3-(3-dimethylaminopropyl) - 2 - thio-2,4-oxazolidinedione were added to 20 ml. of ethanol and 1.4 ml. of triethylamine and the solution heated at reflux for 3 minutes. The dye was precipitated as an oily residue on treatment with 50 ml. of water containing an excess of piperidine and the residue washed with water and made crystalline on stirring with a small amount of methanol. The dye was recrystallized from ethanol and obtained (yield 61%) as dark red needles with gold reflux of M.P. 203–205° C. with decomposition.

DYE NO. 25

3 - (3 - dimethylaminopropyl) - 5 - [(1,3,3 - trimethyl-2-indolinyldene)ethylidene]-2-thio-2,4-oxazolidinedione

1.1 g. (1 mol.) of 2-β-acetanilidovinyl-1,3,3-trimethyl-3H-indolium iodide and 1.3 g. (1 mol.+100%) of N-[(3-dimethylamino)-propyl]thiocarbonyl glycolic acid, potassium salt were added to 5 ml. of acetic anhydride and 5 ml. of triethylamine and the solution heated at reflux for 3 minutes. The reaction mixture was treated with 50 ml. of water containing 1.5 g. of sodium iodide and the dye isolated as a sticky solid. The solid was dissolved in methanol, made basic with piperidine, enough water added to initiate precipitation and the solution chilled and the dye collected. The dye was recrystallized by dissolving in boiling methanol and adding just enough water to initiate precipitation, and chilling. The dye was obtained (yield 37%) as orange crystals with gold reflux of M.P. 137–139° C. with decomposition.

DYE NO. 26

5 - [(1 - ethylnaphthol[1,2 - d]thiazolin - 2 - ylidene)ethylidene]-3-[3-(4-methyl-1-piperazinyl)propyl]rhodanine

1.2 g. (1 mol.) of 2-β-anilinoethyl-1-ethylnaphtho-[1,2-d]thiazolium p-toluenesulfonate and 1.0 g. (1 mol.+10%) of 3-[3-(4-methyl-1-piperazinyl)propyl]rhodanine hydroperchlorate were added to 5 ml. of acetic anhydride and 5 ml. of triethylamine and the solution heated at reflux for 3 minutes. The dye was precipitated as the hydroperchlorate on treatment with a solution containing 5 ml. of acetic acid, 0.6 g. of sodium perchlorate and 25 ml. of water. The dye was then dissolved in dimethylformamide and precipitated with ethanol. The dye was again recrystallized by dissolving in dimethylformamide and precipitating with water containing an excess of piperidine. The dye was obtained (yield 37%) as dark red crystals of M.P. 198–200° C. with decomposition.

DYE NO. 27

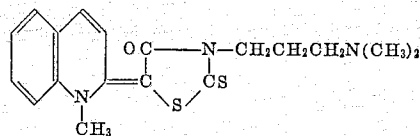
3 - (3 - diethylaminopropyl) - 5 - [(3 - methyl-2-thiazolindinyldene)ethylidene]rhodanine

1.0 g. (1 mol.) of 2-β-anilinoethyl-3-methyl-2-thiazolium iodide and 0.9 g. (1 mol.) of 3-(3-diethylaminopropyl)rhodanine hydroperchlorate were added to 5 ml. of pyridine, 2 ml. of acetic anhydride and 3 ml. of triethylamine and the solution heated at reflux for 3 minutes. The dye was precipitated as a crystalline material on treatment with a solution containing 40 ml. of water and 5 ml. of piperidine. The dye was recrystallized from methanol and obtained (yield 79%) as red crystals with green reflux of M.P. 162–164° C. with decomposition.

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DYE NO. 28

3 - (3 - dimethylaminopropyl)-5-(1-methyl-2(1H)-quinolyldene)rhodanine



0.9 g. (1 mol.) of 1-methyl-2-phenylthioquinolinium iodide and 0.8 g. (1 mol.) of 3-(3-dimethylaminopropyl)-rhodanine hydroperchlorate was added to 7 ml. of pyridine and 3 ml. of triethylamine and the solution heated at reflux for 3 minutes. The reaction mixture was treated with 40 ml. of a 50% methanol-water solution made basic with piperidine and chilled. The dye was twice recrystallized by dissolving in dimethylformamide and precipitating with methanol. The dye was obtained (yield 74%) as orange needles of M.P. 159–160° C. with decomposition.

The intermediates of Formulas III, V and VI are well known in the art. The preparations of intermediates of Formula IV are illustrated with the following typical examples.

3-(2-diethylaminoethyl)rhodanine

45.2 g. (1 mol.) of bis(carboxymethyl)trithiocarbonate and 23.2 g. (1 mol.) of N,N-diethylethylenediamine were added to 250 ml. of water, 21.2 g. (1 mol.) of sodium carbonate was added to the mixture in small portions with vigorous stirring and the resulting solution was heated on a steam bath for 2 hours. The solution was made acid with concentrated hydrochloric acid and heated on the steam bath for 1 hour. The reaction mixture was then concentrated to a heavy oil, taken up in 200 ml. of methanol and chilled overnight. The solution was filtered, the filtrate concentrated to a volume of 150 ml. and passed through a column containing 400 g. of neutral alumina. The product was diluted with methanol and the methanolic solution concentrated to a heavy resinous orange oil (40%) which was used to prepare dye without any further purification.

3-(2-morpholinoethyl)rhodanine

45.20 g. (1 mol.) of bis(carboxymethyl)trithiocarbonate and 26.04 g. (1 mol.) of N-(2-aminoethyl)morpholine were suspended in 200 ml. of water. 24.8 g. (1 mol.) of sodium carbonate monohydrate was added slowly with stirring. The reaction mixture was heated for 2 hours on a steam bath and then was chilled to 10° C., 30 ml. (ca. 1.5 mol.) of concentrated hydrochloric acid was added slowly with stirring and the reaction mixture was concentrated on a rotary evaporator. The viscous oily residue was twice extracted with methanol, filtered through Celite filter aid to remove suspended sodium chloride and the filtrate was concentrated to give a red gum. The red gum was dissolved in 225 ml. of methanol and chromatographed on 1 kg. of neutral alumina with methanol as the solvent. The 3-(2-morpholinoethyl)rhodanine was obtained as a yellow oil from the first fraction which was eluted from the column. This oil was used directly for preparing the dyes.

3-(2-diethylaminoethyl)-2-thio-2,4-oxazolidinedione

116 g. (2 mol.) of N,N-diethylethylenediamine was added to a solution of 35 g. of 5% potassium hydroxide in 150 ml. of water. 105 g. (1 mol.) of acetamidocarbothiolglycolic acid was added in small portions with rapid stirring and external cooling of the flask. The resultant solution was stirred at room temperature for 5 hours, made acid with concentrated sulfuric acid and chilled overnight. The solution was filtered and the filtrate concentrated to a thick yellow oil under reduced pressure. The residue was boiled with 250 ml. of methanol, chilled, the solid separated by filtration and the filtrate concentrated to a volume of 150 ml. under reduced pressure.

The solution was passed through a column containing 400 g. of neutral alumina, eluted with methanol and the methanolic solution concentrated to a heavy yellow oil (39%) under reduced pressure. The product was used to prepare dyes without further purification.

1-(2-diethylaminoethyl)-3-ethyl-2-thiohydantoin hydrobromide

11.6 g. (1 mol.) of N,N-diethylethylenediamine was added to 40 ml. of ethyl acetate. 16.7 g. (1 mol.) of ethyl bromoacetate was added and the solution cooled externally until the reaction subsided. The product was precipitated with ether, washed with ether, dissolved in 40 ml. of acetone and treated with 13.0 g. (2 mol.) of ethyl isothiocyanate. The acetone solution was heated under reflux for 1 hour, chilled and precipitated as an oil with ether. The product was washed with ether and obtained (86%) as a highly viscous yellow oil which was used to prepare dyes without further purification.

1-(2-diethylaminoethyl)-3-ethylurea

71 g. (1 mol.) of ethylisocyanate in 100 ml. of benzene was added dropwise to a stirred solution of 116 g. (1 mol.) of 1,1-diethylethylene-diamine in 300 ml. of benzene. After the addition was complete the reaction mixture was stirred at room temperature for 2 hours. The benzene was then removed using a rotary evaporator. The oily 1-(2-diethylaminoethyl)-3-ethylurea was used directly for making 1-(2-diethylaminoethyl)-3-ethylbarbituric acid.

1-(2-diethylaminoethyl)-3-ethylbarbituric acid

24.6 g. (1 mol.) of 1-(2-diethylamino)-3-ethylurea in 100 ml. of glacial acetic acid, 20.4 g. (1.5 mol.) of malonic acid and 100 ml. of acetic anhydride were added and the whole was allowed to stand at about 5° C. for four days. The excess acetic acid and acetic anhydride were removed using a rotary evaporator at 40° C. The residue was stirred in ether and the ether layer decanted. The residue was dissolved in water and ammonium hydroxide added until the solution was alkaline. The water was removed using a rotary evaporator at 40° C. The resulting crude 1-(2-diethylaminoethyl)-3-ethylbarbituric acid was used directly in making dyes.

1-ethyl-3-(2-morpholinoethyl)urea

52.08 g. (1 mol.) of N-(2-aminoethyl)morpholine was dissolved in 600 ml. of benzene and with stirring 31.6 ml. (1 mol. of ethylisocyanate in 50 ml. of benzene was added dropwise. Upon completion of the addition the reaction mixture was heated under reflux for 2 hours. The cooled reaction mixture was concentrated to 400 ml. and poured into 1500 ml. of ligroin (B.P. 100–115° C. with stirring. The 1-ethyl-3-(2-morpholinoethyl)urea separated as a white solid (95%) of melting point 80–85° C. with decomposition.

1-ethyl-3-(2-morpholinoethyl)barbituric acid

4.6 g. (2 mol.) of sodium was dissolved in 350 ml. of absolute ethanol with stirring. 20.12 g. (1 mol.) of 1-ethyl-3-(2-morpholinoethyl)urea and 18.2 ml. (1.2 mol.) of diethylmalonate were added to the sodium ethoxide solution and the mixture was heated under reflux for 24 hours. The mixture was chilled to 10° and neutralized by the addition of 20 ml. of concentrated hydrochloric acid. The solution was filtered through a bed of Celite filter aid to remove suspended sodium chloride and the filtrate was concentrated on a rotary evaporator to give the crude 1-ethyl-3-(2-morpholinoethyl) barbituric acid which was used directly in making dyes.

3-(3-dimethylaminopropyl)rhodanine hydroperchlorate

This compound was prepared by the method used to make 3-(2-diethylaminoethyl)rhodanine except that N,N-dimethyl-1,3-propanediamine was substituted for the N,N-diethylethylenediamine and the resulting compound was

treated with an aqueous solution containing sodium perchlorate to produce the quaternary ammonium salt as yellow crystals of M.P. 128–130° C. with decomposition.

N-[(dimethylamino)propyl]thiocarbonyl glycolic acid potassium salt

52.2 g. (1 mol.) of carbamoylmethylthiothiocarbonyl glycolic acid was added to a solution containing 16.5 g. (1 mol.) of 85% potassium hydroxide and 75 ml. of water. The solution was then treated slowly with external cooling with 25.5 g. (1 mol.) of N,N-dimethyl-1,3-propanediamine. After the addition was complete the solution was allowed to stand at room temperature for 2 hours and then treated with 150 ml. of ethanol and chilled overnight. The solid was collected on a filter and washed with 200 ml. of boiling ethanol. The product was obtained (yield 59%) as a colorless solid of M.P. 115–118° C. with decomposition.

3-[3-(4-methyl-1-piperazinyl)propyl]rhodanine hydroperchlorate

14.4 g. (1 mol.) of bis(carboxymethyl)trithiocarbonate was suspended in 150 ml. of water and treated with 6.8 g. of sodium carbonate. 10.0 g. (1 mol.) of 1-(3-amino-propyl)-4-methylpiperazine was added and the solution heated on the steam bath of 1½ hours. The solution was then made strongly acid with concentrated hydrochloric acid and heated for ½ hour more. The solution was chilled overnight and an oil separated which was not the desired product. The solution was allowed to slowly evaporate for several days at room temperature and the product separated (yield 51%) as a sticky solid which was used directly to prepare dyes.

3-(3-diethylaminopropyl)rhodanine hydroperchlorate

This compound was prepared by the method used to make 3-(2-diethylaminoethyl)rhodanine except that N,N-diethyl-1,3-propanediamine was substituted for the N,N-diethylethylenediamine and the resulting compound was treated with an aqueous sodium perchlorate solution to form the quaternary ammonium salt as pinkish crystals of M.P. 102–104° C. with decomposition.

Our optical sensitizing dyes are used to advantage to sensitize silver halides e.g., silver chloride, silver bromide, silver iodide, silver chlorobromide, silver bromoiodide, silver chlorobromoiodide, etc., which have been dispersed in any hydrophilic colloid 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 cellulose acetate, etc.

The concentration of our dyes in the emulsions can vary widely, i.e., from about 5 to about 100 mg. 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 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, allyl-isothiocyanate, cystine, etc.), various gold compounds (e.g., potassium chloraurate, auric trichloride, etc.) (see U.S. Patents 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. Patent 2,423,730, Spence and Carroll U.S. application 771,380, filed August 29, 1947 (now U.S. Patent 2,640,776), etc.; or mixtures of such addenda. Dispersing agents for color couplers, such as those set forth in U.S. Patents 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 example will serve to further illustrate our invention by showing the sensitizing effects of representative dyes of our invention on silver halide emulsions.

EXAMPLE I

Portions of a gelatino-silver bromiodide emulsion containing 0.77 mole percent iodide of the type described by Trivelli and Smith, Phot. Journal, 79, 330 (1939) or a silver chlorobromide emulsion containing 40 mole percent bromide were sensitized with representative dyes at the indicated concentration. Aqueous solutions of the dyes were added to the emulsions. 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 and on a wedge spectrograph, processed for 3 minutes in Kodak Developer D-19, fixed in a conventional sodium thiosulfate fixing bath, washed and dried. The spectral sensitivity data obtained are summarized in Table 1.

TABLE 1

Dye number	Type of emulsion	Spectral sensitization	
		λ_{max} , (m μ)	Range (m μ)
1.....	Silver bromiodide....	570	to 640
2.....	do.....	560	to 600
3.....	Silver chlorobromide....	545	to 590
4.....	do.....	615	to 670
6.....	do.....	595	to 650
7.....	do.....	495, 590	to 610
8.....	do.....	490, 590	to 610
9.....	do.....	530	490-560
10.....	Silver bromiodide....	605	to 655
11.....	do.....	600	to 645
12.....	do.....	625	to 675
13.....	do.....	625	to 690
14.....	do.....	550	to 600
15.....	do.....	610	to 650
16.....	Silver chlorobromide....	475	to 530
17.....	do.....	585	to 630
18.....	do.....	545	to 590
20.....	do.....	500	to 535
21.....	do.....	500	to 535

The following example will serve to illustrate the superiority of our dyes over corresponding prior art dyes as to the improved stain level in developed color print material.

EXAMPLE II

Portions of a fine grain silver chlorobromide emulsion containing a magenta-forming pyrazolone coupler of the type described in Bush et al. U.S. Patent 2,908,573, issued Oct. 13, 1959, were sensitized with the indicated representative dyes of our invention and their alkyl substituted analogs (used in equimolar amounts) were coated on a

paper support. Unexposed portions of each coating were processed through the Kodak P-122 Ektacolor Paper process and the stain was read spectrophotometrically as percent reflectance at the wavelength of maximum dye stain. The results are summarized in Table 2.

TABLE 2

	Wavelength (mμ)	Percent reflectance
Dye:		
A.....	530	77.8
No. 22.....	530	81.0
B.....	492	80.7
No. 23.....	492	84.3
C.....	508	82.0
No. 18.....	508	85.2

The dyes identified as A, B and C are the alkyl analogs of Dyes No. 22, 23 and 18, respectively, e.g.:

- A. 5-[(3-ethyl-2-benzothiazolynilidene)ethylidene]-3-ethylrhodanine
- B. 5-[(3-ethyl-2-benzoxazolynilidene)ethylidene]-3-ethylrhodanine
- C. 1,3-diethyl-5-[(3-ethyl-2-benzoxazolynilidene)ethylidene]-2-thiohydantoin.

From these data it can be seen that significant reflectance gains of from 3.2 to 3.6 percent are obtained by sensitizing color print materials with our dyes in place of the alkyl analogs of our dyes. It should be noted that in one of our three color elements the reflectance gain illustrated in this example would be about three times that shown above for a single layer element, i.e., a three color element sensitized with our dyes would have about 9.6 to about 10.8 percent gain in reflectance over an element sensitized with the alkyl analogs of our dyes.

The improved solubility of our dyes is illustrated in the following example.

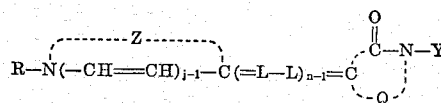
EXAMPLE III

A comparison was made of the solubility of Dyes No. 25, 26, 27 and 28, and their alkyl substituted analogs (i.e., an ethyl group was substituted on the acid nucleus in place of the dialkylaminoalkyl or 4-methyl-1-piperazinyl propyl of our dyes). In each instance a 5 mg. portion of the dye was added to 50 ml. of water containing 5 drops of acetic acid. Our dyes were completely soluble while the corresponding alkyl analogs were either insoluble or only slightly soluble.

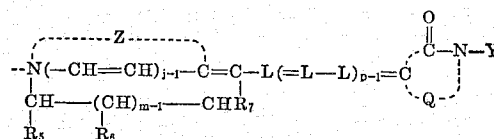
The invention has been described in detail with particular reference to preferred embodiments thereof but it will be understood that variations and modifications can be effected within the spirit and scope of the invention as described hereinabove and as defined in the appended claims.

We claim:

1. In a photographic silver halide emulsion containing a coupler compound, the improvement comprising the use in said emulsion of a merocyanine dye selected from those having the formulas:



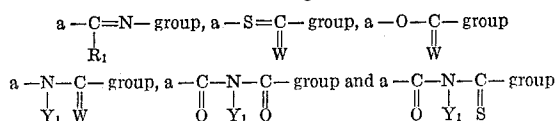
and



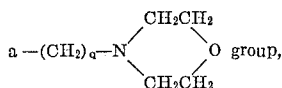
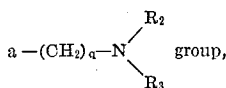
wherein R represents a group selected from the class consisting of an alkyl group and an aryl group; Z represents the nonmetallic atoms required to complete a 5- to 6-membered heterocyclic nucleus; L represents a methine group; j represents an integer of from 1 to 2; n repre-

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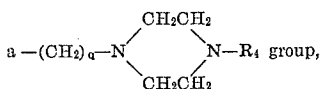
sents an integer of from 1 to 4; Q represents a group selected from the class consisting of



R₁ represents a member selected from the class consisting of the hydrogen atom, an alkyl group, an aryl group, an amino group, a carbonamido group, a sulfonamido group, a sulfamyl group and a carbamyl group; W represents an atom selected from the class consisting of oxygen, selenium, and sulfur; Y and Y₁ each represent a group selected from the class consisting of the hydrogen atom, an alkyl group, an aryl group,

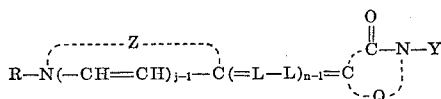


and

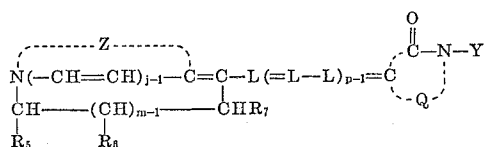


such that at least one of the groups Y and Y₁ contains a group with a tertiary nitrogen atom; q represents an integer of from 2 to 4; R₂, R₃ and R₄ each represents an alkyl group; R₅, R₆, and R₇ each represents a member selected from the class consisting of the hydrogen atom and an alkyl group; m represents an integer of from 1 to 2; and p represents an integer of from 1 to 3.

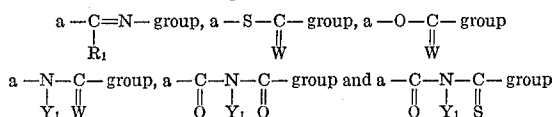
2. In a photographic silver halide emulsion containing a coupler compound, the improvement comprising the use in said emulsion of a merocyanine dye selected from those having the formulas:



and

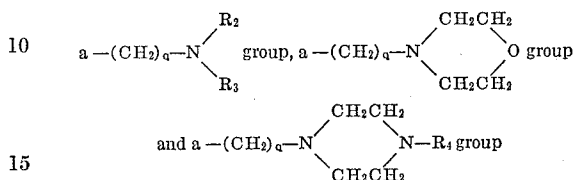


wherein R represents a group selected from the class consisting of an alkyl group and an aryl group; Z represents the nonmetallic atoms required to complete a 5- to 6-membered heterocyclic nucleus selected from the class consisting of a thiazole nucleus, a benzothiazole nucleus, a naphthothiazole nucleus, a thianaphtheno-7',6',4,5-thiazole nucleus, and 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-dialkylindolenine nucleus, an imidazole nucleus, a benzimidazole nucleus, and a naphthimidazole nucleus; L represents a methine group; j represents an integer of from 1 to 2; n represents an integer of from 1 to 4; Q represents a group selected from the class consisting of



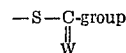
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R₁ represents a member selected from the class consisting of the hydrogen atom, an alkyl group, an aryl group, an amino group, a carbonamido group, a sulfonamido group, a sulfamyl group and a carbamyl group; W represents an atom selected from the class consisting of oxygen, selenium, and sulfur; Y and Y₁ each represent a group selected from the class consisting of the hydrogen atom, an alkyl group, an aryl group,

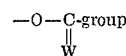


such that at least one of the groups Y and Y₁ contains a group with a tertiary nitrogen atom; q represents an integer of from 2 to 4; R₂, R₃ and R₄ each represents an alkyl group; R₅, R₆ and R₇ each represents a member selected from the class consisting of the hydrogen atom and an alkyl group; m represents an integer of from 1 to 2; and p represents an integer of from 1 to 3.

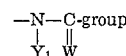
3. An improved silver halide emulsion of claim 2 in which the Q group of the merocyanine dye represents a



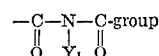
4. An improved silver halide emulsion of claim 2 in which the Q group of the merocyanine dye represents a



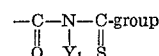
5. An improved silver halide emulsion of claim 2 in which the Q group of the merocyanine dye represents a



6. An improved silver halide emulsion of claim 2 in which the Q group of the merocyanine dye represents a



7. An improved silver halide emulsion of claim 2 in which the Q group of the merocyanine dye represents a



8. An improved silver halide emulsion of claim 2 in which the merocyanine dye is 3-(3-dimethylaminopropyl)-5-[(3-ethyl-2-benzothiazolinyldene)ethylidene]-2-thio-2,4-oxazolidinedione.

9. An improved silver halide emulsion of claim 2 in which the merocyanine dye is 1-(2-diethylaminoethyl)-3-ethyl-5-[(3-ethyl-2-benzoxazolinyldene)ethylidene]-2-thiohydantoin.

10. An improved silver halide emulsion of claim 2 in which the merocyanine dye is 3-(3-dimethylaminopropyl)-5-[(3-ethyl-2-benzothiazolinyldene)ethylidene]rhodanine.

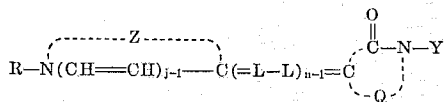
11. An improved silver halide emulsion of claim 2 in which the merocyanine dye is 1-(2-diethylaminoethyl)-5-[(3-ethyl-2-benzothiazolinyldene)ethylidene]-3-methyl-2-thiohydantoin.

12. An improved silver halide emulsion of claim 2 in which the merocyanine dye is 3-(3-diethylaminopropyl)-5-[(3-methyl-2-thiazolidinyldene)ethylidene]rhodanine.

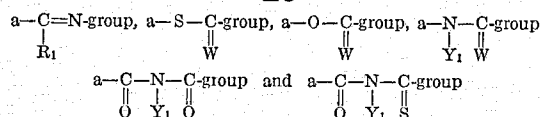
13. An improved silver halide emulsion of claim 2 in which the merocyanine dye is 1-(2-diethylaminoethyl)-5-[(3-ethylnaphtho[2,1-d]oxazoline-2-ylidene)ethylidene]-3-phenyl-2-thiohydantoin.

14. An improved silver halide emulsion of claim 2 in which the merocyanine dye is 1-ethyl-5-[(3-ethyl-2-benzo-

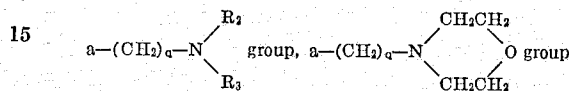
15. In a multilayer color photographic element containing differently sensitized emulsion layers containing color-forming couplers, the improvement comprising the use in at least one of said emulsion layers of a merocyanine dye having the formulas:


$$\begin{array}{c} \text{Z} \\ \text{N}-(\text{CH}=\text{CH})_{j-1}-\text{C}=\text{C}-\text{L}(=\text{L}-\text{L})_{p-1}=\text{C} \begin{array}{l} \text{O} \\ \parallel \\ \text{C}-\text{N}-\text{Y} \\ \text{Q} \end{array} \\ | \qquad \qquad \qquad | \\ \text{CH}-(\text{CH})_{m-1}-\text{CH} \text{R}_7 \\ | \qquad \qquad \qquad | \\ \text{R}_5 \qquad \qquad \text{R}_6 \end{array}$$

20



R₁ represents a member selected from the class consisting of the hydrogen atom, an alkyl group, an aryl group, an amino group, a carbonamido group, a sulfonamido group, a sulfamyl group and a carbamyl group; W represents an atom selected from the class consisting of oxygen, selenium and sulfur; Y and Y₁ each represent a group selected from the class consisting of the hydrogen atom, an alkyl group, an aryl group,


$$20 \quad \begin{array}{c} \text{CH}_2\text{CH}_2 \\ | \quad | \\ \text{a}-(\text{CH}_2)_6-\text{N} \quad \text{N}-\text{R}_1 \text{ group} \\ | \quad | \\ \text{CH}_2\text{CH}_2 \end{array}$$

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_2 , R_3 and R_4 each represents an alkyl group; R_5 , R_6 and R_7 each represents a member selected from the class consisting of the hydrogen atom and an alkyl group; m represents an integer of from 1 to 2; and p represents an integer of from 1 to 3.

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J. TRAVIS BROWN, *Primary Examiner.*