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3,497,502

PHOTOGRAPHIC ELEMENTS CONTAINING A LIGHT SENSITIVE LAYER

Original Filed May 4, 1964

FIG. 1

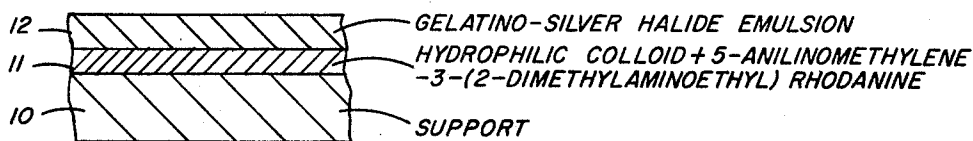


FIG. 2

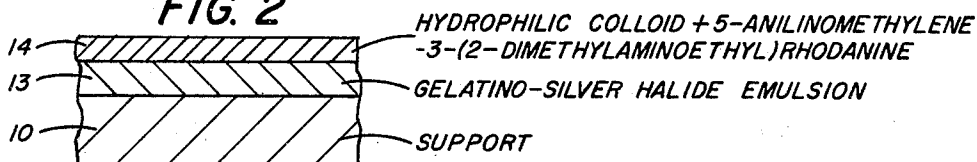
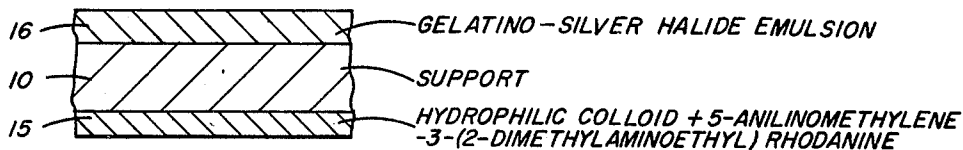


FIG. 3



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PHOTOGRAPHIC ELEMENTS CONTAINING A LIGHT SENSITIVE LAYER

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Original application May 4, 1964, Ser. No. 364,451, now Patent No. 3,352,680, dated Nov. 17, 1967. Divided and this application June 2, 1967, Ser. No. 643,097

Int. Cl. C09b 23/00; G03c 1/10

U.S. Cl. 260-240

10 Claims

ABSTRACT OF THE DISCLOSURE

New photographic elements which have a support, a hydrophilic colloid layer containing light-sensitive silver halide and a hydrophilic layer containing at least one sensitizing and/or filter dye selected from a new class of oxonol, hemioxonol, benzylidene and cinnamylidene dyes containing a secondary amino substituted alkyl group attached to an acidic nucleus in the dye are described.

This application is a division of our copending application Ser. No. 364,451, filed May 4, 1964, now U.S. Patent 3,352,680, granted Nov. 17, 1967.

This invention relates to dyes and more particularly to oxonol, hemioxonol, benzylidene and cinnamylidene dyes containing at least one secondary amino substituted alkyl group attached to the acidic nucleus, and to photographic elements containing said dyes in a hydrophilic colloid layer.

Certain dyes are known to alter the sensitivity of photographic silver halide emulsions.

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.

In order that dyes be useful in photographic elements they should not only either sensitize silver halide to light in the desired range of wavelengths or absorb light in the desired part of the spectrum if the dye is to be used in a light filtering layer, but the dye must be easy to incorporate in the photographic element, be firmly held in the photographic element but completely bleached or removed by the normal processing solutions. Dyes available for use do not always have all these properties in the desired degree. New sensitizing and/or light-filtering dyes are desired for use in photographic elements.

It is therefore an object of our invention to provide a new class of oxonol, hemioxonol, benzylidene and cinnamylidene dyes containing at least one secondary amino substituted alkyl group attached to the acidic nucleus or nuclei in the dye, and which are valuable for use in making photographic elements.

Another object is to provide a synthesis for preparing our new dyes which have desirable sensitizing and/or light absorbing characteristics as well as good solubility in aqueous solutions.

Another object is to provide photographic silver halide emulsions containing our dyes.

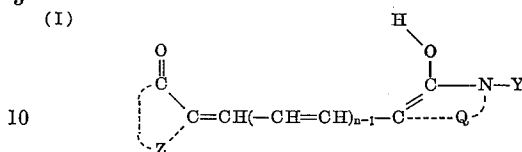
Still another object is to provide photographic elements comprising a support, at least one hydrophilic colloid layer containing light-sensitive silver halide and at least one hydrophilic layer containing at least one of our dyes.

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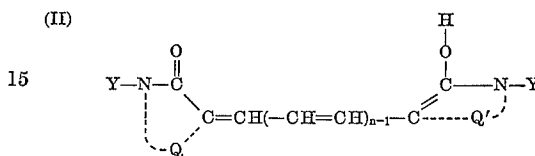
Still other objects will become apparent from a consideration of the following specification and claims.

These and other objects are accomplished according to our invention by providing and using dyes included in the formulas:

(I)

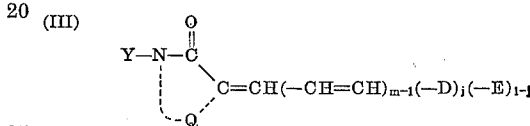


(II)



and

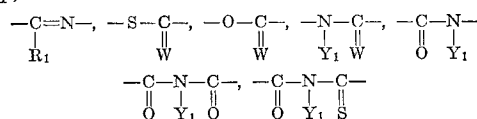
(III)



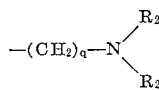
wherein Z represents the nonmetallic atoms required to complete a 5- to 6-membered heterocyclic nucleus such as those of the 2-pyrazolin-5-one series (e.g., 3-methyl-1-phenyl-2-pyrazolin-5-one, 1-phenyl-2-pyrazolin-5-one, 1-(2-benzothiazolyl)-3-methyl-2-pyrazolin-5-one, etc.), those of the 2-isoxazolin-5-one series (e.g., 3-phenyl-2-isoxazolin-5-one, 3-methyl-2-isoxazolin-5-one, etc.), those of the 2-indolinone series (e.g., 1-alkyl-2-indolinone, etc.), those of the barbituric acid and 2-thiobarbituric acid series as well as their 1-alkyl (e.g., 1-methyl, 1-ethyl, 1-propyl, 1-heptyl, etc.), or 1,3-dialkyl (e.g., 1,3-dimethyl, 1,3-diethyl, 1,3-di-n-propyl, 1,3-diisopropyl, 1,3-dicyclohexyl, 1,3-di(β-methoxyethyl), etc.), or 1,3-diaryl (e.g., 1,3-diphenyl, 1,3-di(p-chlorophenyl), 1,3-di(p-ethoxycarbonylphenyl), etc.), or 1-aryl (e.g., 1-phenyl, 1-p-chlorophenyl, 1-p-ethoxycarbonylphenyl, etc.) or 1-alkyl-3-aryl (e.g., 1-ethyl-3-phenyl, 1-n-heptyl-3-phenyl, etc.) derivatives, those of the rhodanine series (i.e., 2-thio-2,4-thiazolidinedione, series), such as rhodanine, 3-alkylrhodanines (e.g., 3-ethylrhodanine, 3-allylrhodanine, etc.) or 3-arylrhodanines (e.g., 3-phenylrhodanine, etc.), those of the 3H-imidazo[1,2-a]pyridin-2-one series, those of the 5,7-dioxo-6,7-dihydro-5H-thiazolo[3,2-a]pyrimidine series (e.g., 5,7-dioxo-3-phenyl-6,7-dihydro-5-thiazolo[3,2-a]pyrimidine, etc.), those of the 2-thio-2,4-oxazolidinedione series (i.e., those of the 2-thio-2,4-(3H,5H)-oxazolidinedione series) e.g., 3-ethyl-2-thio-2,4-oxazolidinedione, etc.), those of the thianaphthenone series (e.g., 3-(2H)-thianaphthenone, etc.), those of the 2-thio-2,5-thiazolidinedione series (i.e., the 2-thio-2,5-(3H,4H)thiazolidinedione series) (e.g., 3-ethyl-2-thio-2,5-thiazolidinedione, etc.), those of the 2,4-thiazolidinedione series (e.g., 2,4-thiazolidinedione, 3-ethyl-2,4-thiazolidinedione, 3-phenyl-2,4-thiazolidinedione, 3-α-naphthyl-2,4-thiazolidinedione, etc.), those of the thiazolidinone series (e.g., 4-thiazolidinone, 3-ethyl-3-thiazolidinone, 3-phenyl-4-thiazolidinone, 3-α-naphthyl-4-thiazolidinone, etc.), those of the thiazolin-4-one series (e.g., 2-ethylthiothiazolin-4-one, 2-alkylphenylaminothiazolin-4-ones, 2-diphenylaminothiazolin-4-one, etc.), those of the 2-imino-2,4-oxazolidinedione (i.e., pseudohydantoin) series, those of the hydantoin series (e.g., hydantoin, 3-ethylhydantoin, 3-phenylhydantoin, 3-α-naphthylhydantoin, 1,3-diethylhydantoin, 1-ethyl-3-phenylhydantoin, 1-ethyl-3-α-naphthylhydantoin, 1,3-diphenylhydantoin, etc.), those of the thiohydantoin series (e.g., 2-thiohydantoin, 3-ethylthiohydantoin, 3-phenyl-2-thiohydantoin, 3-α-naphthyl-2-thiohy-

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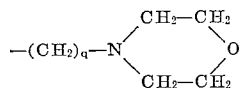
dantoin, 1,3-diethyl-2-thiohydantoin, 1-ethyl-3-phenyl-2-thiohydantoin, 1-ethyl-3- α -naphthyl-2-thiohydantoin, 1,3-diphenyl-2-thiohydantoin, etc.), those of the 2-imidazolin-5-one series (e.g., 2-propylthio-2-imidazolin-5-one, etc.), etc., (especially a heterocyclic nucleus containing 5 atoms in the heterocyclic ring, 3 of said atoms being carbon atoms, 1 of said atoms being a nitrogen atom, and 1 of said atoms being selected from the group consisting of a nitrogen atom, an oxygen atom, a selenium atom and a sulfur atom); n represents an integer of from 1 to 3; Q and Q' each represents the same or different group, such as



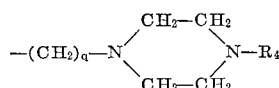
etc.; R_1 represents any of the groups used on the 3-position of 2-pyrazolin-5-ones, e.g., hydrogen, alkyl (e.g., methyl, isopropyl, tertiary butyl, hexyl, etc.), aryl (e.g., phenyl, tolyl, halophenyl, etc.), amino (e.g., methylamino, diethylamino, phenylamino, etc.), carbonamido (e.g., ethylcarbonamido, phenylcarbonamido, etc.), sulfonamido (e.g., butylsulfonamido, phenylsulfonamido, etc.), sulfamoyl (e.g., propylsulfamoyl, phenylsulfamoyl, etc.), carbamoyl (e.g., ethylcarbamoyl, phenylcarbamoyl, etc.); W represents the sulfur atom, the selenium atom or the oxygen atom; Y and Y_1 each represents a group selected from the class consisting of the hydrogen atom, an alkyl group (e.g., methyl, ethyl, butyl, etc.), an aryl group (e.g., phenyl, tolyl, etc.), a



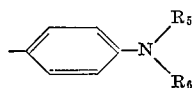
group, a



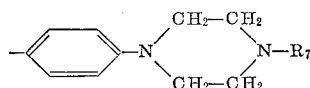
group, and a



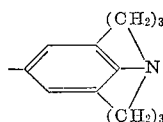
group, such that at least one of the groups Y and Y_1 contains a group with a tertiary nitrogen atom; q represents an integer of from 2 to 4; R_2 , R_3 , and R_4 each represents an alkyl group (e.g., methyl, propyl, butyl, hexyl, etc.); m represents an integer of from 1 to 2; D represents a group selected from the class consisting of a



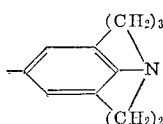
group, a 4-(N-pyrrolidinyl)phenyl group, a 4-(N-morpholino)phenyl group, a 4-(N-piperidino)phenyl group, a



group, the

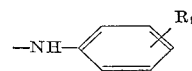


group, the

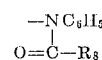


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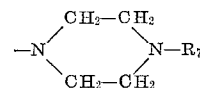
group, etc.; R_5 and R_6 each represents an alkyl group (e.g., methyl, 2-hydroxyethyl, 2-chloroethyl, benzyl, butyl, hexyl, etc.), an aryl group (e.g., phenyl, tolyl, chlorophenyl, etc.), etc.; R_7 represents an alkyl group (e.g., methyl, ethyl, butyl, etc.); E represents a group, such as a



group, a



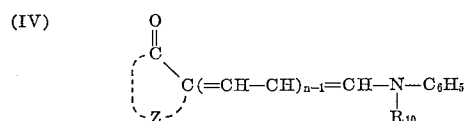
group, a N-pyrrolidinyl group, a N-morpholino group, a N-piperidino group, and a



group; R_8 represents an alkyl group (e.g., methyl, ethyl, butyl, etc.), an aryl group (e.g., phenyl, tolyl, etc.), etc.; R_9 represents a group such as, hydroxyl, halo (e.g., chloro, bromo, etc.), alkyl (e.g., methyl, ethyl, butyl, etc.), alkoxy (e.g., methoxy, propoxy, butoxy, etc.), etc.; and j represents an integer of from 0 to 1.

Our dyes are used to advantage in photographic elements comprising a support, at least one hydrophilic colloid layer containing a light-sensitive silver halide emulsion, and at least one hydrophilic colloid layer containing one or more of our dyes. Certain of our dyes are used to advantage as sensitizers in the colloid layer containing the silver halide emulsion, while our other dyes are used to advantage as light filtering dyes in hydrophilic colloid layers of photographic elements.

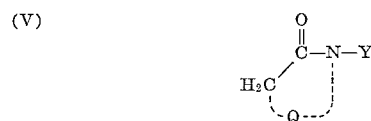
The dyes of Formula I can be prepared to advantage by condensing a compound having the formula:



wherein Z and n are as defined previously and R_{10} represents the hydrogen atom or a



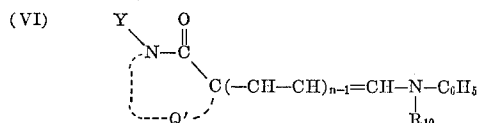
group in which R_{11} represents an alkyl group (e.g., methyl, ethyl, butyl, etc.), with a compound having the formula:



wherein Y and Q are as defined previously. The reaction is carried out advantageously by heating the reactants in an inert solvent in the presence of a basic condensing agent at a temperature between room temperature and the reflux temperature of the reaction mixture. Inert solvents used to advantage include pyridine, ethanol, butanol, dimethylformamide, etc. Basic condensing agents used to advantage include the trialkylamines (e.g., triethylamine, 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 methylate, sodium ethylate, etc.), etc.

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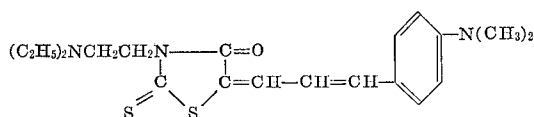
The dyes of Formula II in which Q and Q' are different are prepared advantageously by condensing a compound having the formula:



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DYE 7

3-(2-diethylaminoethyl)-5-p-dimethylamino-cinnamylidenerhodanine



8.8 g. (1 mol.) of 3-(2-diethylaminoethyl)rhodanine and 7.0 g. (1 mol.) of p-dimethylaminocinnamaldehyde were added to 75 ml. of ethanol, 5.6 ml. of triethylamine added, and the solution heated under reflux for 30 minutes. The reaction mixture was filtered and the filtrate chilled. The dye separated and was recrystallized by dissolving in pyridine and precipitating with ethanol. The dye was obtained (yield 4%) as red needles M.P. 157–159° C. with decomposition.

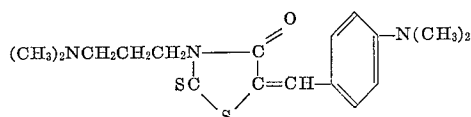
DYE 8

3-(2-dimethylaminoethyl)-5-p-dimethylaminobenzylidenerhodanine

1.50 g. (1 mol.) of 3-(2-dimethylaminoethyl)rhodanine hydroperchlorate and 0.75 g. (1 mol.) of p-dimethylaminobenzaldehyde were added to 7 ml. of acetic acid and 3 ml. of acetic anhydride. The reaction mixture was heated at reflux for 3 minutes, the solution chilled and the dye collected on a filter. The dye was dissolved in ethanol, made basic with piperidine, chilled and collected. The dye was recrystallized from ethanol and obtained (yield 32%) as scarlet needles of M.P. 141–143° with decomposition.

DYE 9

3-(3-dimethylaminopropyl)-5-p-dimethylaminobenzylidenerhodanine

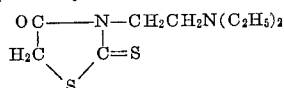


1.60 g. (1 mol.) of 3-(3-dimethylaminopropyl)rhodanine hydroperchlorate and 0.75 g. (1 mol.) of p-dimethylaminobenzaldehyde were added to 7 ml. of acetic acid and 3 ml. of acetic anhydride and the reaction mixture refluxed for 3 minutes. The solution was chilled and the dye collected on a filter. The dye was dissolved in ethanol, made basic with piperidine, chilled and collected. The dye was recrystallized from ethanol and obtained (yield 22%) as light orange crystals of M.P. 136–138° with decomposition.

Intermediates of Formula IV are well known in the art.

The preparation of typical intermediates of Formula V will still further illustrate the preparation of our dyes.

3-(2-diethylaminoethyl)rhodanine

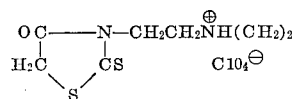


45.2 g. (1 mol.) of bis(carboxymethyl)trithiocarbonate and 23.2 g. (1 mol.) of N,N-diethylethylenediamine were added to 250 ml. of water. 21.2 g. (1 mol.) of sodium carbonate was added to the mixture in small portions with vigorous stirring and the resulting solution was heated on a steam bath for 2 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

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a heavy resinous orange oil (yield 40%) which was used to prepare dye without any further purification.

3-(2-dimethylaminoethyl)rhodanine hydroperchlorate

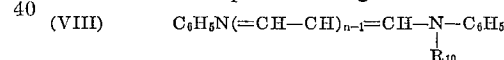


22.6 g. (1 mol.) of bis(carboxymethyl)trithiocarbonate was dissolved in a solution containing 11.1 g. of sodium carbonate and 250 ml. of water. The resulting solution was treated with 13.2 g. (1 mol.+50%) of N,N-dimethylethylenediamine and heated on the steam bath for 1½ hours. The solution was then made strongly acid with concentrated hydrochloric acid and heated on the steam bath for ½ hour. A solution of 18.3 g. of sodium perchlorate in 50 ml. of water was added to the reaction mixture and the solution chilled. The product was collected on a filter and obtained (yield 74%) as pinkish orange crystals of M.P. 166–168° with decomposition.

3-(3-dimethylaminopropyl)rhodanine hydroperchlorate

22.6 g. (1 mol.) of bis(carboxymethyl)trithiocarbonate was dissolved in a solution containing 11.1 g. of sodium carbonate and 150 ml. of water. The resulting solution was treated with 15.3 g. (1 mol.+100%) of N,N-dimethyl-1,3-propanediamine and heated on a steam bath for 1½ hours. The solution was then made strongly acid with concentrated hydrochloric acid, heated on the steam bath for ½ hour and then concentrated to a heavy yellow oil on a rotary evaporator. The oil was redissolved in 50 ml. of water, treated with a solution containing 18.3 g. of sodium perchlorate in 50 ml. of water and chilled. The product was collected on a filter and obtained (yield 81%) as yellow crystals of M.P. 128–130° with decomposition.

Intermediates of Formula VI are advantageously prepared from compounds of Formula V by condensing them with a compound having the formula:



and their hydrochloride salts, wherein R₁₀ is as defined previously. The reaction of a compound of Formula V with diphenylformamidine is advantageously conducted in the presence of a petroleum fraction, e.g., kerosene, while the corresponding reaction with compounds, such as, β-anilinoacrolein anil or glutaric aldehyde or their hydrochlorides (or other salts) are advantageously conducted by heating in the presence of a strong tertiary organic base, such as, have been described herein previously.

In the preparation of photographic emulsions, the new dyes of the invention are advantageously incorporated in the finished silver halide emulsion and should be uniformly distributed throughout the emulsion. The methods for incorporating dyes in emulsions are relatively simple and well known in the art of emulsion making. For example, it is convenient to add the dyes from aqueous solution preferably in the presence of an equivalent of an acid, such as, acetic acid. Methanol, ethanol, isopropanol and other solvents having no deleterious effect on the ultimate light-sensitive materials may also be used but are not usually needed.

Our dyes are used advantageously to sensitize silver halides, e.g., silver chloride, silver bromide, silver iodide, silver chlorobromide, silver bromiodide, silver chlorobromiodide, etc. The silver halide may be deposited as a film by evaporation under vacuum and then coated with a protective hydrophilic colloid layer or dispersed in a hydrophilic colloid. Hydrophilic colloids used to advantage include natural materials, e.g., gelatin, albumin, agar-agar, gum arabic, alginic acid, etc., and synthetic hydrophilic resins, e.g., polyvinyl alcohol, polyvinyl pyrrolidone, cellulose ethers, partially hydrolyzed cellulose

acetate, etc. Certain of our dyes are also used to advantage in filter layers in which any of the hydrophilic colloids listed can be used as the carrier.

Our dyes are used over a wide range of concentrations in hydrophilic colloid layers with or without silver halide. The optimum concentrations will depend upon the particular photographic element and the effect desired, and can be determined readily by methods well known in the art.

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

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, allylthiocyanate, cystine, etc.), various gold compounds (e.g., potassium chloroaurate, 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 Aug. 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.

The following examples will still further illustrate our invention.

EXAMPLE 1

Portions of a gelatino-silver chlorobromide emulsion containing 40 mole percent bromide of the type described by Trivelli and Smith, Photo. Journal, 79, 330 (1939) were sensitized with representative dyes indicated in Table 1. 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 No.	Spectral sensitization	
	λ_{Max} (m μ)	Range (m μ)
1-----	605	to 710
2-----	605	470 to 630
3-----	610	470 to 635
7-----	520	to 710
9-----	565	to 600

Similarly it can be shown that still other dyes of our invention can be used to advantage for spectrally sensitizing other silver halide emulsions.

The following example will illustrate the use of representative hemioxonol dyes as filter dyes.

EXAMPLE II

Coatings were made of portions of a gelatin solution containing the indicated amount of representative hemi-

oxonol dyes on pieces of glass plate. After drying, absorption measurements were made and listed in Table 2.

TABLE 2

Dye No.	Concentration of dye, mg./ft. ²	D _{max}	Wavelength, m μ
4-----	19.2	2.56	412
5-----	18.3	1.37	387
6-----	18.8	2.11	395

The dyes in each of the coatings were bleached effectively in an alkaline developer solution, such as Kodak Developer D-19.

Similarly it can be shown that other dyes of our invention can be used to advantage in bleachable light filter layers for photographic elements. These and other dyes of our invention are valuable for use in light filtering layers because of the ease with which they can be incorporated during manufacture of the photographic element and the ease with which they are removed from the element during photographic development.

The accompanying drawings FIGS. 1, 2 and 3 illustrate enlarged cross sectional views of photographic elements containing our filter layers.

FIG. 1 shows support 10 coated with filter layer 11 comprising a hydrophilic colloid and our dye 5-anilino-methylene-3-(2-dimethylaminoethyl)rhodanine, over which is coated gelatin silver halide layer 12.

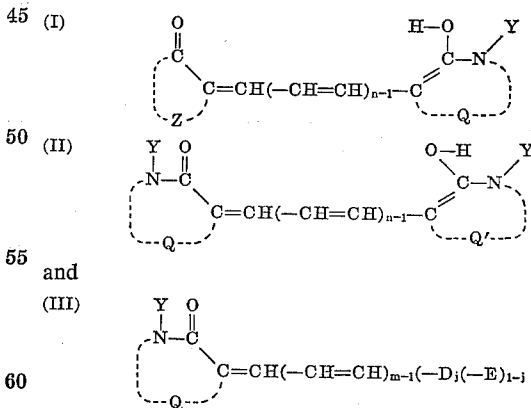
FIG. 2 shows support 10 coated with gelatino-silver halide layer 13 over which is coated filter layer 14 comprising a hydrophilic colloid and 5-anilino-methylene-3-(2-dimethylaminoethyl)rhodanine.

FIG. 3 shows support 10 coated on one side with anti-halation backing layer 15 comprising a hydrophilic colloid and 5-anilino-methylene-3-(2-dimethylaminoethyl)rhodanine, and coated on the other side with gelatino-silver halide emulsion layer 16.

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 of the invention as described hereinabove.

We claim:

1. A dye selected from those having the formulas:



wherein Z represents the nonmetallic atoms required to complete a 5- to 6-membered heterocyclic nucleus selected from the class consisting of a 2-pyrazolin-5-one nucleus, a 2-isoxazolin-5-one nucleus, a 2-indolinone nucleus, a barbituric acid nucleus, a thiobarbituric acid nucleus, a rhodanine nucleus, a 3H-imidazo-[1,2-a]pyridin-2-one nucleus, a 5,7-dioxo-6,7-dihydro-5H-thiazolo-[3,2-a]pyrimidine nucleus, a 2-thio-2,4-oxazolidinedione nucleus, a thianaphthenone nucleus, a 2-thio-2,5-thiazolidinedione nucleus, a 2,4-thiazolidinedione nucleus, a thiazolidinone nucleus, a thiazolin-4-one nucleus, a 2-imino-2,4-oxazolidinedione nucleus, a hydantoin nucleus, a thiohydantoin nucleus, and a 2-imidazolin-5-one nucleus; n represents an

11

integer of from 1 to 3; Q and Q' each represent a group selected from the class consisting of a



group,

a



group,

a



group,

a



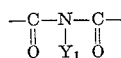
group,

a

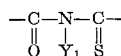


group,

a

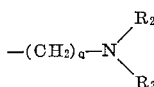


group and a

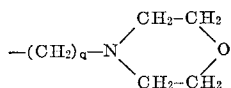


group;

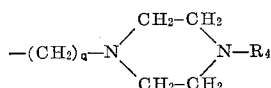
R₁ represents a group selected from the class consisting of the hydrogen atom, an alkyl group, an aryl group, an amino group, a carbonamido group, a sulfonamido group, a sulfamoyl group, and a carbamoyl group; W represents an atom selected from the class consisting of sulfur, selenium, and oxygen; Y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



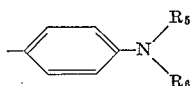
group, a



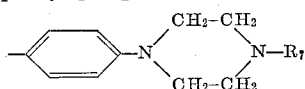
group, and a



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; m represents an integer of from 1 to 2; D represents a group selected from the class consisting of a

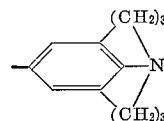


group, the 4-(N-pyrrolidinyl)phenyl group, the 4-(N-morpholino) phenyl group, a



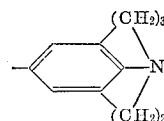
12

group, the



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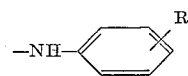
group and the



10

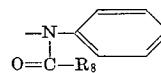
group; R₅ and R₆ each represent a group selected from the class consisting of an alkyl group and an aryl group; R₇ represents an alkyl group; j represents an integer of from 0 to 1; E represents a member selected from the class consisting of a

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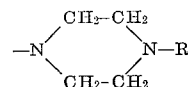
group, a

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group, the N-pyrrolidinyl group, the N-morpholino group and a

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group; R₉ represents a member selected from the class consisting of the hydroxyl group, a halogen atom, an alkoxy group and an alkyl group; and R₈ represents a group selected from the class consisting of an alkyl group, and an aryl group.

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2. A dye of claim 1 having Formula I.
3. A dye of claim 1 having Formula II.
4. A dye of claim 1 having Formula III.
5. The dye compound bis[3-(2-diethylaminoethyl)-5-rhodanine]-trimethineoxonol.
6. The dye compound bis[3-(2-dimethylaminoethyl)-5-rhodanine]-methineoxonol hydroperchlorate.
7. The dye compound 3-(2-diethylaminoethyl)-5-p-dimethylaminocinnamylidenerhodanine.
8. The dye compound 3-(3-dimethylaminopropyl)-5-p-dimethylaminobenzylidenerhodanine.
9. The dye compound 5-anilinomethylene-3-(2-dimethylaminoethyl)-rhodanine.
10. The dye compound 3-(2-dimethylaminoethyl)-5-piperidinomethylenerrhodanine.

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JOHN D. RANDOLPH, Primary Examiner

U.S. Cl. X.R.

70 96—84, 106; 260—240.2, 240.3, 240.9, 306.7, 566