Jan. 9, 1940. L. G. S. BROOKER 2,186,624

MEROTRICARBOCYANINE DYE AND PHOTOGRAPHIC EMULSION

Filed April 26, 1937

Fig. 1. 3-ethyl-5-[(2-ethyl-1(2)-benzothiazylidene) hexadienylidene]-2-thio-2, 4-oxazoledione.

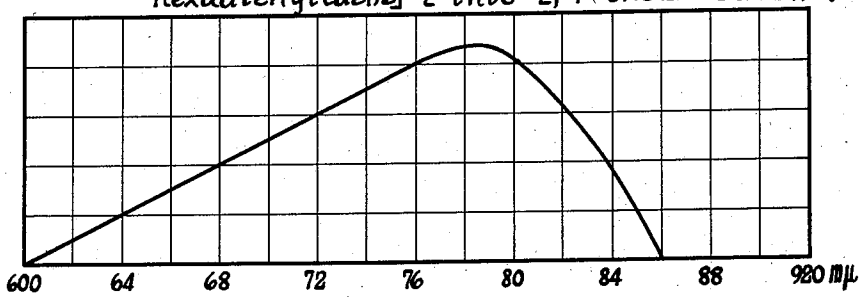


Fig. 2. 3-ethyl-5-[(3-ethyl-4-phenyl-2(3)-thiazylidene hexadienylidene]-rhodanine.

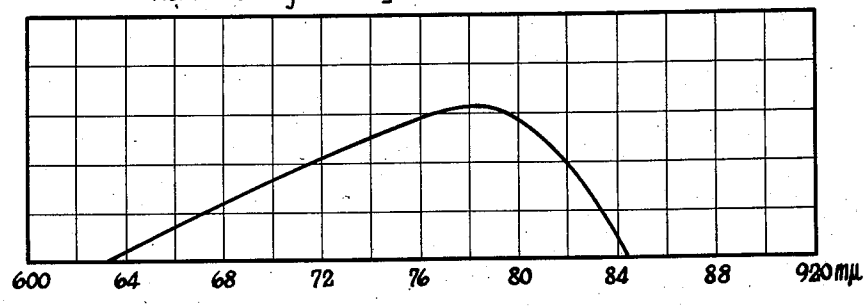
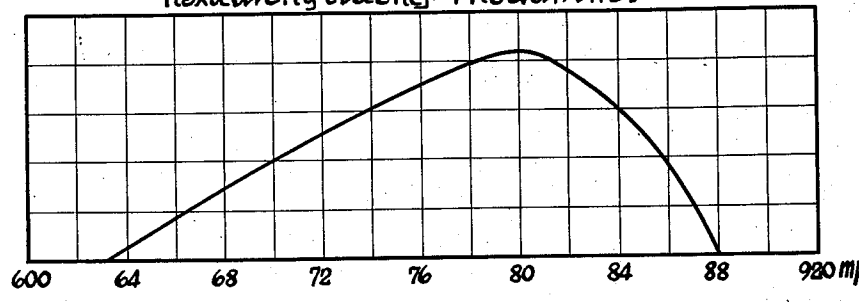


Fig. 3. 3-ethyl-5-[(2-ethyl-1(2)-benzoselenazylidene) hexadienylidene]-rhodanine.



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Patented Jan. 9, 1940

2,186,624

UNITED STATES PATENT OFFICE

2,186,624

MEROTRICARBOCYANINE DYE AND PHOTOGRAPHIC EMULSION

Leslie G. S. Brooker, Rochester, N. Y., assignor to Eastman Kodak Company, Rochester, N. Y., a corporation of New Jersey

Application April 26, 1937, Serial No. 138,953

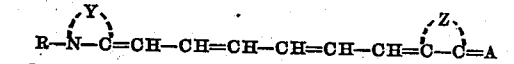
9 Claims. (Cl. 95—7)

This invention relates to merotricarbocyanine dyes and photographic emulsions containing the same.

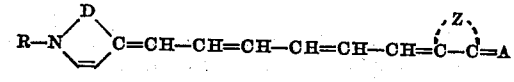
The application is a continuation-in-part of my copending application Serial No. 752,036, filed November 8, 1934, (United States Patent No. 2,078,233, dated April 27, 1937) which is in turn a continuation-in-part of my copending application Serial No. 739,502, filed August 11, 1934.

An object of my invention is to provide new dyes which can be called merotricarbocyanine dyes. A further object is to provide a process for the preparation of such dyes. A still further object is to provide photographic emulsions containing such dyes. A still further object is to provide photographic emulsions sensitized for the far-red and infra-red region of the spectrum. Other more specific objects will be apparent hereinafter from the specification and claims.

My new dyes can be represented by the following general formulas:



and



wherein A represents a divalent atom of the oxygen group, such as oxygen or sulfur, for example, D represents a vinylene or phenylene group, R represents an alkyl group, Y represents the non-metallic atoms necessary to complete a heterocyclic nucleus and Z represents the non-metallic atoms necessary to complete a heterocyclic nucleus.

More specifically, in the above formulas, R can represent an alkyl group, such as methyl, ethyl, n-butyl, isoamyl or allyl for example, Y can represent the non-metallic atoms necessary to complete a five-membered heterocyclic nucleus, such as one of the thiazole series, for example 4-methylthiazole, 4-phenylthiazole, 4,5-diphenylthiazole, benzothiazole, 5-chlorobenzothiazole or naphthothiazoles, or one of the oxazole series, for example 4-methyloxazole, 4-phenyloxazole, benzoxazole, or naphthoxazoles, or one of the selenazole series, for example 4-methylselenazole, 4-phenylselenazole or benzoselenazole, or one of the indolenine series, for example 3,3-dialkylindoline, or a thiazoline nucleus, or a selenazoline nucleus for example. Y can also represent the non-metallic atoms necessary to complete a six-membered heterocyclic nucleus, such as one of the pyridine series or one of the quinoline series, for example 5-methylquinoline or 5,6-benzoquinoline. Z can represent the non-metallic atoms necessary to complete a five-membered heterocyclic nucleus, particularly a five-membered heterocyclic nucleus containing a nuclear nitrogen and nuclear sulfur atom as in the case of a rhodanine nucleus, for example. Z can represent the non-metallic atoms necessary to complete an oxazoledione nucleus, for example a 3-alkyl-2-thio-2,4-oxazoledione nucleus or a 1-alkyl oxindole nucleus, such as 1-ethyloxindole or 1-ethyl-2-thio-oxindole or like five-membered or six-membered heterocyclic nuclei.

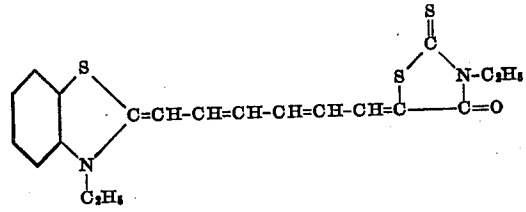
My new dyes can be prepared by reacting a cyclammonium quaternary salt containing an acylanilino-$\Delta^{1,3,5}$-hexatrienyl group in the alpha or gamma position, i. e. one of the so-called reactive positions, with a heterocyclic compound containing a nuclear reactive methylene group adjacent to a nuclear carbonyl group, such as a nuclear oxocarbonyl (commonly called merely carbonyl) or a nuclear thiocarbonyl group. The reactions are advantageously carried out in the presence of a diluent which allows of a homogeneous reaction mixture and from which the dye will separate at least upon chilling. Lower aliphatic alcohols, i. e. alcohols of one to four carbon atoms, are suitable. The reactions are further advantageously carried out in the presence of a basic condensing agent. The quantity of condensing agent is advantageously sufficient to bind the elements of acid eliminated from the reacting molecules. Sodium hydroxide, sodium ethylate or potassium acetate can be employed for example. However, the condensing agent is advantageously a strong organic base, i. e. one having a dissociation constant substantially greater than that of pyridine. Trialkylamines, such as triethylamine or triethanolamine, dibutylamine, N-methylpiperidine, piperidine and diethylamine are suitable, for example. Heat accelerates the formation of my new dyes.

My new dyes can also be prepared by reacting an acylated condensation product of a heterocyclic compound containing a reactive nuclear methylene group adjacent to a nuclear carbonyl group with a glutaconic aldehyde dianilide salt with a cyclammonium quaternary salt having a reactive alkyl group in the alpha or gamma position. The diluents and condensing agents mentioned above are advantageously employed as above. This second stated method is advan-

tageously employed in preparing certain of my new dyes, for example those containing a quinoline nucleus linked through its 4-position or those dyes containing a 4-methylthiazole or 4-phenylthiazole nucleus or a benzoselenazole nucleus.

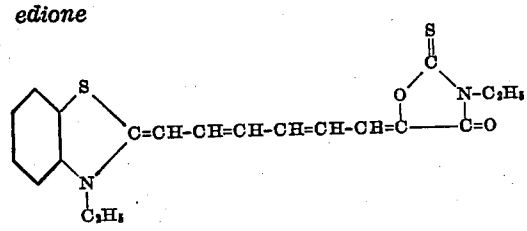
While the process of preparing my new dyes is subject to variation, particularly with respect to the natures and proportions of the reactants, the nature and proportion of the condensing agent, the nature and quantity of the diluent, the temperature, the time of reaction and the method of isolation and purification of the dyes, the following examples will serve to teach those skilled in the art the manner of obtaining my new dyes.

EXAMPLE 1.—*3-ethyl-5-[(2-ethyl-1(2)-benzothiazylidene) hexadienylidene]-rhodanine*



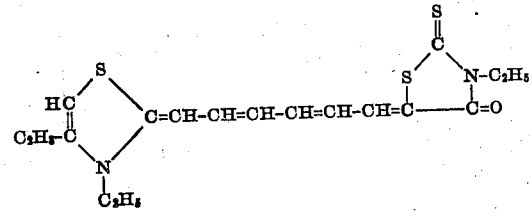
1.25 g. (1 mol.) of 1-(6-acetanilido-$\Delta^{1,3,5}$-hexatrienyl)-benzothiazole ethiodide and 0.4 g. (1 mol.) of 3-ethylrhodanine were refluxed in 10 cc. of absolute ethyl alcohol containing 0.25 g. (1 mol.) of triethylamine for about 15 minutes. The dye separated from the chilled reaction mixture. It was filtered and washed well with methyl alcohol. It was recrystallized from glacial acetic acid and then from 95% ethyl alcohol and obtained as minute green crystals melting at 231° to 233° C. with decomposition. Its ethyl alcoholic solution was blue.

EXAMPLE 2.—*3-ethyl-5-[(2-ethyl-1(2)-benzothiazylidene) hexadienylidene]-2-thio-2,4-oxazoledione*



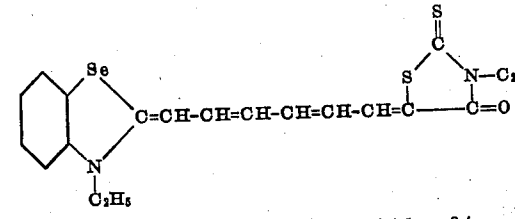
1.25 g. (1 mol.) of 1-(6-acetanilido-$\Delta^{1,3,5}$-hexatrienyl)-benzothiazole ethiodide and 0.75 g. of 3-ethyl-2-thio-2,4-oxazoledione were refluxed in about 10 cc. of absolute ethyl alcohol containing 0.2 g. (1 mol.) of piperidine for about 10 minutes. The dye separated from the chilled reaction mixture. It was washed well with methyl alcohol. It was recrystallized first from methyl alcohol and then from 95% ethyl alcohol and obtained as minute green crystals having a silvery reflex and melting at 214° to 216° C. with decomposition. Its ethyl alcoholic solution was blue.

EXAMPLE 3.—*3-ethyl-5-[(3-ethyl-4-phenyl-2(3)-thiazylidene)-hexadienylidene] rhodanine*



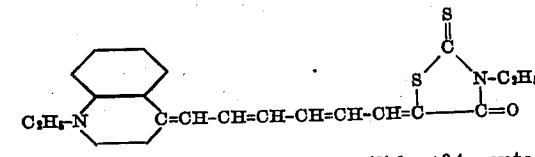
0.9 g. (1 mol.) of 5-(5-acetanilido-$\Delta^{2,4}$-pentadienylidene)-3-ethylrhodanine and 1.6 g. (2 mol.) of 2-methyl-4-phenylthiazole ethiodide were refluxed in 20 cc. of absolute ethyl alcohol containing 1.0 g. (1 mol.+300% excess) of triethylamine for about 30 minutes. The dye separated from the chilled reaction mixture. It was filtered and washed well with methyl alcohol. It was twice recrystallized from a mixture of methyl alcohol and pyridine and obtained as green crystals, melting at 206° to 209° C. with decomposition. Its methyl alcohol-pyridine solution was blue.

EXAMPLE 4.—*3-ethyl-5-[(2-ethyl-1(2)-benzoselenazylidene) hexadienylidene]-rhodanine*



0.9 g. (1 mol.) of 5-(5-acetanilido-$\Delta^{2,4}$-pentadienylidene)-3-ethylrhodanine and 1.8 g. (2 mol.) of 1-methylbenzoselenazole ethiodide were refluxed in 20 cc. of absolute ethyl alcohol containing 1.0 g. (1 mol.+300% excess) for about 15 minutes. The dye separated from the cooled reaction mixture. It was filtered and washed well with methyl alcohol. It was recrystallized from a mixture of methyl alcohol and pyridine and then from pyridine and obtained as green crystals, melting at 242° to 245° C. with decomposition. Its pyridine solution was deep blue.

EXAMPLE 5.—*3-ethyl-5-[(1-ethyl-1(4)-quinolylidene) hexadienylidene]-rhodanine*



0.9 g. (1 mol.) of 5-(5-acetanilido-$\Delta^{2,4}$-pentadienylidene)-3-ethylrhodanine and 1.5 g. (2 mol.) of lepidine ethiodide were refluxed in about 20 cc. of absolute ethyl alcohol containing 1.0 g. (1 mol.+300% excess) of triethylamine for about 15 minutes. The dye separated from the chilled reaction mixture. It was filtered and washed well with methyl alcohol. It was twice recrystallized from a mixture of methyl alcohol and pyridine and obtained as green crystals, melting at 198° to 200° C. with decomposition. Its methyl alcohol-pyridine solution was blue.

Instead of 3-ethylrhodanine, unsubstituted rhodanine, 3-phenylrhodanine, 3-carbethoxymethylrhodanine, 3-(p-aminophenyl)-rhodanine, 1-ethyl-oxindole, 1-ethyl-2-thio-oxindole, 3-alkyl-2-thio-2,4-oxazoledione or like five-membered or six-membered heterocyclic compounds can be employed, e. g. thiobarbituric acid.

In the above last three examples, the excess of basic condensing agent is advantageous, giving rise to a higher yield of the dye. Likewise the excess of cyclammonium quaternary salt is advantageous in order to secure better yields. The cyclammonium quaternary salt is advantageously an alkiodide though other quaternary salts can be employed, e. g. alkylsulfates or p-toluenesulfonates.

The cyclammonium quaternary salts contain-

ing a 6-acylanilido-$\Delta^{1,3,5}$-hexatrienyl group in a reactive position can be prepared from cyclammonium quaternary salts containing a reactive alkyl group in a reactive position and a glutaconic aldehyde dianilide salt by heating the materials together in an organic acid anhydride, advantageously acetic anhyride. The following procedure is illustrative:

5.8 g. (1 mol.) of 1-methylbenzoxazole ethiodide or 6.1 g. (1 mol.) of 1-methylbenzothiazole ethiodide and 5.5 g. (1 mol.) of glutaconic aldehyde dianilide hydrochloride were heated in about 25 cc. of acetic anhydride for from 5 to 10 minutes. The reaction mixture was chilled and the hexatrienyl compound precipitated by adding diethyl ether. The precipitated product was stirred with acetone, filtered and finally washed with acetone.

Cyclammonium alkyl halides, particularly alkiodides, are advantageously employed though other quaternary salts can be employed, for example the alkyl sulfates or toluenesulfonates.

The acylanilido-$\Delta^{2,4}$-pentadienylidene compounds can be prepared by reacting a glutaconic aldehyde dianilide salt with a compound containing a nuclear reactive methylene group adjacent to a nuclear carbonyl or thiocarbonyl group by heating the materials in the presence of a basic condensing agent advantageously employing a diluent, such as a lower aliphatic alcohol. The condensation product so obtained is then acylated. The following procedure is illustrative:

6.4 g. (1 mol.) of 3-ethylrhodanine, 11.2 g. (1 mol.) of glutaconic aldehyde dianilide hydrochloride, 50 cc. of absolute ethyl alcohol and 4 g. (1 mol.) of triethylamine were refluxed for from 3 to 5 minutes. The reaction product separated from the chilled reaction mixture. It was filtered off and dried. The dried reaction product was placed in 150 cc. of acetic anhydride and the mixture heated to boiling and then quickly chilled. The acylated compound separated. It was filtered off and dried. Strong organic bases, particularly triethylamine are advantageously employed in preparing these intermediates.

My new dyes, particularly those containing a rhodanine nucleus, sensitize photographic emulsions for the far-red and infra-red regions of the spectrum in a novel and useful manner. My invention is particularly directed to the customarily employed silver halide emulsions, especially the silver chloride and bromide emulsions, which can contain other salts which may be light-sensitive. My invention is further particularly directed to the customarily employed gelatin emulsions. However, the gelatin can be replaced with any other carrier which has substantially no deleterious effect on the light-sensitive materials, e. g. a cellulose derivative or a resin.

In the preparation of photographic emulsions sensitized with my new dyes, it is only necessary to thoroughly disperse a small amount of the dyes in an ordinary photographic emulsion. The suitable and most economical concentration for any given emulsion will be apparent to those skilled in the art, upon making the ordinary tests and observations customarily used in the art of emulsion making. To prepare a gelatino-silver-halide emulsion the following procedure is satisfactory: A quantity of the dye is dissolved in a suitable solvent, for example methyl alcohol, ethyl alcohol or pyridine, and a volume of this solution (which may be diluted with water) containing from ⅕ to 5 mg. of dye is slowly added to about 1000 cc. of an ordinary flowable gelatino-silver-halide emulsion, with stirring. The dye is thoroughly incorporated. With the more powerful of my new sensitizing dyes 1 mg. of dye per 1000 cc. of emulsion will suffice to produce maximum sensitizing effects with the ordinary gelatino-silver-halide emulsions.

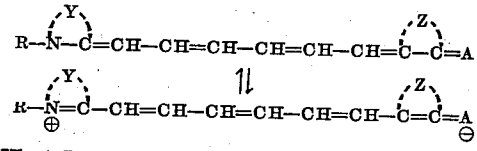
The above statements are only illustrative and are not to be understood as limiting my invention in any sense, as it will be apparent that these dyes can be incorporated by other methods in many of the photographic emulsions customarily employed in the art, such, for instance, as by bathing a plate or film, upon which an emulsion has been coated, in a solution of the dye in an appropriate solvent, although such a method is ordinarily not to be preferred. The claims are intended to cover any combination of these new dyes with a photographic emulsion, whereby the dye exerts a sensitizing effect upon the emulsion as well as a photographic element comprising a support, ordinarily transparent, upon which the light-sensitive emulsion is coated or spread and permitted to set or dry.

The accompanying drawing is by way of illustration. Each figure is a diagrammatic reproduction of a spectrogram showing the sensitivity of an ordinary gelatino-silver-bromide emulsion containing one of my new dyes. In Fig. 1, the curve represents the sensitivity of an ordinary gelatino-silver-bromide emulsion containing 3-ethyl-5-[(2-ethyl-1(2)-benzothiazylidene) hexadienylidene]-2-thio-2,4-oxazoledione. In Fig. 2, the curve represents the sensitivity of an ordinary gelatino-silver-bromide emulsion containing 3-ethyl-5-[(3-ethyl-4-phenyl-2(3)-thiazylidene) hexadienylidene]-rhodanine. In Fig. 3, the curve represents the sensitivity of an ordinary gelatino-silver-bromide emulsion containing 3-ethyl-5-[(2-ethyl-1(2)-benzoselenazylidene) hexadienylidene]-rhodanine.

Still further illustrations of my new emulsions sensitized for the infra-red could be given, but the foregoing will suffice to teach those skilled in the art the principles of sensitizing photographic emulsions for the far-red and infra-red with my new dyes.

My new dyes can be employed in the construction of light filters.

My new dyes can probably exist in two forms, illustrated as follows:



What I claim as my invention and desire to be secured by Letters Patent of the United States is:

1. A photographic silver halide emulsion containing a sensitizing merotricarbocyanine dye.

2. A photographic gelatino-silver-halide emulsion containing a sensitizing merotricarbocyanine dye.

3. A photographic gelatino-silver-halide emulsion sensitized with a 3-alkyl-5-[(2-alkyl-1(2)-benzothiazylidene) hexadienylidene]-rhodanine.

4. A photographic gelatino-silver-halide emulsion sensitized with 3-ethyl-5-[(2-ethyl-1-(2)-benzothiazylidene) hexadienylidene]-rhodanine.

5. A photographic gelatino-silver-halide emulsion sensitized with a 3-alkyl-5-[(2-alkyl-1(2)-benzoxazylidene) hexadienylidene]-rhodanine.

6. A photographic gelatino-silver-halide emul-

sion sensitized with 3-ethyl-5-[(2-ethyl-1(2)-benzoxazylidene) hexadienylidene]-rhodanine.

7. A photographic gelatino-silver-halide emulsion sensitized with a 3-alkyl-5-[(2-alkyl-1(2)-benzothiazylidene) hexadienylidene]-2-thio-2,4-oxazoledione.

8. A photographic gelatino-silver-halide emulsion sensitized with a 3-ethyl-5-[(2-ethyl-1(2)-benzothiazylidene) hexadienylidene]-2-thio-2,4-oxazoledione.

9. A photographic element comprising a support coated with a photographic gelatino-silver-halide emulsion containing a sensitizing merotricarbocyanine dye.

LESLIE G. S. BROOKER.