United States Patent Office

3,515,722

Patented June 2, 1970

3,515,722

CYANINE DYES

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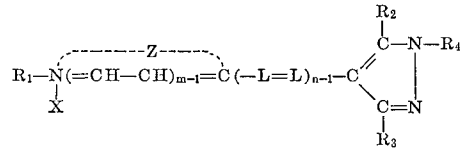
No Drawing. Filed Dec. 23, 1966, Ser. No. 604,161
Int. Cl. C09b 23/00
U.S. Cl. 260—240 11 Claims

ABSTRACT OF THE DISCLOSURE

Cyanine dyes are provided which have the following general formula:



wherein *m* represents a positive integer of from 1 to 2; *n* represents a positive integer of from 2 to 3; L represents a methine linkage; R_1 represents a member selected from the group consisting of an alkyl group of from 1 to 4 carbon atoms, an alkenyl group, and a phenyl group; R_2 and R_3 each represents a member selected from the group consisting of a hydrogen atom, an alkyl group of from 1 to 4 carbon atoms and a phenyl group; R_4 represents a member selected from the group consisting of an alkyl group of from 1 to 4 carbon atoms and a phenyl group; X represents an acid anion; and, Z represents the non-metallic atoms necessary to complete a desensitizing heterocyclic nucleus containing 5 to 6 atoms in the heterocyclic ring, said desensitizing nucleus being selected from the group consisting of nitrobenzothiazole, nitrobenzoselenazole, imidazo[4,5-b]quinoxaline, 3,3-dialkyl-3H-pyrrolo[2,3-b]pyridine, 3,3-dialkyl-3H-dialkyl-3H-nitroindole, thiazolo[4,5-b]quinoline, nitroquinoline, nitrothiazole, nitronaphthothiazole, nitrooxazole, nitronaphthoxazole, nitroselenazole, nitronaphthoselenazole and nitropyridine nuclei. The dyes of this invention are electron acceptors and spectral sensitizers for fogged direct positive silver halide emulsions.

This invention relates to novel photographic materials, and more particularly to a new class of cyanine dyes containing a 4-pyrazolyl nucleus that are especially useful as electron acceptors and spectral sensitizers for direct positive photographic silver halide emulsions, and to means for the preparation of such new dyes.

It is known that direct positive images can be obtained with certain types of photographic silver halide emulsions. For example, photographic emulsions have been proposed for this purpose comprising an electron acceptor and silver halide grains that have been fogged with a combination of a reducing agent and a compound of a metal more electropositive than silver. One of the advantages of such direct positive emulsions is that the highlight areas of the images obtained with these materials are substantially free from fog. However, known materials of this type have not exhibited the high speed required for many applications of photography. Also, such known materials have not shown the desired selective sensitivity, especially to radiation in the green to red region of the spectrum. It is evident, therefore, that there is need in the art for improved direct positive photographic materials having both good speed and desirable sensitivity to longer wavelength radiations.

I have now found that certain cyanine dyes containing certain pyrazole nuclei are outstanding electron acceptors

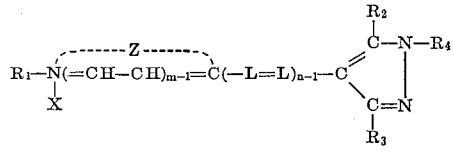
and spectral sensitizers in direct positive type photographic silver halide emulsions. They provide superior reversal systems, especially with fogged silver halide emulsions that are characterized by both good speed and desired sensitivity to radiation in the green to red region of the spectrum with maximum sensitivity occurring in most cases in the region of about 460–550 mμ. The images produced with these new direct positive photographic emulsions are clear and sharp.

It is, accordingly, an object of this invention to provide a new class of cyanine dyes that function as electron acceptors and spectral sensitizers for photographic silver halide emulsions, and more particularly for direct positive photographic emulsions, such as fogged, direct positive emulsions. Another object is to provide means for preparing the new cyanine dyes of this invention. Other objects of this invention will be apparent from this disclosure and the appended claims.

The new class of cyanine dyes of the invention include those comprising first and second 5- to 6-membered nitrogen heterocyclic nuclei joined by methine linkage; the first of said nuclei being a pyrazole nucleus joined, by the 4-carbon atom thereof, to the methine linkage, said second nucleus being a desensitizing quaternary salt nucleus joined by a carbon atom thereof to the methine linkage; and, said methine linkage being selected from the group consisting of a dimethine linkage and a tetramethine linkage.

One highly useful class of the novel cyanine dye compounds of the invention include those represented by the following general formula:

I.



wherein *m* represents a positive integer of from 1 to 2; *n* represents a positive integer of from 2 to 3; L represents a methine linkage, e.g., —CH=, —C(CH_3)=, —C(C_6H_5)=, etc.; R_1 represents an alkyl group, including substituted alkyl (preferably a lower alkyl containing from 1 to 4 carbon atoms), e.g., methyl, ethyl, propyl, isopropyl, butyl, hexyl, cyclohexyl, decyl, dodecyl, etc., or a substituted alkyl group (preferably a substituted lower alkyl containing from 1 to 4 carbon atoms), such as a hydroxyalkyl group, e.g., β-hydroxyethyl, ω-hydroxybutyl, etc., an alkoxyalkyl group, e.g., β-methoxyethyl, ω-butoxybutyl, etc., a carboxyalkyl group, e.g., β-carboxyethyl, ω-carboxybutyl, etc., a sulfoalkyl group, e.g., β-sulfoethyl, ω-sulfobutyl, etc., a sulfatoalkyl group, e.g., β-sulfatoethyl, ω-sulfatobutyl, etc., an acryloxyalkyl group, e.g., β-acetoxyethyl, γ-acetoxypropyl, ω-butyryloxybutyl, etc., an alkoxycarbonylalkyl group, e.g., β-methoxycarbonylethyl, ω-ethoxycarbonylbutyl, etc., or an aralkyl group, e.g., benzyl, phenethyl, etc., and the like, or an alkenyl group, e.g., allyl, 1-propenyl, 2-butenyl, etc., or an aryl group, e.g., phenyl, tolyl, naphthyl, methoxyphenyl, chlorophenyl, etc.; R_2 and R_3 each represents a hydrogen atom, or an alkyl group (preferably a lower alkyl containing from 1 to 4 carbon atoms), e.g., methyl, ethyl, propyl, isopropyl, butyl, hexyl, cyclohexyl, decyl, dodecyl, etc., or an aryl group e.g., phenyl, tolyl, xylyl, methoxyphenyl, chlorophenyl, naphthyl, etc.; R_4 represents an alkyl group, preferably a lower alkyl containing from 1 to 4 carbon atoms, e.g., methyl, ethyl, propyl, isopropyl, butyl, hexyl, cyclohexyl, decyl, dodecyl, etc., or an aryl group e.g., phenyl, tolyl, xylyl, methoxyphenyl, chlorophenyl, naphthyl, trifluorophenyl, pentafluorophenyl, etc.; X represents an acid anion, e.g., chloride,

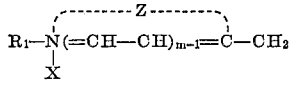
bromide, iodide, p-toluenesulfonate, thiocyanate, sulfamate, methyl sulfate, ethyl sulfate, perchlorate, etc.; and Z represents the nonmetallic atoms necessary to complete a densensitizing heterocyclic nucleus selected from the group including a nitrobenzothiazole nucleus, e.g., 5-nitrobenzothiazole, 6-nitrobenzothiazole, 5 - chloro-6-nitrobenzothiazole, etc.; a nitrobenzoxazole nucleus, e.g., 5-nitrobenzoxazole, 6-nitrobenzoxazole, 5-chloro-6-nitrobenzoxazole, etc.; nitrobenzoselenazole nucleus, e.g., 5-nitrobenzoselenazole, 6-nitrobenzoselenazole, 5-chloro-6-nitrobenzoselenazole, etc.; an imidazo[4,5-b]quinoxaline nucleus, e.g., imidazo[4,5-b]quinoxaline, 1,3-dialkylimidazo[4,5-b]quinoxaline such as 1,3-diethylimidazo-[4,5-b]quinoxaline, 6 - chloro-1,3-diethylamidazo[4,5-b] quinoxaline, etc., 1,3-dialkenylimidazo[4,5-b]quinoxaline such as 1,3-diallylimidazo[4,5-b]quinoxaline, 6-chloro-1,3 - diallylimidazo[4,5-b]quinoxaline, etc., 1,3-diarylimidazo[4,5-b]quinoxaline such as 1,3-diphenylimidazo-[4,5-b]quinoxaline, 6-chloro-1,3-diphenylimidazo[4,5-b] quinoxaline, etc.; a 3,3-dialkyl-3H-pyrrolo[2,3-b]pyridine nucleus, e.g., 3,3-dimethyl-3H-pyrrolo[2,3-b]pyridine, 3,3-diethyl-3H-pyrrolo[2,3-b]pyridine, etc.; a 3,3-dialkyl-3H-nitroindole, e.g., 3,3-dimethyl-5-nitro-3H-indole, 3,3-diethyl-5-nitro-3H-indole, 3,3-dimethyl-6-nitro-3H-indole, etc., a thiazolo[4,5-b]quinoline nucleus; or a nitroquinoline, e.g., 5-nitroquinoline, 6-nitroquinoline, etc. Other nuclei containing nitro groups that are useful as desensitizers include nitrothiazole, nitronaphthothiazole, nitrooxazole, nitronaphthoxazole, nitroselenazole, nitronaphthoselenazole, and nitropyridine nuclei. The desensitizing nuclei wherein Z in above Formula I represents the atoms necessary to complete a nitro substituted heterocyclic nucleus form particularly efficacious desensitizing dyes and are a preferred dye species of the invention.

The cyanine dyes of the invention are powerful desensitizers for preparing direct positive photographic silver halide emulsions. In addition, they are also useful desensitizers in emulsions used in the process described in Stewart and Reeves, U.S. Pat. No. 3,250,618, issued May 10, 1966.

As used herein and in the appended claims, "desensitizing nucleus" refers to those nuclei which, when converted to a symmetrical carbocyanine dye and added to gelatin silver chlorobromide emulsion containing 40 mole percent chloride and 60 mole percent bromide, at a concentration of from 0.01 to 0.2 gram dye per mole of silver, cause by electron trapping at least about an 80 percent loss in the blue speed of the emulsion when sensitometrically exposed and developed three minutes in Kodak developer D–19 at room temperature. Advantageously, the desensitizing nuclei are those which, when converted to a symmetrical carbocyanine dye and tested as just described, essentially completely desensitize the test emulsion to blue radiation (i.e., cause more than about 90 to 95% loss of speed to blue radiation).

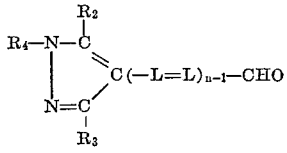
The cyanine dyes defined by Formula I above are conveniently prepared by heating a mixture of (1) a heterocyclic compound of the formula:

II.



wherein *m*, R_1, X and Z are as previously defined, and (2) a pyrazole compound of the formula:

III.



wherein *n*, L, R_2, R_3 and R_4 are as previously defined, in approximately equimolar proportions, in the presence of a condensing agent, if desired, such as anhydrous sodium acetate, a trialkylamine such as triethylamine, etc., piperidine, N-methylpiperidine, etc., in an inert solvent medium such as ethanol, acetic anhydride, glacial acetic acid, etc. The crude dyes are then separated from the reaction mixtures and purified by one or more recrystallizations from appropriate solvents such as benzene, petroleum ether, ethanol, methanol, etc.

In the preparation of direct positive photographic silver halide emulsions, one or more of the new dyes of the invention, as defined by Formula I above, are incorporated into direct positive type emulsions, especially into a suitably fogged silver halide emulsion. The emulsion can be fogged in any suitable manner, such as by light or with chemical fogging agents, e.g., stannous chloride, formaldehyde, thiourea dioxide and the like. The emulsion may be fogged by the addition thereto of a reducing agent such as thiourea dioxide and a compound of a metal more electropositive than silver such as a gold salt, for example, potassium chloroaurate, as described in British Pat. 723,019 (1955).

Typical reducing agents that are useful in providing such emulsions include stannous salts, e.g., stannous chloride, hydrazine, sulfur compounds such as thiourea dioxide, phosphonium salts such as tetra (hydroxymethyl) phosphonium chloride, and the like. Typical useful metal compounds that are more electropositive than silver include gold, rhodium, platinum, palladium, iridium, etc., preferably in the form of soluble salts thereof, e.g., potassium chloroaurate, auric chloride, $(NH_4)_2PdCl_6$ and the like.

The concentration of added dye can vary widely, e.g., from about 50 to 2000 mg. and preferably from about 400 to 800 mg. per mole of silver halide in the direct positive emulsions.

As used herein, and in the appended claims, "fogged" refers to emulsions containing silver halide grains which produce a density of at least 0.5 when developed, without exposure, for 5 minutes at 68°F. in developer Kodak DK–50 having the composition set forth below, when the emulsion is coated at a silver coverage of 50 mg. to 500 mg. per square foot.

DEVELOPER

N-methyl-p-aminophenol sulfate—2.5 g.
Sodium sulfite (anhydrous)—30.0 g.
Hydroquinone—2.5 g.
Sodium metaborate—10.0 g.
Potassium bromide—0.5 g.
Water to make—1.0 l.

The dyes of this invention are also advantageously incorporated in direct positive emulsions of the type in which a silver halide grain has a water-insoluble silver salt center and an outer shell composed of a fogged water-insoluble silver salt that develops to silver without exposure. The dyes of the invention are incorporated, preferably, in the outer shell of such emulsions. These emulsions can be prepared in various ways, such as those described in Berriman U.S. Pat. application Ser. No. 448,467, filed Apr. 15, 1965. For example, the shell of the grains in such emulsions may be prepared by precipitating over the core grains a light-sensitive water-insoluble silver salt that can be fogged and which fog is removable by bleaching. The shell is of sufficient thickness to prevent access of the developer used in processing the emulsions of the invention to the core. The silver salt shell is surface fogged to make developable to metallic silver with conventional surface image developing compositions. The silver salt of the shell is sufficiently fogged to produce a density of at least about 0.5 when developed for 6 minutes at 68° F. in Developer A below when the emulsion is coated at a silver coverage of 100 mg. per square foot. Such fogging can be effected by chemically sensitizing to fog with the sensitizing agents described for chemically sensitizing the core emulsion, high intensity light and the like fogging means well known to those

skilled in the art. While the core need not be sensitized to fog, the shell is fogged. Fogging by means of a reduction sensitizer, a noble metal salt such as gold salt plus a reduction sensitizer, a sulfur sensitizer, high pH and low pAg silver halide precipitating conditions, and the like can be suitably utilized. The shell portion of the subject grains can also be coated prior to fogging.

DEVELOPER A

N-methyl-p-aminophenol sulfate—2.5 grams
Ascorbic acid—10.0 grams
Potassium metaborate—35.0 grams
Potassium bromide—1.0 grams
Water to—1 liter
pH of—9.6

Before the shell of water-insoluble silver salt is added to the silver salt core, the core emulsion is first chemically or physically treated by methods previously described in the prior art to produce centers which promote the deposition of photolytic silver, i.e., latent image nucleating centers. Such centers can be obtained by various techniques as described herein. Chemical sensitization techniques of the type described by Antoine Hautot and Henri Saubeneir in Science et Industries Photographiques, vol. XXVIII, January 1957, pages 1 to 23 and January 1957, pages 57 to 65 are particularly useful. Such chemical sensitization includes three major classes, namely, gold or noble metal sensitization, sulfur sensitization, such as by a labile sulfur compound, and reduction sensitization, e.g., treatment of the silver halide with a strong reducing agent which introduces small specks of metallic silver into the silver salt crystal or grain.

In the preparation of the above photographic emulsions, the dyes, reducing agents and metal compounds of the invention are advantageously incorporated in the washed, finished silver halide emulsion and should, of course, be uniformly distributed throughout the emulsion. The methods of incorporating dyes and other addenda in emulsions are relatively simple and well known to those skilled in the art of emulsion making. For example, it is convenient to add them from solutions in appropriate solvents, in which case the solvent selected should be completely free from any deleterious effect on the ultimate light-sensitive materials. Methanol, isopropanol, pyridine, water, etc., alone or in admixtures, have proven satisfactory as solvents for this purpose. The type of silver halide emulsions that can be sensitized with the new dyes include any of those prepared with hydrophilic colloids that are known to be satisfactory for dispersing silver halides, for example, emulsions comprising natural materials such as gelatin, albumin, agar-agar, gum arabic, alginic acid, etc. and hydrophilic synthetic resins such as polyvinyl alcohol, polyvinyl pyrrolidone, cellulose esthers, partially hydrolyzed cellulose acetate, and the like.

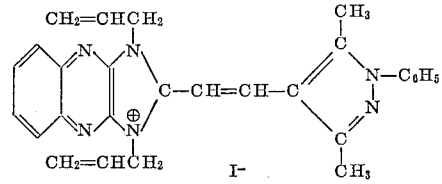
The dyes, reducing agents and metal compounds of the invention can be used with emulsions prepared with any of the light-sensitive silver halide salts including silver chloride, silver bromide, silver chlorobromide, silver bromoiodide, silver chlorobromoiodide, etc. Particularly useful are direct positive fogged emulsions in which the silver salt is a silver bromohalide comprising more than 50 mole percent bromide. As indicated previously, certain dyes of this invention are also useful in emulsions which contain color formers. This is unexpected since related prior art dyes cannot be used in emulsions containing a color former.

The novel emulsions of this invention may be coated on any suitable photographic support, such as glass, film base such as cellulose acetate, cellulose acetate butyrate, polyesters such as polyethylene terephthalate, paper, baryta coated paper, polyolefin coated paper, e.g., polyethylene or polypropylene coated paper, which may be electron bombarded to promote emulsion adhesion, to produce the novel photographic elements of the invention.

The invention is further illustrated by the following examples.

EXAMPLE 1

1,3-diallyl-2-[(3,5-dimethyl-1-phenyl-4-pyrazolyl)-vinyl] imidazo[4,5-b]quinoxalinium iodide



I-

A mixture of 2.2 g. (1 mol.) of 1,3-diallyl-2-methyl-imidazo[4,5-b]quinoxalinium p-toluenesulfonate, 1.1 g. (1 mol.+10% excess) of 3,5-dimethyl-1-phenyl-4-pyrazole carboxaldehyde, and 15 ml. of acetic anhydride was refluxed for 10 minutes. The reaction mixture was chilled and treated with 100 ml. of ether. The oily layer was separated from the supernatant liquid by decantation and then washed with ether. The oily layer was dissolved in acetone and treated with an aqueous solution of sodium iodide. After chilling, the crude dye was collected on a filter and washed with water and then acetone. After recrystallization from methyl alcohol, 1.1 g. (38%) of pure dye was obtained as yellow crystals, M.P. 202–203° C., decomposes.

Analysis.—Calc'd for $C_{28}H_{27}IN_6$ (percent): I, 22.10. Found (percent): I, 22.0.

The above prepared dye containing the desensitizing 1,3-diallylimidazo[4,5-b]quinoxalinium salt nucleus was photographically tested for its usefulness as an electron acceptor and spectral sensitizer for fogged direct positive photographic silver halide emulsions by the following procedure.

A gelatin silver bromoiodide emulsion is reduction and gold sensitized, i.e., fogged, by first adding stannous chloride and heating for 60 minutes at 55° C. and then adding potassium chloroaurate and heating for 20 minutes at 55° C., as described in British Pat. 723,019. The above prepared dye 1,3-diallyl-2-[3,5-dimethyl-1-phenyl-4-pyrazolyl)vinyl]imidazo[4,5-b]quinoxalinium iodide is then added to the above fogged emulsion in amount sufficient to give a concentration of 0.50 gram of the dye per mole of silver. The resulting emulsion is then coated on a cellulose acetate film support at a coverage of 100 mg. of silver and 400 mg. of gelatin per square foot of support.

A sample of the coated support is then exposed on an Eastman Ib sensitometer using a tungsten light source and processed for 6 minutes at room temperature in Kodak D–19 developer which has the following composition:

N-methyl-p-aminophenol sulfate—2.0 g.
Sodium sulfite (anhydrous)—90.0 g.
Hydroquinone—8.0 g.
Sodium carbonate (monohydrate)—52.5 g.
Potassium bromide—5.0 g.
Water to make 1.0 liter

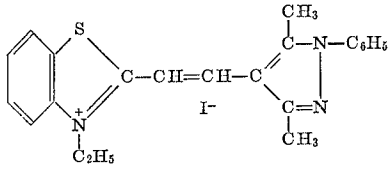
then fixed, washed and dried. The results are listed in Table I hereinafter. Referring thereto, it will be seen that the dye of this example has a maximum density in the unexposed areas of 1.76 and a minimum density in exposed areas of 0.03, a maximum sensitivity of 485 mμ and a relative speed of 603. This result indicates that the dye compound of the above example is especially well suited to function as both an electron acceptor and spectral sensitizer. It thus provides excellent quality direct positive photographic silver halide emulsions. Excellent magenta images are obtained when the color former 1-(2,4,6-trichlorophenyl) - 3,3' - (2'',4'' - di - t - amylphenoxyacetamido)benzimidazo-5-pyrazolone is incorporated in the emulsion of this example, the emulsion is coated on a support, exposed to a tungsten source through Wratten filter No. 61 and No. 16, and reversal processed as de-

scribed in Graham et al. U.S. Pat. 3,046,129, issued July 24, 1962, in Example (a) col. 27, lines 27 et seq. except that black-and-white (MQ) development is omitted, the color development is reduced to one minute and is conducted in total darkness until after fixing.

The following Example A containing a sensitizing 3-ethylbenzothiazolium iodide nucleus in place of the desensitizing 1,3-diallylimidazo[4,5-b]quinoxalinium iodide nucleus of above Example 1, but otherwise of similar structure, is included here for comparison purposes.

EXAMPLE A

2-[(3,5-dimethyl-1-phenyl-4-pyrazolyl)vinyl]-3-ethylbenzothiazolium iodide



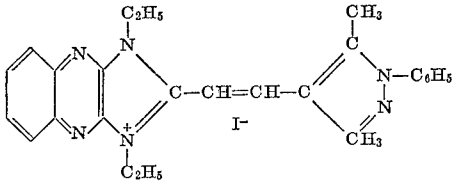
A mixture of 1.5 g. (1 mol.) of 3-ethyl-2-methylbenzothiazolium iodide, 1 g. (1 mol.) of 3,5-dimethyl-1-phenyl-4-pyrazole carboxaldehyde, 1.2 g. (1 mol.+200% excess) of anhydrous sodium acetate, and 10 ml. of ethyl alcohol was refluxed one hour. After adding 100 ml. of water and chilling, a reddish tar was separated from the supernatant liquor by decantation. The tar was treated with 100 ml. of chloroform and chilled. The crude dye was collected on a filter and washed with chloroform. The dye was purified by recrystallization from methyl alcohol. A yield of 0.9 g. (38%) of pure dye was obtained as bright yellow crystals, M.P. 225–226° C., dec.

Analysis.—Cal'd for $C_{22}H_{22}IN_3S$ (percent): I, 26.05. Found (percent): I, 26.3.

The above dye was photographically tested by the exact procedure described in above Example 1. The results are shown in Table 1 hereinafter. Referring to the table, it will be seen that the dye of Example A containing the sensitizing nucleus had a relative speed of only 191 as compared with 603 for the dye of Example 1 containing the specified desensitizing nucleus. It will be further noted that the dye of Example A had a maximum density in the unexposed areas of only 1.50 and a relatively high minimum density in the exposed areas of 0.14, whereas the dye of Example 1 showed densities of 1.76 and 0.03, respectively, thereby indicating a marked superiority in contrast over that of Example A. The maximum sensitization for Example A was 455 mμ, while that of Example 1 was at 485 mμ. Accordingly, these results indicate that the dye of Example 1 containing a desensitizing nucleus is markedly superior to dyes containing a sensitizing nucleus, as exemplified by Example A, as an electron acceptor and spectral sensitizer for fogged direct positive photographic silver halide emulsions.

EXAMPLE 2

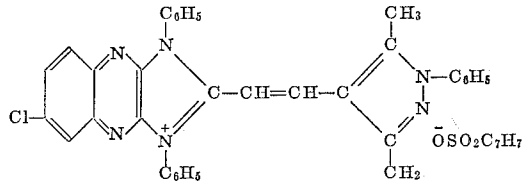
2-[(3,5-dimethyl-1-phenyl-4-pyrazolyl)vinyl]-1,3-diethyl-imidazo[4,5-b]quinoxalinium iodide



A mixture of 2.1 g. (1 mol.) of 1,3-diethyl-2-methylimidazo[4,5-b])quinoxalinium p-toluenesulfonate, 1.1 g. (1 mol.+10% excess) of 3,5-dimethyl-1-phenyl-4-pyrazole carboxaldehyde, and 15 ml. of acetic anhydride was refluxed for ten minutes. The reaction mixture was chilled and treated with ether. The oily layer was separated from the supernatant liquid by decantation and then washed with ether. The oily layer was dissolved in acetone and treated with an aqueous solution of sodium iodide. After chilling, the crude dye was collected on a filter and washed with water and then with acetone. After recrystallization from ethyl alcohol, 0.45 g. (16%) of pure dye was obtained as yellow needles, M.P. 237–238° C., dec.

EXAMPLE 3

6-chloro-2-[(3,5-dimethyl - 1 - phenyl-4-pyrazolyl)vinyl]-1,3-diphenylimidazo[4,5-b]quinoxalinium p-toluenesulfonate

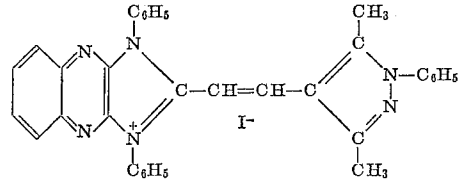


A mixture of 2.7 g. (1 mol.) of 6-chloro-2-methyl-1,3-diphenylimidazo[4,5-b]quinoxalinium p-toluenesulfonate, 1.1 g. (1 mol.+10% excess) of 3,5-dimethyl-1-phenyl-4-pyrazole carboxaldehyde, and 10 ml. of acetic anhydride was refluxed for ten minutes. The reaction mixture was chilled and then treated with 100 ml. of ether. The oily layer was separated from the supernatant liquid by decantation, and then washed with ether, whereupon it became crystalline. The crude dye was collected on a filter and washed with ether. After recrystallization from ethyl alcohol, 1.6 g. (42%) of pure dye was obtained as small bright yellow crystals, M.P. 283–284° C., dec.

Analysis.—Calc'd for $C_{41}H_{33}ClN_6O_3S$ (percent): C, 67.88; H, 4.59. Found (percent): C, 68.0; H, 4.7.

EXAMPLE 4

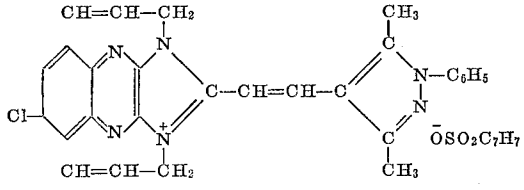
2-[(3,5-dimethyl-1-phenyl-4-pyrazolyl)vinyl]-1,3-diphenylimidazo[4,5-b]quinoxalinium iodide



A mixture of 2.6 g. (1 mol.) of 2-methyl-1,3-diphenylimidazo[4,5-b]quinoxalinium p-toluenesulfonate, 1.1 g. (1 mol.+10% excess) of 3,5-dimethyl-1-phenyl-4-pyrazolecarboxaldehyde and 15 ml. of acetic anhydride was refluxed ten minutes. The reaction mixture was chilled and treated with 100 ml. of ether. The oily layer was separated from the supernatant liquid by decantation and then washed with ether. The oily layer was dissolved in acetone and treated with an aqueous solution of sodium iodide. After chilling, the crude dye was collected on a filter and washed with water and then acetone. After recrystallization from methyl alcohol, 1.5 g. (47%) of pure dye was obtained as yellow crystals, M.P. 319–320° C., dec.

EXAMPLE 5

1,3 - diallyl-6-chloro-2-[(3,5-dimethyl-1-phenyl-4-pyrazolyl)vinyl]imidazo[4,5-b]quinoxalinium p-toluenesulfonate

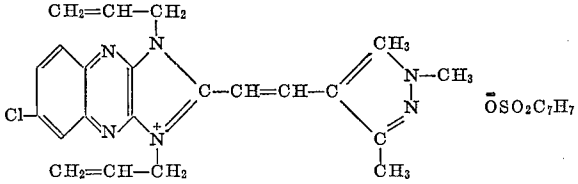


A mixture of 2.35 g. (1 mol.) of 1,3-diallyl-6-chloro-2-methylimidazo[4,5-b]quinoxalinium p-toluenesulfonate, 1 g. (1 mol.) of 3,5-dimethyl-1-phenyl-4-pyrazole car-

boxaldehyde, and 10 ml. of acetic anhydride was refluxed for ten minutes. The reaction mixture was chilled, and the crude dye collected on a filter and washed with acetone. After recrystallization from ethyl alcohol, 1.25 g. (37%) of pure dye was obtained as yellow crystals, M.P. 189–190° C., dec.

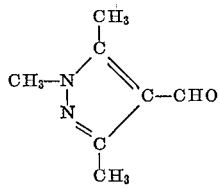
EXAMPLE 6

1,3-diallyl-6-chloro-2-[(1,3,5-trimethyl-4-pyrazolyl) vinyl]imidazo[4,5-b]quinoxalinium p-toluenesulfonate



A mixture of 2.3 g. (1 mol.) of 1,3-diallyl-6-chloro-2-methylimidazo[4,5 - b]quinoxalinium p-toluenesulfonate, 0.75 g. (1 mol.) of 1,3,5-trimethyl-4-pyrazole carboxaldehyde, and 10 ml. of acetic anhydride was refluxed ten minutes. The reaction mixture was chilled and treated with 100 ml. of ether. The crude dye was collected on a filter and washed with ether. After recrystallization from ethyl alcohol, 1.7 g. (57%) of pure dye was obtained as yellow-orange crystals, M.P. 122–124° C., dec.

The intermediate 1,3,5-trimethyl-4-pyrazole carboxaldehyde employed in above Example 6 was prepared as follows:



A solution of 42 g. (1 mol.+10% excess) of phosphoryl chloride in 100 ml. of dioxane was added to a solution of 20 g. (1 mol.+10% excess) of dimethylformamide in 100 ml. of dioxane. Then, a solution of 27.5 g. (1 mol.) of 1,3,5-trimethylpyrazone in 50 ml. of dioxane was added dropwise with stirring. After the addition was complete, the reaction mixture was heated two hours on a steam bath. After cooling, a solution of 120 ml. of about 8% sodium hydroxide was added. The reaction mixture was cooled and the solid collected on a filter and then discarded. Solid sodium carbonate was added until effervescence ceased. The reaction mixture separated into three layers and the bottom aqueous layer was discarded. The upper two layers were continuously extracted with ether for two hours. The ether extract was concentrated and the residue distilled under reduced pressure. When the temperature of the vapors reached 115°/15 mm. distillation was stopped and the residue considered good material. A yield of 17.3 g. (50%) of brownish solid was obtained. A sample recrystallized from ethyl alcohol had M.P. 82–83° C.

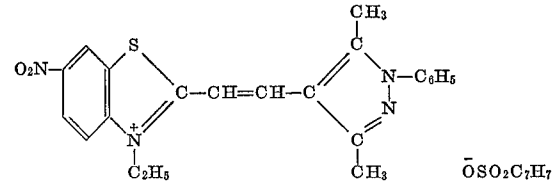
The 1,3,5-trimethylpyrazole intermediate was prepared as follows:

To a solution of 23 g. (1 mol.) of methyl hydrazine in 100 ml. of ethyl alcohol was added 50 g. (1 mol.) of 2,4-pentanedione over a period of 30 minutes with stirring, keeping the temperature below 40° by means of an ice bath. After the addition was complete, the reaction mixture was refluxed one hour. The reaction mixture was then fractionated through a column. A yield of 44 g. (80%) of colorless liquid with a B.P. of 167–168° C. was obtained.

The above prepared dyes of Examples 2 to 6 containing in each case a desensitizing imidazo[4,5-b]quinoxalinium salt nucleus were tested by the exact procedure described in above Example 1 and found, as shown in Table 1, to have relative speeds of 295, 575, 398, 380 and 436, respectively. These results indicate, together with the other data of Table 1, that the above dyes are markedly superior to the comparison dye of Example A which had a speed of only 191. Accordingly, the dyes of the above examples qualify as good electron acceptors and spectral sensitizers for fogged, direct positive photographic emulsions.

EXAMPLE 7

2-[(3,5-dimethyl-1-phenyl-4-pyrazolyl)vinyl]-3-ethyl-6-nitro-benzothiazolium p-toluenesulfonate



A mixture of 4 g. (1 mol.) of 3-ethyl-2-methyl-6-nitrobenzothiazolium p-toluenesulfonate, 2 g. (1 mol.) of 3,5-dimethyl-1-phenyl-4-pyrazole carboxaldehyde, and 20 ml. of acetic anhydride was refluxed for ten minutes. The reaction mixture was chilled and then treated with 100 ml. of ether. The oily layer was separated from the supernatant liquid by decantation and washed with ether and then treated with acetone and chilled. The crude dye was collected on a filter and washed with acetone. After recrystallization from ethyl alcohol, 4.5 g. (79%) of pure dye was obtained as brownish yellow needles, M.P. 202–204° C., dec.

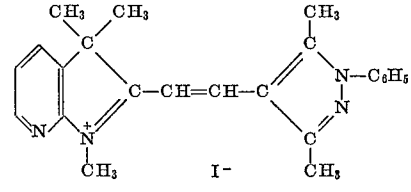
Analysis.—Calc'd for $C_{29}H_{28}N_4O_5S_2$ (percent): C, 60.39; H, 4.89. Found (percent): C, 60.1; H, 4.7.

This dye contains the desensitizing 6-nitrobenzothiazolium salt nucleus and as indicated by the photographic test procedure of Example 1, and as shown in Table 1, it constitutes an excellent electron acceptor and spectral sensitizer, having a speed of 692 and maximum sensitivity at 500 mμ, for fogged, photographic reversal emulsions.

In place of the 3-ethyl-2-methyl-6-nitrobenzothiazolium p-toluenesulfonate in the above example, there can be substituted an equivalent amount of other intermediates such as a 3-alkyl (e.g., methyl, ethyl, propyl, isopropyl, butyl, hexyl, decyl, dodecyl, etc.) -2-methyl - 6 - nitrobenzoxazolium quanternary salt, e.g., the chloride, bromide, iodide, perchlorate, p-toluenesulfonate, etc. salts, or a 3-alkyl (e.g., methyl, ethyl, propyl, isopropyl, butyl, hexyl, decyl dodecyl, etc.) -2-methyl-6-nitrobenzoselenazolium quanternary salts, e.g., the chloride, bromide, iodide, perchlorate, p-toluenesulfonate, etc. salts, and the like, to give the corresponding cyanine dyes having generally similar electron acceptor and spectral sensitizer properties, for example, the dye 2-[(3,5-dimethyl - 1 - phenyl - 4 - pyrazolyl)vinyl] - 3 - ethyl - 6-nitrobenzoxazolium p-toluenesulfonate, the dye 2-[(3,5-dimethyl - 1 - phenyl - 4 - pyrazolyl) - vinyl] - 3 - ethyl-6-nitrobenzoselenazolium p-toluenesulfonate, etc. The 3,5-dimethyl - 1 - phenyl - 4 - pyrazole carboxaldehyde can also be substituted in the above example by an equivalent amount of other related aldehydes such as, for example, 3,5 - dimethyl - 1 - phenyl - 4 - pyrazole acrylaldehyde to give the corresponding cyanine dye 2-[(3,5 - dimethyl-1-phenyl - 4 - pyrazolyl)butadienyl] - 3 - ethyl - 6 - nitrobenzothiazolium p - toluenesulfonate having generally similar properties as an electron acceptor and spectral sensitizer for fogged, direct positive photographic silver halide emulsions.

EXAMPLE 8

2-[(3,5-dimethyl-1-phenyl-4-pyrazolyl)vinyl]1,3,3-trimethyl-3H-pyrrolo[2,3-b]pyridinium iodide



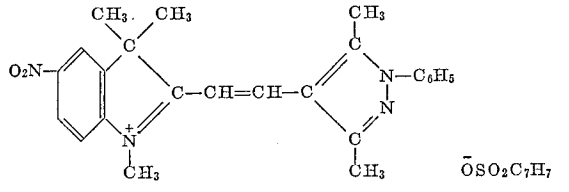
A mixture of 1.8 g. (1 mol.) of 1,3,3-trimethyl-2-methylene-1,2-dihydro-3H-pyrrolo[2,3-b]pyridine, 2 g. (1 mol.) of 3,5-dimethyl-1-phenyl-4-pyrazole carboxaldehyde, 2.1 g. (mol.) of p-toluenesulfonic acid, and 10 ml. of acetic anhydride was refluxed for ten minutes. The reaction mixture was chilled and then treated with 100 ml. of ether. The oily layer was separated from the supernatant liquid by decantation, and washed with ether. The oily layer was disolved in acetone and treated with an aqueous solution of sodium iodide. After chilling, the crude dye was collected on a filter and washed with water and then with acetone. After recrystallization from ethyl alcohol, 1.4 g. (29%) of pure dye was obtained as orange plates, M.P. 233–235° d.

Analysis.—Calc'd for $C_{23}H_{25}IN_4$ (percent): C, 57.01; H, 5.20; I, 26.21. Found (percent): C, 57.3; H, 5.4; I, 26.4.

The above prepared dye containing the desensitizing 3H-pyrrolo[2,3-b]pyridinium salt nucleus was tested by the exact procedure of Example 1 and found, as shown in Table 1, to have a relative speed of 955, together with other desirable properties set forth in the table, which results indicate that this dye is an excellent electron acceptor and spectral sensitizer for fogged, photographic reversal emulsions.

EXAMPLE 9

2-[(3,5-dimethyl-1-phenyl-4-pyrazolyl)vinyl]-1,3,3-trimethyl-5-nitro-3H-indolium p-toluenesulfonate

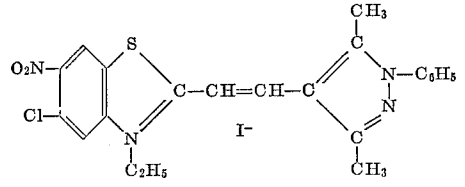


A mixture of 2.4 g. (1 mol.) of 1,2,3,3-tetramethyl-5-nitro-3H-indolium p-toluenesulfonate, 1.25 g. (1 mol.) of 3,5-dimethyl-1-phenyl-4-pyrazole carboxaldehyde, and 10 ml. of acetic anhydride was refluxed for ten minutes. The reaction mixture was chilled and the crude dye collected on a filter, washed with acetic anhydride and then with acetone. After recrystallization from ethyl alcohol, 1 g. (28%) of pure dye was obtained as yellow crystals, 218–221° D., dec.

Analysis.—Calc'd for $C_{31}LH_{32}N_4O_5S$ (percent): C, 64.99; H, 5.64. Found (percent): C, 64.7; H, 5.5.

EXAMPLE 10

5-chloro-2-[(3,5-dimethyl-1-phenyl-4-pyrazolyl)vinyl]-3-ethyl-6-nitrobenzothiazolium iodide

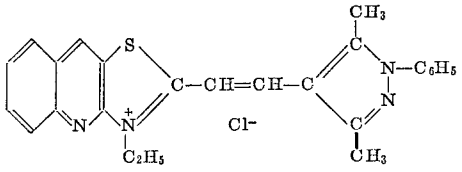


A mixture of 3.9 g. (1 mol.) of 5-chloro-3-ethyl-2-methyl-6-nitrobenzothiazolium iodide, 2 g. (1 mol.) of 3,5-dimethyl - 1 - phenyl - 4 - pyrazole carboxaldehyde, and 20 ml. of acetic anhydride was refluxed ten minutes. The reaction mixture was chilled and the crude dye collected on a filter and washed with acetone. After recrystallization from methyl alcohol, 2.2 g. (38%) of pure dye was obtained as brownish needles, M.P. 229–230° C., dec.

Analysis.—Calc'd for $C_{22}H_{20}ClIN_4O_2S$ (percent): C, 46.59; H, 3.56; I, 22.39. Found (percent): C, 46.4; H, 3.3; I, 22.5.

EXAMPLE 11

2-[(3,5-dimethyl-1-phenyl-4-pyrazolyl)vinyl]-3-ethylthiazolo[4,5-b]quinolinium chloride

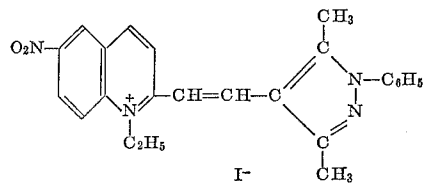


A mixture of 2.7 g. (1 mol.) of 3-ethyl-2-methylthiazolo[4,5-b]quinolinium chloride, 2 g. (1 mol.) of 3,5-dimethyl-1-phenyl-4-pyrazole carboxaldehyde, and 10 ml. of acetic anhydride was refluxed two minutes. The reaction mixture was chilled and the crude dye collected on a filter, washed with acetic anhydride and then with acetone. After recrystallization from methyl alcohol, 1.8 g. (40%) of pure dye was obtained as orange crystals, M.P. 188–189° C., dec.

The above prepared dyes of Examples 9, 10 and 11 containing the desensitizing 5-nitro-3H-indolium salt nucleus, the 5-chloro-6-nitrobenzothiazolium salt nucleus and the thiazolo[4,5-b]quinolinium salt nucleus, respectively, were tested by the exact procedure of Example 1 and found, as shown in Table 1, to be relatively good to excellent electron acceptors and spectral sensitizers for direct positive photographic silver halide emulsions. It should be noted that the indicated relative speeds are 1000, 603, and 1820, respectively, the indicated maximum density in the unexposed areas are 1.62, 1.48 and 1.12 respectively, the indicated minimum density in the exposed areas are 0.05, 0.02 and 0.03, respectively, and the indicated maximum sensitization at 545, 500 and 535 mμ, respectively. These results are markedly superior to the comparison dye of Example A with indicated values of only 1.91 for relative speed, 0.14 for minimum density in the unexposed areas, and maximum sensitization at only 455 mμ. From the foregoing, it will be apparent that the dye of above Example 9 is outstanding in all the desired properties for preparing superior fogged, photographic reversal emulsions.

EXAMPLE 12

2-[(3,5-dimethyl-1-phenyl-4-pyrazolyl)vinyl]-1-ethyl-6-nitroquinolinium iodide

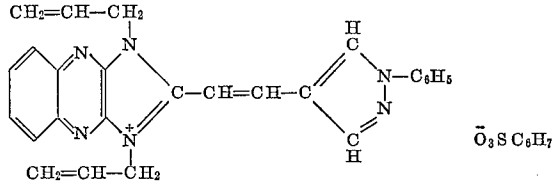


A mixture of 3.4 g. (1 mol.) of 1-ethyl-6-nitro-quinaldinium iodide, 2 g. (1 mol.) of 3,5-dimethyl-1-phenyl-4-pyrazole carboxaldehyde, and 15 ml. of acetic anhydride was refluxed ten minutes. The reaction mixture was chilled and treated with 100 ml. of ether. The oily layer was separated from the supernatant liquid by decantation and then treated with ethyl alcohol. The crude dye was extracted with 450 ml. of methyl alcohol. The filtrate was concentrated to 25 ml. and chilled, and the dye collected on a filter. After recrystallization from methyl alcohol, 0.2 g. (4%) of pure dye was obtained as brownish crystals, M.P. 128–131° D., dec.

Photographic testing in accordance with the procedure of Example 1 indicated that the above prepared dye containing the desensitizing 6-nitroquinolinium salt nucleus, is a moderately good electron acceptor and spectral sensitizer for fogged, photographic reversal emulsions. The results are listed in Table 1 hereinafter.

EXAMPLE 13

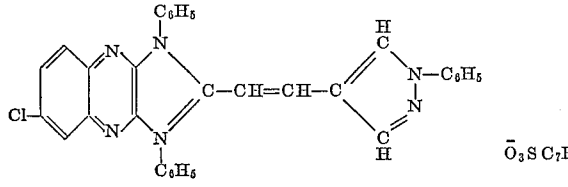
1,3-diallyl-2-[(1-phenyl-4-pyrazolyl)vinyl]imidazo[4,5-b]quinoxalinium p-toluenesulfonate



A mixture of 4.4 g. (1 mol.) of 1,3-diallyl-2-methylimidazo[4,5-b]quinoxalinium p-toluenesulfonate, 1.7 g. (1 mol.) of 1-phenyl-4-pyrazole carboxaldehyde, and 10 ml. of acetic anhydride was refluxed ten minutes. The reaction mixture was chilled and the crude dye collected on a filter and washed with acetone. After recrystallization from methyl alcohol, 3.2 g. (54%) of pure dye was obtained as brownish crystals, M.P. 232–233° C., dec.

EXAMPLE 14

6-chloro-1,3-diphenyl-2-[(1-phenyl-4-pyrazolyl)vinyl]imidazo[4,5-b]quinoxalinium p-toluenesulfonate

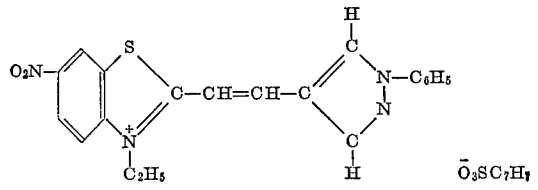


A mixture of 5.4 g. (1 mol.) of 6-chloro-1,3-diphenyl-2-methylimidazo[4,5-b]quinoxalinium p-toluenesulfonate, 1.7 g. (1 mol.) of 1-phenyl-4-pyrazole carboxaldehyde, and 10 ml. of acetic anhydride was refluxed ten minutes. The reaction mixture was chilled and the crude dye collected on a filter and washed with acetone. After recrystallization from methyl alcohol, 3.4 g. (49%) of pure dye was obtained as yellowish plates, M.P. 291–292° C., dec.

The dyes of above Examples 13 and 14, each containing a desensitizing 1,3-diallylimidazo[4,5-b]quinoxalinium salt nucleus, were tested by the exact procedure of Example 1 and found, as shown in Table 1 hereinafter, to be relatively good electron acceptors and spectral sensitizers for fogged, direct positive photographic silver halide emulsions. The dye of Example 13 showed the best relative speed of 603 as compared to 263 for the dye of Example 14. In all other properties both dyes were about the same.

EXAMPLE 15

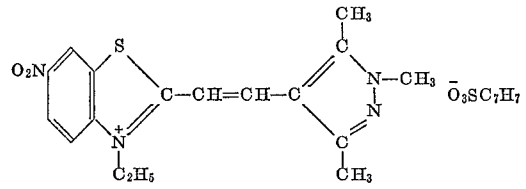
3-ethyl-6-nitro-2-[(1-phenyl-4-pyrazolyl)vinyl]benzothiazolium p-toluenesulfonate



A mixture of 4 g. (1 mol.) of 1-ethyl-2-methyl-6-nitrobenzothiazolium p-toluenesulfonate, 1.7 g. (1 mol.) of 1-phenyl-4-pyrazole carboxaldehyde, and 15 ml. of acetic anhydride was refluxed ten minutes. The reaction mixture was chilled and the crude dye collected on a filter and washed with acetone. After recrystallization from methyl alcohol, 3.9 g. (71%) of pure dye was obtained as orange crystals, M.P. 276–277° C., dec.

EXAMPLE 16

3-ethyl-6-nitro-2-[(1,3,5-trimethyl-4-pyrazolyl)vinyl]benzothiazolium p-toluenesulfonate



A mixture of 4 g. (1 mol.) of 3-ethyl-2-methyl-6-nitrobenzothiazolium p-toluenesulfonate, 1.4 g. (1 mol.) of 1,3,5-trimethyl-4-pyrazole carboxaldehyde, and 15 ml. of acetic anhydride was refluxed ten minutes. The reaction mixture was chilled and the crude dye collected on a filter and washed with acetone. After recrystallization from methyl alcohol, 3.5 g. (69%) of pure dye was obtained as brown needles, M.P. 253–254° C., dec.

The above prepared dyes of Examples 15 and 16 containing the desensitizing 6-nitrobenzothiazolium salt nucleus were tested by the procedure described in Example 1 and found, as shown in Table 1 hereinafter, to be moderately good electron acceptors and spectral sensitizers (with relative speeds of 398 and 479, respectively) for fogged, direct positive photographic silver halide emulsions.

The dyes prepared according to the above Examples 1 to 16, together with the comparison dye of Example A, as indicated previously, were photographically tested by the exact procedure described in Example 1 herein. The results are shown in Table 1 immediately below.

TABLE 1

Example No.	Dye conc., g./mole silver	Relative density: White light clear speed	Maximum in unexposed areas	Minimum in exposed areas	Sensitizing max. (mμ)
1	0.500	603	1.76	0.03	485
2	0.685	295	1.74	0.06	485
3	0.310	575	1.96	0.04	510
4	0.790	398	1.71	0.05	490
5	0.970	380	1.78	0.04	500
6	0.860	436	1.84	0.04	500
7	0.700	692	1.56	0.02	500
8	0.700	955	1.76	0.02	508
9	0.700	1,000	1.62	0.05	545
10	0.700	603	1.48	0.02	500
11	0.700	1,820	1.12	0.03	535
12	0.700	240	1.11	0.08	450
13	0.700	603	1.54	0.03	500
14	0.700	263	1.58	0.10	500
15	0.700	398	1.52	0.03	485
16	0.700	479	1.40	0.03	490
Example A	0.350	191	1.50	0.14	455

The following examples further illustrate the preparation of fogged, direct positive photographic emulsions and elements with the cyanine dyes of the invention.

EXAMPLE 17

To 9.0 pounds of a silver chloride gelatin emulsion containing an equivalent of 100 grams of silver nitrate is added 0.017 gram of 1,3-diallyl-2-[(3,5-dimethyl-1-phenyl-4-pyrazolyl)vinyl]imidazo[4,5-b]quinoxalinium iodide (dye of Example 1). The emulsion is coated on a non-glossy paper support, and is flashed with white light to give a density of 1.2 when developed in the following developer, diluted 1 part to 2 parts of water:

N-methyl-p-aminophenol sulfate—3.1 grams
Sodium sulfite, des.—45 grams
Hydroquinone—12 grams
Sodium carbonate, des.—67.5 grams
Potassium bromide—1.9 grams
Water to—1 liter

The light fogged material can be exposed to an image with light modulated by a Wratten No. 15 filter to give a direct positive image. Similar results are obtained when the dye of Example 3 is substituted for the 1,3-diallyl-2-

[(3,5 - dimethyl-1-phenyl-4-pyrazolyl)vinyl]imidazo[4,5-b]quinoxalinium iodide.

EXAMPLE 18

Seven pounds of a silver chloride gelatin emulsion containing the equivalent of 100 g. of silver nitrate is heated to 40° C. and the pH is adjusted to 7.8. Eight cc. of full strength (40%) Formalin solution is added and the emulsion is held at 40° C. for 10 minutes. At the end of the holding period, the pH is adjusted to 6.0 and 0.125 g. of 2-[(3,5 - dimethyl-1-phenyl-4-pyrazolyl)vinyl]-3-ethyl-6-nitrobenzothiazolium-p-toluenesulfonate (dye of Example 7) is added to the emulsion. The emulsion is coated on a support, and provides good direct positive images. Similar results are obtained when the dye of Example 9 is substituted for the 2-[3,5-dimethyl-1-phenyl-4-pyrazolyl) vinyl]-3-ethyl-6-nitrobenzothiazolium-p-toluenesulfonate.

By substituting other dye compounds of the invention, into the procedure of the above Examples 17 and 18, and more particularly the dyes of Examples 2, 4–6, 8 and 10–16, generally similar fogged, direct positive photographic silver halide emulsions and photographic elements may be prepared.

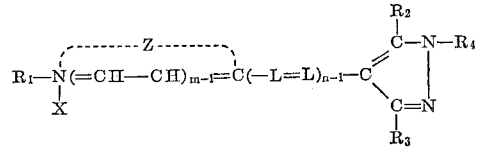
The photographic silver halide emulsion and other layers present in the photographic elements made according to the invention can be hardened with any suitable hardener, including aldehyde hardeners such as formaldehyde, and mucochloric acid, aziridine hardeners, hardeners which are derivatives of dioxane, oxypolysaccharides such as oxy starch or oxy plant gums, and the like. The emulsion layers can also contain additional additives, particularly those known to be beneficial in photographic emulsions, including, for example, lubricating materials, stabilizers, speed increasing materials, absorbing dyes, plasticizers, and the like. These photographic emulsions can also contain in some cases additional spectral sensitizing dyes. Furthermore, these emulsions can contain color forming couplers or can be developed in solutions containing couplers or other color generating materials. Among the useful color formers are the monomeric and polymeric color formers, e.g. pyrazolone color formers, as well as phenolic, heterocyclic and open chain couplers having a reactive methylene group. The color forming couplers can be incorporated into the direct positive photographic silver halide emulsion using any suitable technique, e.g., techniques of the type shown in Jelley et al. U.S. Pat. 2,322,027, issued June 15, 1943, Fierke et al. U.S. Pat. 2,801,171, issued July 30, 1957, Fisher U.S. Pats. 1,055,155 and 1,102,028, issued Mar. 4, 1913, and June 30, 1914, respectively, and Wilmanns U.S. Pat. 2,186,849, issued Jan. 9, 1940. They can also be developed using incorporated developers such as polyhydroxybenzenes, aminophenols, 3-pyrazolidones, and the like.

Light sensitive photographic silver halide emulsions containing the novel dyes of this invention are claimed in my U.S. patent application Ser. No. 604,146, titled "Photographic Emulsions," filed concurrently with the instant application.

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

I claim:

1. A cyanine dye selected from those represented by the following general formula:



wherein *m* represents a positive integer of from 1 to 2; *n* represents a positive integer of from 2 to 3; L represents a methine linkage; R_1 represents a member selected from the group consisting of an alkyl group of from 1 to 4 carbon atoms, an alkenyl group, and a phenyl group; R_2 and R_3 each represents a member selected from the group consisting of a hydrogen atom, an alkyl group of from 1 to 4 carbon atoms and a phenyl group; R_4 represents a member selected from the group consisting of an alkyl group of from 1 to 4 carbon atoms and a phenyl group; X represents an acid anion; and, Z represents the non-metallic atoms necessary to complete a desensitizing heterocyclic nucleus containing 5 to 6 atoms in the heterocyclic ring, said desensitizing nucleus being selected from the group consisting of nitrobenzothiazole, nitrobenzoselenazole, imidazo[4,5-b]quinoxaline, 3,3-dialkyl-3H-pyrrolo[2,3-b]pyridine, 3,3-dialkyl - 3H - nitroindole, thiazolo[4,5 - b]quinoline, nitroquinoline, nitrothiazole, nitronaphthothiazole, nitrooxazole, nitronaphthoxazole, nitroselenazole, nitronaphthoselenazole and nitropyridine nuclei, the alkyl groups in said desensitizing nuclei containing from 1 to 4 carbon atoms.

2. A cyanine dye as defined in claim **1** wherein said *n* represents the integer 2.

3. A cyanine dye as defined by claim **1** wherein said Z represents the non-metallic atoms necessary to complete a nitrobenzothiazole nucleus.

4. A cyanine dye as defined by claim **1** wherein said Z represents the non-metallic atoms necessary to complete a nitrobenzoxazole nucleus.

5. A cyanine dye as defined by claim **1** wherein said Z represents the non-metallic atoms necessary to complete a nitrobenzoselenazole nucleus.

6. A cyanine dye as defined by claim **1** wherein said Z represents the non-metallic atoms necessary to complete an imidazo[4,5-b]quinoxaline nucleus.

7. A cyanine dye as defined by claim **1** wherein said Z represents the non-metallic atoms necessary to complete a 3,3-dialkyl-3H-pyrrolo[2,3-b]pyridine nucleus.

8. A cyanine dye as defined by claim **1** wherein said Z represents the non-metallic atoms necessary to complete a 3,3-dialkyl-3H-nitroindole nucleus.

9. A cyanine dye as defined by claim **1** wherein said Z represents the non-metallic atoms necessary to complete a thiazolo[4,5-b]quinoline nucleus.

10. A cyanine dye as defined by claim **1** wherein said Z represents the non-metallic atoms necessary to complete a nitroquinoline nucleus.

11. A cyanine dye selected from the group consisting of

1,3-diallyl-2-[(3,5-dimethyl-1-phenyl-4-pyrazolyl)vinyl] imidazol[4,5-b]quinoxalinium salt,
2-[(3,5-dimethyl-1-phenyl-4-pyrazolyl)vinyl]-1,3-diethylimidazo[4,5-b]quinoxalinium salt,
6-chloro-2-[(3,5-dimethyl-1-phenyl-4-pyrazolyl)vinyl]-1,3-diphenylimidazo[4,5-b]quinoxalinium salt,
2-[(3,5-dimethyl-1-phenyl-4-pyrazolyl)vinyl]-1,3-diphenylimidazo[4,5-b]quinoxalinium salt,
1,3-diallyl-6-chloro-2-[(3,5-dimethyl-1-phenyl-4-pyrazolyl)vinyl]imidazo[4,5-b]quinoxalinium salt,
1,3-diallyl-6-chloro-2-[(1,3,5-trimethyl-4-pyrazolyl) vinyl]imidazo[4,5-b]quinoxalinium salt,
2-[(3,5-dimethyl-1-phenyl-4-pyrazolyl)vinyl]-3-ethyl-6-nitrobenzothiazolium salt,
2-[(3,5-dimethyl-1-phenyl-4-pyrazolyl)vinyl]1,3,3-trimethyl-3H-pyrrolo[2,3-b]pyridinium salt,
2-[(3,5-dimethyl-1-phenyl-4-pyrazolyl)vinyl]-1,3,3-trimethyl-5-nitro-3H-indolium salt,
5-chloro-2-[(3,5-dimethyl-1-phenyl-4-pyrazolyl)vinyl]-3-ethyl-6-nitrobenzothiazolium salt,
2-[(3,5-dimethyl-1-phenyl-4-pyrazolyl)vinyl]-3-ethylthiazolo[4,5-b]quinolinium salt,
2-[(3,5-dimethyl-1-phenyl-4-pyrazolyl)vinyl]-1-ethyl-6-nitroquinolinium salt,

1,3-diallyl-2-[(1-phenyl-4-pyrazolyl)vinyl]imidazo[4,5-b]quinoxalinium salt,
6-chloro-1,3-diphenyl-2-[(1-phenyl-4-pyrazolyl)vinyl]imidazo[4,5-b]quinoxalinium salt,
3-ethyl-6-nitro-2-[(1-phenyl-4-pyrazolyl)vinyl]benzothiazolium salt, and
3-ethyl-6-nitro-2-[(1,3,5-trimethyl-4-pyrazolyl)vinyl]benzothiazolium salt.

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JOHN D. RANDOLPH, Primary Examiner

U.S. Cl. X.R.

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