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3,574,629

DIRECT POSITIVE SILVER HALIDE EMULSIONS CONTAINING 2-IMINO-3-THIAZOLINE CYANINE DYES

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17 Claims

ABSTRACT OF THE DISCLOSURE

Novel cyanine dyes are provided which comprise first and second 5- to 6-membered nitrogen containing heterocyclic nuclei joined by a methine linkage; the first of said nuclei being a 2-arylimino (or alkylimino)-4-aryl (or alkyl)-3- thiazoline nucleus joined at the 5-carbon atom thereof to said linkage; and said second nucleus being joined at a carbon thereof to said linkage, to complete said cyanine dye.

This invention relates to novel photographic materials, and more particularly to a new class of cyanine dyes, to photographic silver halide emulsions containing these new dyes, and to photographic elements prepared with such novel emulsions.

Direct positive images have been prepared hitherto 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 high-light 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 selective sensitivity to longer wavelength radiations.

It is, accordingly, an object of this invention to provide a new class of photographically useful cyanine dyes. Another object is to provide improved and novel photographic silver halide emulsions, and more particularly direct positive emulsions, containing at least one of the novel dyes of the invention. Another object of this invention is to provide such novel emulsions containing, in addition, a photographic color former. Another object of this invention is to provide novel photographic elements comprising a support material having thereon at least one layer of the novel emulsions of the invention. Still another object of this invention is to provide novel filter dyes for photographic filter layers. Other objects of this invention will be apparent from this disclosure and the appended claims.

I have now found that certain cyanine dyes derived from 2-substituted amino-4-substituted thiazoles are especially useful electron acceptors and in most instances as spectral sensitizers, in photographic silver halide emulsions. In direct positive type of photographic emulsions, for example, 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 or red region of the spectrum with maximum sensitivity occurring in most cases in the region of about 550 to 600 nm. The images produced with these new direct positive emulsions are clear and sharp, and of excellent contrast.

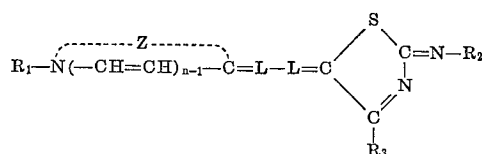
The novel cyanine dyes of the invention comprise first

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and second 5- to 6-membered nitrogen containing heterocyclic nuclei joined by a methine linkage; the first of said nuclei being a 2-arylimino (or alkylimino)-4-aryl (or alkyl)-3-thiazoline nucleus joined at the 5-carbon atom thereof to said linkage; and said second nucleus being joined at a carbon thereof to said linkage, to complete said cyanine dye.

The preferred cyanine dyes of the invention that are especially useful as electron acceptors and spectral sensitizers in photographic silver halide emulsions include those represented by the following general formula:

I.



wherein n represents a positive integer of from 1 to 2; 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., and substituted alkyl groups (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 acyloxyalkyl group, e.g., β -acetoxylethyl, γ -acetoxypentyl, ω -butyryloxybutyl, etc., an alkoxyalkyl group, e.g., β -methoxycarbonyl, ω -ethoxycarbonylbutyl, etc., or an aralkyl group, e.g., benzyl, phenethyl, etc., and the like; an alkenyl group, e.g., allyl, 1-propenyl, 2-butenyl, etc., or, any aryl group, e.g., phenyl, tolyl, naphthyl, methoxyphenyl, chlorophenyl, etc.; R_2 and R_3 each represents an alkyl group, including a substituted alkyl (preferably a lower alkyl containing from 1 to 4 carbon atoms) e.g., methyl, ethyl, propyl, isopropyl, butyl, decyl, dodecyl, etc., or an aralkyl group, e.g., benzyl, phenethyl, etc., or an aryl group, e.g., phenyl, tolyl, naphthyl, methoxyphenyl, chlorophenyl, etc.; and Z represents the non-metallic atoms necessary to complete a sensitizing or a desensitizing heterocyclic nucleus containing from 5 to 6 atoms in the heterocyclic ring, which nucleus may contain a second hetero atom such as oxygen, sulfur, selenium or nitrogen, such as the following nuclei: a thiazole nucleus, e.g., thiazole, 4-methylthiazole, 4-phenylthiazole, 5-methylthiazole, 5-phenylthiazole, 4,5-dimethylthiazole, 4,5-diphenylthiazole, 4-(2-thienyl)thiazole, benzothiazole, 4-chlorobenzothiazole, 4- or 5-nitrobenzothiazole, 5-chlorobenzothiazole, 6-chlorobenzothiazole, 7-chlorobenzothiazole, 4-methylbenzothiazole, 5-methylbenzothiazole, 6-methylbenzothiazole, 6-nitrobenzothiazole, 5-bromobenzothiazole, 6-bromobenzothiazole, 5-chloro-6-nitrobenzothiazole, 4-phenylbenzothiazole, 5-phenylbenzothiazole, 4-methoxybenzothiazole, 5-methoxybenzothiazole, 6-methoxybenzothiazole, 5-iodobenzothiazole, 6-iodobenzothiazole, 4-ethoxybenzothiazole, 5-ethoxybenzothiazole, tetrahydrobenzothiazole, 5,6-dimethoxybenzothiazole, 5,6-dioxymethylenebenzothiazole, 5-hydroxybenzothiazole, 6-hydroxybenzothiazole, α -naphthothiazole, β -naphthothiazole, β,β -naphthothiazole, 5-methoxy- β,β -naphthothiazole, 5-ethoxy- β -naphthothiazole, 8-methoxy- α -naphthothiazole, 7-methoxy- α -naphthothiazole, 4'-methoxythianaphtho-7',6',4,5-thiazole, nitro group substituted naphthothiazoles, etc.; an oxazole nucleus, e.g., 4-methyloxazole, 4-nitro-oxazole, 5-methyloxazole, 4-phenyloxazole, 4,5-diphenyloxazole, 4-ethyloxazole,

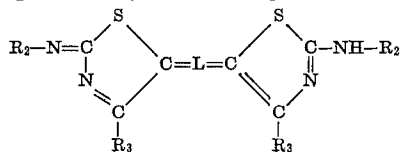
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zole, 4,5-dimethoxazole, 5-phenyloxazole, benzoxazole, 5-chlorobenzoxazole, 5-methylbenzoxazole, 5-phenylbenzoxazole, 5- or 6-nitrobenzoxazole, 5-chloro-6-nitrobenzoxazole, 6-methylbenzoxazole, 5,6-dimethylbenzoxazole, 4,6-dimethylbenzoxazole, 5-methoxybenzoxazole, 5-ethoxybenzoxazole, 5-chlorobenzoxazole, 6-methoxybenzoxazole, 5-hydroxybenzoxazole, 6-hydroxybenzoxazole, α -naphthoxazole, β -naphthoxazole, nitro group substituted naphthoxazoles, etc.; a selenazole nucleus, e.g., 4-methylselenazole, 4-nitroselenazole, 4-phenylselenazole, benzoselenazole, 5-chlorobenzoselenazole, 5-methoxybenzoselenazole, 5-hydroxybenzoselenazole, 5- or 6-nitrobenzoselenazole, 5-chloro-6-nitrobenzoselenazole, tetrahydrobenzoselenazole, α -naphthoselenazole, β -naphthoselenazole, nitro group substituted naphthoselenazoles, etc.; a thiazoline nucleus, e.g., thiazoline, 4-methylthiazoline, 4-nitrothiazoline, etc.; a pyridine nucleus, e.g., 2-pyridine, 5-methyl-2-pyridine, 4-pyridine, 3-methyl-4-pyridine, nitro group substituted pyridines, etc.; a quinoline nucleus, e.g., 2-quinoline, 3-methyl-2-quinoline, 5-ethyl-2-quinoline, 6-chloro-2-quinoline, 6-nitro-2-quinoline, 8-chloro-2-quinoline, 6-methoxy-2-quinoline, 8-ethoxy-2-quinoline, 8-hydroxy-2-quinoline, 4-quinoline, 6-methoxy-4-quinoline, 6-nitro-4-quinoline, 7-methyl-4-quinoline, 8-chloro-4-quinoline, 1-isoquinoline, 6-nitro-1-isoquinoline, 3,4-dihydro-1-isoquinoline, 3-isoquinoline, etc.; a 3,3-dialkylindolenine nucleus, preferably having a nitro or cyano substituent, e.g., 3,3-dimethyl-5 or 6-nitroindolenine, 3,3-dimethyl-5- or 6-cyanoindolenine, etc.; and, an imidazole nucleus, e.g., imidazole, 1-alkylimidazole, 1-alkyl-4-phenylimidazole, 1-alkyl-4,5-dimethylimidazole, benzimidazole, 1-alkyl-benzimidazole, 1-aryl-5,6-dichlorobenzimidazole, 1-alkyl- α -naphthimidazole, 1-aryl- β -naphthimidazole, 1-alkyl-5-methoxy- α -naphthimidazole, etc., an imidazo[4,5-b]quinoxaline nucleus, e.g., 1,3-dialkylimidazo[4,5-b]quinoxaline such as 1-ethylimidazo[4,5-b]quinoxaline, 6-chloro-1-ethylimidazo[4,5-b]quinoxaline, etc., 1,3-dialkenylimidazo[4,5-b]quinoxaline such as 1-allylimidazo[4,5-b]quinoxaline, 6-chloro-1-allylimidazo[4,5-b]quinoxaline, etc., 1,3-diaryl-imidazo[4,5-b]quinoxaline such as 1-phenylimidazo[4,5-b]quinoxaline, 6-chloro-1-phenylimidazo[4,5-b]quinoxaline, and the like. Nuclei wherein Z completes an imidazo[4,5-b]quinoxaline nucleus, or a nitro group substituted thiazole, oxazole, selenazole, thiazoline, pyridine, quinoline or imidazole nucleus are termed desensitizing nuclei. From the foregoing, it will be apparent that Z constitutes the atoms necessary to complete the heterocyclic nitrogen containing nucleus of the type used in the production of cyanine dyes.

As used herein "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 0.10 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).

In another embodiment of the invention, novel cyanine dyes are provided which are primarily useful as filter dyes in photographic filter layers. This class of cyanine dyes are represented by the following general formula:

II.

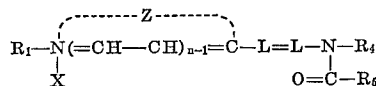


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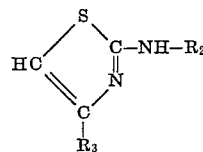
wherein L, R₂, and R₃ are as previously defined. The above defined dyes are primarily useful as filter dyes in photographic filter layers.

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

III.



wherein n, L, R₁ and Z are as previously defined, X represents an acid anion, e.g., chloride, bromide, iodide, p-toluenesulfonate, perchlorate, thiocyanate, sulfamate, methyl sulfate, ethyl sulfate, etc., R₄ represents an aryl group, e.g., phenyl, tolyl, etc., and R₅ represents an alkyl group, e.g., methyl, ethyl, butyl, etc., and (2) a heterocyclic compound of the formula:



wherein R₂ and R₃ are as previously defined, in approximately equimolar proportions, in the presence of a basic condensing agent such as an alkali metal alkoxide, e.g., sodium ethoxide, in an inert solvent such as ethanol. The crude dyes are separated from the reaction mixtures and purified by one or more recrystallizations from appropriate solvents. Typical compounds defined by Formula IV above include, for example, 2-anilino-4-phenylthiazole, 2-anilino-4-methylthiazole, 2-methylamino-4-phenylthiazole, 2-methylamino-4-tert-butylthiazole, 2-benzylamino-4-methylthiazole, etc.

The preparation of the cyanine dyes defined by Formula II above are prepared in generally similar manner as described immediately above by heating a mixture comprising (1) a compound of Formula IV above and (2) chloral ethylate, in the proportions of approximately 2 moles of (1) to each mole of (2).

In accordance with the invention, novel and improved direct positive photographic silver halide emulsions are prepared by incorporating one or more of the cyanine dyes of the invention into a suitable 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 Patent 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, (NH₄)₂PdCl₆ and the like.

Useful concentrations of reducing agent and metal compound (e.g., metal salt) can be varied over a considerable range. As a general guideline, good results are obtained using about .05 to 40 mg. reducing agent per mole of silver halide and 0.5 to 15.0 mg. metal compound per mole of silver halide. Best results are obtained at lower concentration levels of both reducing agent and metal compound.

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.

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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

	G.
N-methyl-p-aminophenol sulfate -----	2.5
Sodium sulfite (anhydrous) -----	30.0
Hydroquinone -----	2.5
Sodium metaborate -----	10.0
Potassium bromide -----	0.5
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. patent application Ser. No. 448,467, filed Apr. 15, 1965, now U.S. Pat. 3,367,778, issued Feb. 6, 1968. 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 it 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

	G.
N-methyl-p-aminophenol sulfate -----	2.5
Ascorbic acid -----	10.0
Potassium metaborate -----	35.0
Potassium bromide -----	1.0
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 Sauvenier 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.

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The dyes of this invention are highly useful electron acceptors in high speed direct positive emulsions comprising fogged silver halide grains and a compound which accepts electrons, as described and claimed in Illingsworth U.S. patent application Ser. No. 609,794, filed Jan. 17, 1967, and titled "Photographic Reversal Materials III." (U.S. patent application, Ser. No. 609,794 is a continuation-in-part of U.S. patent application, Ser. No. 533,448, filed Mar. 11, 1966; and U.S. patent application, Ser. No. 619,936, filed Mar. 2, 1967, now U.S. Pat. 3,501,307, issued Mar. 17, 1970, is a continuation-in-part of Ser. No. 533,448.) The fogged silver halide grains of such emulsions are such that a test portion thereof, when coated as a photographic silver halide emulsion on a support to give a maximum density of at least about one upon processing for six minutes at about 68° F. in Kodak DK-50 developer, has a maximum density which is at least about 30% greater than the maximum density of an identical coated test portion which is processed for six minutes at about 68° F. in Kodak DK-50 developer after being bleached for about 10 minutes at about 68° F. in a bleach composition of:

Potassium cyanide—50 mg.
Acetic acid (glacial)—3.47 cc.
Sodium acetate—11.49 g.
Potassium bromide—119 mg.
Water to 1 liter

The grains of such emulsions will lose at least about 25% and generally at least about 40% of their fog when bleached for ten minutes at 68° F. in a potassium cyanide bleach composition as described herein. This fog loss can be illustrated by coating the silver halide grains as a photographic silver halide emulsion on a support to give a maximum density of at least 1.0 upon processing for six minutes at about 68° F. in Kodak DK-50 developer and comparing the density of such a coating with an identical coating which is processed for six minutes at 68° F. in Kodak DK-50 developer after being bleached for about 10 minutes at 68° F. in the potassium cyanide bleach composition. As already indicated, the maximum density of the unbleached coating will be at least 30% greater, generally at least 60% greater, than the maximum density of the bleached coating.

The silver halides employed in the preparation of the photographic emulsions useful herein include any of the photographic silver halides as exemplified by silver bromide, silver iodide, silver chloride, silver chlorobromide, silver bromiodide, silver chlorobromiodide, and the like. Silver halide grains having an average grain size less than about one micron, preferably less than about 0.5 micron, give particularly good results. The silver halide grains can be regular and can be any suitable shape such as cubic or octahedral, as described and claimed in Illingsworth U.S. patent application Ser. No. 609,778, filed Jan. 17, 1967, and titled "Direct Positive Photographic Emulsions I." (U.S. patent application, Ser. No. 609,778 is a continuation-in-part of U.S. patent application, Ser. No. 533,400, filed Mar. 11, 1966; and U.S. patent application, Ser. No. 619,909, filed Mar. 2, 1967 now U.S. Pat. 3,501,306, issued Mar. 17, 1970 is a continuation-in-part of Ser. No. 533,400.) Such grains advantageously have a rather uniform diameter frequency distribution, as described and claimed in Illingsworth U.S. patent application Ser. No. 609,790, filed Jan. 17, 1967, and titled "Photographic Reversal Emulsions II." (U.S. patent application, Ser. No. 609,790 is a continuation-in-part of U.S. patent application, Ser. No. 533,440, filed Mar. 11, 1966; and U.S. patent application Ser. No. 619,948, filed Mar. 2, 1967, now U.S. Pat. 3,501,305, issued Mar. 17, 1970 is a continuation-in-part of Ser. No. 533,440.) For example, at least 95%, by weight, of the photographic silver halide grains can have a diameter which is within about 40%, preferably within about 30% of the mean grain diameter. Mean grain diameter, i.e., average grain size, can be determined using conventional

methods, e.g., as shown in an article by Trivelli and Smith entitled "Empirical Relations Between Sensitometric and Size-Frequency Characteristics in Photographic Emulsion Series" in The Photographic Journal, vol. LXXIX, 1949, pages 330-338. The fogged silver halide grains in these direct-positive photographic emulsions of this invention produce a density of at least 0.5 when developed without exposure for five minutes at 68° F. in Kodak DK-50 developer when such an emulsion is coated at a coverage of 50 to about 500 mg. of silver per square foot of support. The preferred photographic silver halide emulsions comprise at least 50 mole percent bromide, the most preferred emulsions being silver bromoiodide emulsions, particularly those containing less than about ten mole percent iodide. The photographic silver halides can be coated at silver coverages in the range of about 50 to about 500 milligrams of silver per square foot of support.

In the preparation of the above photographic emulsions, the dyes 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 ethers, partially hydrolyzed cellulose acetate, and the like.

The binding agents for the emulsion layer of the photographic element can also contain dispersed polymerized vinyl compounds. Such compounds are disclosed, for example, in U.S. Pats. 3,142,568; 3,193,386; 3,062,674 and 3,220,884 and include the water insoluble polymers of alkyl acrylates and methacrylates, acrylic acid, sulfoalkyl acrylates or methacrylates and the like.

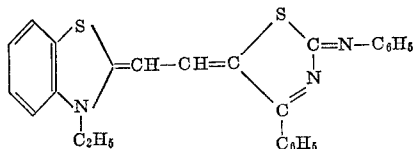
The dyes, reducing agents and metal compounds of the invention can be used with emulsions prepared, as indicated above, with any of the light-sensitive silver halide salts including silver chloride, silver bromide, silver chlorobromide, silver bromoiodide, silver chlorobromoiodide, etc. Particularly useful are direct positive fogged emulsions in which the silver salt is a silver bromohalide comprising more than 50 mole percent bromide. Certain dyes of this invention are also useful in emulsions which contain color formers.

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 poly(ethylene 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

5-[(3-ethyl-2-benzothiazolinyldiene)ethylidene]-4-phenyl-2-phenylimino-3-thiazoline



To a stirred solution of sodium ethoxide in ethanol prepared from ethanol (40 ml.) and sodium (0.95 g., 0.04 g. atom) is added first 2-anilino-4-phenylthiazole (5.00 g., 0.02 mole) and then 2-(2-acetanilidovinyl)-3-ethylbenzothiazolium iodide (9.00 g., 0.02 mole). The mixture is heated under reflux for fifteen minutes, transferred to a beaker and chilled. The crude product is collected by filtration, dried and amounts to 3.50 g. (40%) of solid. The filtrate is diluted with water (250 ml.) and the resulting suspension is chilled overnight. The suspension is filtered, washed with water and after drying the weight of this second crop of crude dye is 6.00 g. (68%). After recrystallizing separately, the two portions of crude product are recrystallized at least once from methanol or ethanol, all fractions are combined and amounts to 5.20 g. (59%) of partially purified dye. This material is boiled with two portions of benzene (100 ml.) filtering hot each time. Two recrystallizations of the benzene insoluble material are carried out by dissolving the dye in small amounts of warm cresol, filtering and reprecipitating by the addition of methanol, the yield of pure dye is 0.49 g. (6%), M.P. 239.5-241.5° C., dec.

Analysis.—Calc'd for $C_{26}H_{21}N_3S_2$ (percent): C, 71.0; H, 4.8; N, 9.6; S, 14.6. Found (percent): C, 70.6; H, 4.6; N, 9.3; S, 14.4.

The benzene extracts above, after chilling and filtration give a second dye. After two recrystallizations from benzene, the yield of the pure dye, 2-anilino-4-phenyl-5-[(4-phenylimino-3-thiazolin-5-ylidene)methyl]thiazole (see Example 2 hereinafter) is 0.49 g. (10%).

The above prepared dye containing the sensitizing 3-ethylbenzothiazole nucleus is 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 (2.5 mole percent of the halide being iodide and having an average grain size of about 0.2 micron is prepared by adding an aqueous solution of potassium bromide and potassium iodide, and an aqueous solution of silver nitrate, simultaneously to a rapidly agitated aqueous gelatin solution at a temperature of 70° C., over a period of about 35 minutes. The emulsion is chill-set, shredded and washed by leaching with cold water in the conventional manner. The emulsion is reduction-gold fogged by first adding 0.2 mg. of thiourea dioxide per mole of silver and heating for 60 minutes at 65° C. and then adding 4.0 mg. of potassium chloraurate per mole of silver and heating for 60 minutes at 65° C. The dye of the above example, 5-[(3-ethyl-2-benzothiazolinyldiene)ethylidene]-4-phenyl-2-phenylimino-3-thiazoline, is then added to the above fogged emulsion in amount sufficient to give a concentration of 0.08 gram of the dye per mole of silver. The resulting emulsion is 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:

	G.
N-methyl-p-aminophenol sulfate	2.0
Sodium sulfite (anhydrous)	90.0
Hydroquinone	8.0
Sodium carbonate (monohydrate)	52.5
Potassium bromide	5.0
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, depending on the concentration thereof in the emulsion, has a maximum density in the unexposed areas of 0.94 to 1.60 and a minimum density in exposed areas of 0.08 to 0.20, a maximum sensitivity of 560 to 590 nm. and a relative speed of 251 to 457.

This result indicates that the dye compound of the above example is 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-
5 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
10 processed as described 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
15 fixing.

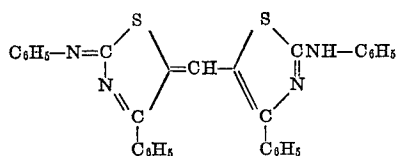
The dye of above Example 1 is also tested for sensitization of negative type emulsions by the following procedure.

The dye is dissolved in suitable solvents and added to separate portions of a fine grain silver chloride emulsion at the concentration of 0.165 gram per mole of silver. The emulsion is digested and then coated on a cellulose acetate support at a coverage of 432 mg. of silver per square foot of support. A sample of the coating is then exposed through Wratten Filter 35 and 38A (see "Kodak Wratten Filters" published 1966) on an Eastman Ib sensitometer using a tungsten light source and processed for 3 minutes in Kodak D-19 developer, fixed, washed and dried. The results are listed in Table 2 hereinafter. Referring thereto, it will be seen that this dye (Example 1) shows an increase in blue sensitization of 100 compared with control arbitrarily set at zero.

In place of the 2-(2-acetanilidovinyl)-3-ethylbenzothiazolium iodide in the above example, there can be substituted an equivalent amount of any other of the intermediates defined by Formula III above to give generally similar cyanine dyes that function as excellent electron acceptors and spectral sensitizers for negative and fogged direct positive photographic emulsions, for example, the dye 5-[(3-methyl-2-benzothiazolinyldene) ethylidene]-4-phenyl-2-phenylimino-3-thiazoline, the dye 5-[(3-ethyl-2-benzoxazolinyldene)ethylidene]-4-phenyl-2-phenylimino-3-thiazoline, the dye 5-[(3-methyl-2-benzoselenazolinyldene)ethylidene]-4-phenyl-2-phenylimino-3-thiazoline, the dye 5-[(1-methyl-4[1H]-quinolinyldene)ethylidene]-4-phenyl-2-phenylimino-3-thiazoline, the dye 5-[(1,3,3-trimethyl-2-indolinyldene)ethylidene]-4-phenyl-2-phenylimino-3-thiazoline, the dye 5-[(1,3-diethyl-2-benzimidazolinyldene)ethylidene]-4-phenyl-2-phenylimino-3-thiazoline, the dye 5-[(1,3-diethylimidazo[4,5-b]quinoxalin-2-ylidene)ethylidene]-4-phenyl-2-phenylimino-3-thiazoline, and the like. Also, in place of the 2-anilino-4-phenylthiazole in the above example, there can be substituted an equivalent amount of any other of the intermediates defined by Formula IV above to give the corresponding cyanine dyes having generally similar properties as electron acceptors and spectral sensitizers for negative and direct positive photographic emulsions.

EXAMPLE 2

2-anilino-4-phenyl-5-[(4-phenylimino-3-thiazolin-5-ylidene)methyl]thiazole



To a warm stirred solution of sodium ethoxide in ethanol prepared from ethanol (50 ml.) and sodium (1.40 g., 0.06 g. atom) was added 2-anilino-4-phenylthiazole (5.05 g., 0.02 mole). After solution was complete 2,2,2-trichloro-1-ethoxyethanol (chloral ethylate) (1.95 g., 0.01

mole) was added, and the mixture was heated under reflux for three hours. The reaction mixture was filtered hot. The precipitate was washed with ethanol and discarded. The combined filtrate and washes were diluted with water (200 ml.) and chilled overnight. The aqueous alcohol was decanted. The residual gum was dissolved in hot methanol (ca. 30 ml.), and the crude dye was precipitated by the addition of water (200 ml.). After chilling the crude dye was collected by filtration and dried. After three recrystallizations from benzene, the yield of purified dye was 0.10 g. (2%), M.P. 256.0-259.0° dec.

Analysis.—Calcd. for $C_{31}H_{22}N_4S_2$ (percent): C, 72.3; H, 4.3; N, 10.9; S, 12.5. Found (percent): C, 72.6; H, 4.5; N, 10.6; S, 12.2.

The above prepared dye is photographically tested by the exact procedures described in above Example 1. The results indicate that this dye is primarily useful as a filter dye for photographic filter layers. Table II shows that this dye can be incorporated in negative emulsions without adversely affecting the speed of the emulsion.

By substituting equivalent amounts of any other of the intermediates defined by Formula IV above for the 2-anilino-4-phenylthiazole in the above Example 2, other dyes having generally similar properties can be prepared.

The cyanine dyes prepared in accordance with above Examples 1 and 2 are photographically tested by the exact procedures described in Example 1 herein. Table I below shows the results with fogged direct positive photographic emulsions, while Table II below shows the results with negative type photographic emulsions.

TABLE I

Dye of Ex. No.	Dye concentration g./mole silver	Relative clear speed	Density		
			Max. in unexposed areas	Minimum in exposed areas	Max. sensitivity (nm.)
1-----	0.25	251	1.60	0.20	560
1-----	0.50	457	1.56	0.17	580
1-----	0.75	457	0.94	0.08	590
Control-----	0.00	<1	1.90	(¹)	-----

¹ No reversal.

TABLE II

Dye of Ex. No.	Dye concentration g./mole silver	Emulsion	Relative blue speed
1-----	0.165	Silver chloride-----	100
2-----	0.165	do-----	-----
2-----	0.083	do-----	0
Control-----	0.00	do-----	(¹)

¹ Arbitrarily set at zero.

EXAMPLE 3

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 5-[(3-ethyl-2-benzothiazolinyldene)ethylidene]-4-phenyl-2-phenylimino-3-thiazoline (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:

	Grams
N-methyl-p-aminophenol sulfate-----	3.1
Sodium sulfite, des.-----	45
Hydroquinone-----	12
Sodium carbonate, des.-----	67.5
Potassium bromide-----	1.9
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.

EXAMPLE 4

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 5-[(3-ethyl-2-benzothiazolinyldene)ethylidene]-4-phenyl-2-phenylimino-3-thiazoline (Example 1).

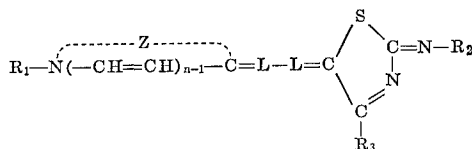
By substituting other dye compounds of the invention, as defined in Formula I above, into the procedure of the above examples, similar fogged, direct positive photographic silver halide emulsions and photographic elements may be prepared.

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.

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 fogged light-sensitive photographic silver halide emulsion containing at least one dye represented by the following formula:



wherein n represents a positive integer of from 1 to 2; L represents a methine linkage; R_1 represents a member selected from the group consisting of an alkyl group, an alkenyl group and an aryl group; R_2 and R_3 each represents a member selected from the group consisting of an alkyl group and an aryl group; and Z represents the non-metallic atoms required to complete a heterocyclic nucleus containing from 5 to 6 atoms in the heterocyclic ring.

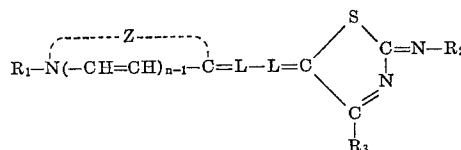
2. A photographic emulsion in accordance with claim 1 wherein said Z completes a nucleus selected from the group consisting of a thiazole nucleus, an oxazole nucleus, a selenazole nucleus, a thiazoline nucleus, a pyridine nucleus, a quinoline nucleus, a 3,3-dialkylindolenine

nucleus, an imidazole nucleus and an imidazo [4,5-b] quinoxaline nucleus.

3. A photographic emulsion in accordance with claim 1 wherein said R_2 and R_3 each represents an aryl group.

4. A photographic emulsion in accordance with claim 1 wherein said cyanine dye is 5-[(3-ethyl-2-benzothiazolinyldene)ethylidene]-4-phenyl-2-phenylimino-3-thiazoline.

5. A fogged direct positive photographic silver halide emulsion containing at least one dye represented by the following formula:



wherein n represents a positive integer of from 1 to 2; L represents a methine linkage; R_1 represents a member selected from the group consisting of an alkyl group, an alkenyl group and an aryl group; R_2 and R_3 each represents a member selected from the group consisting of an alkyl group and an aryl group; and Z represents the non-metallic atoms required to complete a heterocyclic nucleus containing from 5 to 6 atoms in the heterocyclic ring.

6. A direct positive emulsion in accordance with claim 5 wherein said Z completes a nucleus selected from the group consisting of a thiazole nucleus, an oxazole nucleus, a selenazole nucleus, a thiazoline nucleus, a pyridine nucleus, a quinoline nucleus, a 3,3-dialkylindolenine nucleus, an imidazole nucleus and an imidazo [4,5-b] quinoxaline nucleus.

7. A direct positive emulsion in accordance with claim 5 wherein said R_2 and R_3 each represents an aryl group.

8. A direct positive emulsion in accordance with claim 5 wherein said cyanine dye is 5-[(3-ethyl-2-benzothiazolinyldene)ethylidene]-4-phenyl-2-phenylimino-3-thiazoline.

9. A direct positive emulsion in accordance with claim 5 in which the said silver halide is present in the form of chemically fogged silver halide grains.

10. A direct positive emulsion in accordance with claim 5 in which the said silver halide is present in the form of reduction and gold fogged silver halide grains.

11. A direct positive emulsion in accordance with claim 5 containing a photographic color-coupler dissolved in solvents therefor.

12. A direct positive, photographic emulsion in accordance with claim 5 which comprises fogged silver halide grains, said grains being such that a test portion thereof, when coated as a photographic silver halide emulsion on a support to give a maximum density of at least about 1 upon processing for 6 minutes at about 68° F. in Kodak DK-50 developer has a maximum density which is at least about 30% greater than the maximum density of an identical coated test portion which is processed for 6 minutes at about 68° F. in Kodak DK-50 developer after being bleached for about 10 minutes at about 68° F. in a bleach composition of:

potassium cyanide—50 mg.
acetic acid (glacial)—3.47 cc.
sodium acetate—11.49 g.
potassium bromide—119 mg.
water to 1 liter.

13. A direct positive, photographic emulsion in accordance with claim 5 which comprises fogged silver halide grains, at least 95%, by weight, of said grains having a diameter which is within about 40% of the mean grain diameter.

13

14. A photographic element comprising a support having thereon at least one layer containing a photographic emulsion of claim **1**.

15. A photographic element comprising a support having thereon at least one layer containing a direct positive emulsion of claim **5**.

16. A photographic element comprising a support having thereon at least one layer containing a direct positive emulsion of claim **12**.

17. A photographic element comprising a support having thereon at least one layer containing a direct positive emulsion of claim **15**.

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J. TRAVIS BROWN, Primary Examiner

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96—101, 84; 260—240