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PHOTOGRAPHIC EMULSIONS CONTAINING A PYRIMIDINEDIONE AND A DESENSITIZING NUCLEUS LINKED BY A DIMETHINE OR A DOUBLE BOND

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U.S. Cl. 96—64 **28 Claims**

ABSTRACT OF THE DISCLOSURE

Cyanine dyes which contain a complex fused pyrimidinedione nucleus linked by a double bond or a dimethine linkage to a desensitizing nucleus, and light sensitive silver halide emulsions containing such dyes.

This invention relates to novel photographic materials, and more particularly to a new class of dyes. It also relates to light sensitive silver halide emulsions containing these dyes. The dyes of this invention are especially useful as electron acceptors and spectral sensitizers for direct positive photographic silver halide emulsions.

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 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 sensitivity to longer wavelength radiations.

We have now found certain novel dyes which 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 520–560 mμ. The images produced with these new direct positive emulsions are clear and sharp.

It is, accordingly, an object of this invention to provide a new class of cyanine dyes, containing desensitizing nuclei therein, that function as electron acceptors and spectral sensitizers for photographic silver halide emulsions.

Another object of this invention is to provide new and improved light sensitive photographic emulsions, such as fogged, direct positive emulsions, containing one or more of the new cyanine dyes of this invention.

A further object of this invention is to provide photographic elements comprising a support having thereon at least one layer containing a novel light sensitive silver halide emulsion of this invention.

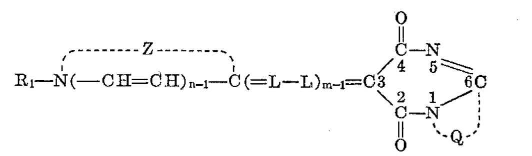
Another object is to provide means for the preparation of such novel dyes and photographic materials of this invention.

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 containing heterocyclic nuclei joined by a linkage consisting of a double bond or a dimethine bridge; the first of said nuclei being a complex fused pyrimidinedione nucleus, joined through the 3-carbon atom thereof, to said linkage; and said second nucleus being a desensitizing nucleus joined at a carbon atom thereof to the said linkage. The "complex fused pyrimidinedione" nuclei employed in the dyes of this invention feature a fused nucleus attached to the 1- and 6-atoms of the pyrimidinedione nucleus. The fused nucleus can be a cyclic nucleus, such as a heterocyclic ring.

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

I.



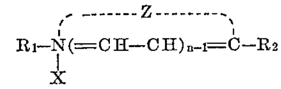
wherein n and m each represent a positive integer of from 1 to 2; L represents a methine linkage, e.g., —CH=, —C(CH$_3$)=, —C(C$_6$H$_5$)=, etc.; R$_1$ represents an alkyl group, including substituted alkyl (preferably a lower alkyl containing from 1 to 4 carbon atoms), e.g., methyl, ethyl, propyl, isopropyl, 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-carbobutyl, 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-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; an alkenyl group, e.g., allyl, 1-propenyl, 2-butenyl, etc., or, any aryl group, e.g., phenyl tolyl, naphthyl, methoxyphenyl, chlorophenyl, etc.; Z represents the non-metallic atoms necessary to complete a desensitizing 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.; a 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 thiazole[4,5-b]quinoline nucleus; or a nitroquinoline, e.g., 5-nitroquinoline, 6-nitroquinoline, etc., and Q represents the non-metallic atoms required to complete a fused heterocyclic ring containing from 5 to 6 atoms in said ring, which ring 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, 5-chlorobenzothiazole, 6-chlorobenzothiazole, 7-chlorobenzothiazole, 4-methylbenzothiazole, 5-methylbenzothiazole, 6-methylbenzothiazole, 5-bromobenzothiazole, 6-bromobenzothiazole, 6-phenylbenzothiazole, 5-phenylbenzothiazole, 4-methoxybenothiazole, 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, 5-metoxy-β,β-naphthothiazole, 5-ethoxy-β-naphthothiazole, 8-methoxy-α-naphthothiazole, 7-methoxy-α-naphthothiazole, 4' - methoxythianaphtheno-7',6',4,5-thiazole, etc.; an oxazole ring, e.g., 4-methyloxazole, 5-methyloxazole, 4-phenyloxazole, 4,5-diphenyloxazole, 4-ethyloxazole, 4,5-dimethyloxazole, 5-phenyloxazole, benzoxazole, 5-chlorobenzoxazole, 5-methylbenzoxazole, 5-phenylbenzoxazole, 6-methylbenzoxazole, 5,6-dimethylbenzoxazole, 4,6-dimethylbenzoxazole, 5-methoxybenzoxazole, 5 - ethoxybenzoxazole, 5-chloronaphthoxazole, 6-methoxybenzoxazole, 5-hydroxybenzoxazole, 6-hydroxybenzoxazole, α-naphthoxazole, β-naphthoxazole, etc.; a selenazole ring, e.g., 4-methylselenazole, 4-phenylselenazole, benzoselenazole, 5 - chlorobenzoselenazole, 5 - methoxybenzoselenazole, 5-hydroxybenzoselenazole, tetrahydrobenzoselenazole, α-naphthoselenazole, β-naphthoselenazole, etc.; a thiazoline ring, e.g., thiazoline, 4-methylthiazoline, etc.; a pyridine ring, e.g., pyridine, 3-methylpyridine, 4-methylpyridine, etc.; a quinoline ring, e.g., quinoline, 3-methylquinoline, 5-ethylquinoline, 6-chloroline, 8-chloroquinoline, 6-methoxyquinoline, etc.; a 3,3 - dialkylindolenine ring, e.g., 3,3-dimethylindolenine, 3,3-diethylindolenine, etc.; an imidazo ring, e.g., imidazole, 1-alkylimidazole, 1-alkyl-4,5-dimethylimidazole, benzimidazole, 1-alkylbenzimidazole, 1-aryl-5,6-dichlorobenzimidazole, 1-alkylnaphthimidazole, 1-aryl-β-naphthimidazole, 1-alkyl-5-methoxy-α-naphthimidazole, etc., and the like. Other densensitizing nuclei defined by Z in above Formula I that are useful include nitrothiazole, nitronaphthothiazole nitrooxazole, nitronaphthoxazole, nitroselenazole, nitronaphthoselenazole, and nitropyridine nuclei. Dyes of Formula I wherein Q represents the atoms required to complete a fused pyridine nucleus are especially useful and are the preferred dye species of the invention.

The cyanine dyes of the invention defined above are powerful electron acceptors for 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 mol 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).

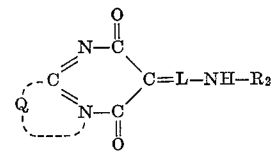
The cyanine dyes defined by Formula I above are conveniently prepared, for example, by heating a mixture of (1) a heterocyclic compound of the formula:

II.



wherein n, R_1, X and Z are as previously defined, and R_2 represents methyl, ethyl, benzyl, etc., and (2) a complex fused pyrimidinedione compound of the formula:

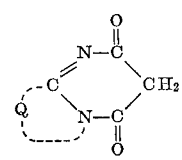
III.



wherein L and Q are as previously defined, and R_2 represents an aryl group, e.g., phenyl, tolyl, etc., in approximately equimolar proportions, in the presence of a condensing agent such as a trialkylamine, e.g., triethylamine, etc., piperidine, N-methylpiperidine, etc., in an inert solvent medium such as acetic anhydride. The crude dyes are then separated from the reaction mixtures and purified by one or more recrystallizations from appropriate solvents such as hot ethanol, m-cresol, pyridine, etc.

The intermediate pyrimidinedione compounds of Formula III above are conveniently prepared, for example, by heating a mixture of approximately equimolar amounts of (1) a compound of the formula:

IV.



and (2) ethylisoformanilide, in an inert solvent medium such as m-cresol, 1-methyl pyrrolidinone, etc., followed by separation and recrystallization from appropriate solvents, e.g., pyridine.

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 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.

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.

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 and now U.S. Pat. No. 3,367,-778. 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.

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, titled "Photographic Reversal Materials III," now abandoned. 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 bromoiodide, silver chlorobromide, 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, titled "Direct Positive Photographic Emulsions I" and now abandoned. 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, titled "Photographic Reversal Emulsions II" and now abandoned. 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 main 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 emusion 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 3,220,844 and include the water insoluble polymers of alkyl acrylates and methacrylates acrylic acid, sulfoalkyl acrylates or methacrylates and the like.

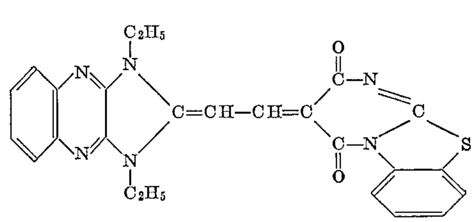
The dyes, reducing agents and metal compounds of the invention can be used with emulsions prepared, as indicated above, with any of the light-sensitive silver halide salts including silver chloride, silver bromide, silver chlorobromide, silver bromoiodide, silver chlorobromoiodide, etc. Particularly 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

3-[(1,3 - diethyl - 2(1H) - imidazo[4,5-b]quinoxalinylidene)ethylidene] - 2H - pyrimido[2,1-b]benzothiazole-2,4(3H)-dione



A mixture of 0.8 g. (1 mol. +50% excess) of 3-anilinomethylene-2H-pyrimido[2,1-b]benzothiazole - 2,4-(3H-dione, 0.7 g. (1 mol.) of 1,3-diethyl-2-methylimidazoquinoxalinium p-toluenesulfonate and 0.2 g. (1 mol. +50%) of triethylamine is refluxed in 20 ml. of acetic anhydride for 15 minutes. The reaction mixture is concentrated to dryness using a rotary evaporator. The residue is stirred in methanol, filtered and the solid is dissolved in hot pyridine, the solution is filtered and methanol is added. After chilling the solution, the resulting crystals are collected on a filter, and washed with methanol. The crude dye is dissolved in chloroform and passed through a neutral alumina column (activity II). The dye is isolated by concentrating the chloroform solution using a rotary evaporator. The yield of red crystals is 16% and they have a melting point greater than 310° C.

The above prepared dye containing the desensitizing 1,3-diethylimidazo[4,5-b]quinoxaline 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 chloroaurate per mole of silver and heating for 60 minutes at 65° C. The dye of the above example, 3-[(1,3 - diethyl - 2(1H)-imidazo[4,5-b]quinoxalinylidene) ethylidene] - 2H-pyrimido[2,1-b]-benzothiazole-2,4(3H)-dione, 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.

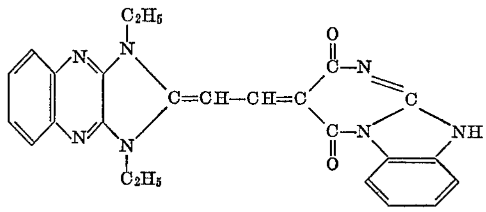
A sample of the coated support is then exposed on an Eastman Ib sensitometer using a tungsten light source and processed for 6 minutes at room temperature in Kodak D–19 developer which has the following composition:

	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 has a maximum density in the unexposed areas of 2.44 and a minimum density in exposed areas of 0.08, a maximum sensitivity of 530 mμ and a relative speed of 295. 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-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 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 fixing.

EXAMPLE 2

3-[(1,3-diethyl-2(1H)-imidazo[4,5-b]quinoxalinylidene)-ethylidene] - 2H - pyrimido[1,2 - a]benzimidazole-2,4-(3H)-dione

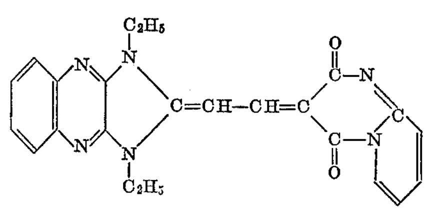


A mixture of 3.06 g. (1 mol.) of 3-anilinomethylene-2H-pyrimido[1,2-a]benzimidazole-2,4(3H)-dione, 0.2 ml. of acetic anhydride and 30 ml. of 1-methylpyrrolidinone are heated to the boiling point. Then 2.76 g. (1 mol.) of 1,3 - diethyl - 2-methylimidazo[4,5-b]quinoxalinium chloride and 2 g. (1 mol. +100% excess) of triethylamine are added and the whole is refluxed for 1 minute, cooled to room temperature and the solid is collected on a filter and washed with methanol. After the solid has been extracted with boiling pyridine it is dissolved in hot m-cresol, filtered and methanol is added. After chilling, the dye is collected on a filter. After another such treatment the yield of orange-red crystals is 8% and they have a melting point greater than 310° C.

The above dye containing the desensitizing 1,3-diethyl-imidazo[4,5-b]quinoxaline nucleus is photographically tested by the exact procedure described in above Example 1. The results as shown in Table 1 hereinafter indicate that this dye qualifies as a moderately good electron acceptor for fogged, direct positive photographic emulsion.

EXAMPLE 3

3-[(1,3-diethyl-2(1H)-imidazo[4,5-b]quinoxalinylidene)-ethylidene] - 2H - pyrido[1,2 - a]pyrimidine-2,4-(3H)-dione



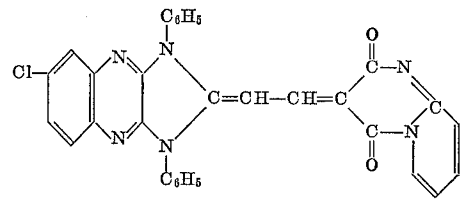
A mixture of 1.3 g. (1 mol.) of 3-anilinomethylene-2H - pyrido[1,2-a]pyrimidine-2,4(3H)-dione, 1.8 g. (1 mol.) of 1,3-diethyl-2-methylimidazo[4,5-b]quinoxalinium iodide, .6 g. (1 mol. +10% excess) of triethylamine is refluxed in 25 ml. of acetic anhydride for 5 minutes, allowed to cool and remain at room temperature for 2 hours. The solid is collected on a filter and washed with acetic anhydride.

The crude dye is dissolved in hot m-cresol, the solution filtered and methanol is added to the filtrate. After chilling and filtering the resulting solid is again treated as above. The yield of orange-red crystals is 27% and they have a melting point of 281–283° C. with decomposition.

This dye containing the desensitizing 1,3-diethylimidazo[4,5-b]quinoxaline nucleus is tested by the exact procedure of above Example 1 and found, as shown in Table 1 hereinafter, to be an excellent electron acceptor and spectral sensitizer for fogged direct positive photographic emulsions. The densities are shown to be 2.38 and 0.04 for the unexposed and exposed areas, respectively, with a maximum sensitivity at 550 mμ and a relative speed of 1000.

EXAMPLE 4

3 - [(6 - chloro-1,3-diphenyl-2(1H)-imidazo[4,5-b]quinoxalinylidene) - ethylidene]-2H-pyrido[1,2-a]pyrimidine-2,4(3H)-dione

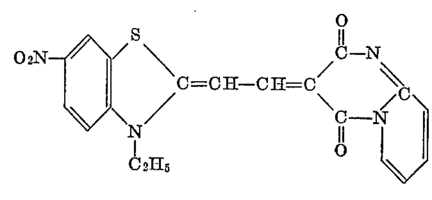


A mixture of 2.6 g. (1 mol.) of 3-anilinomethylene-2H-pyrido[1,2-a]pyrimidine-2,4(3H)-dione, 5.4 g. (1 mol.) of 6-chloro - 2 - methyl-1,3-diphenylimidazo[4,5-b]quinoxolinium p-toluenesulfonate and 1.1 g. (1 mol+10% excess) of triethylamine is refluxed for 5 minutes in 25 ml. of acetic anhydride. The reaction mixture is cooled, the solid is collected on a filter and the solid is washed with acetic anhydride. The crude dye is dissolved in 400 ml. of hot ethanol, the solution is filtered and 5 ml. of triethylamine is added to the solution. After chilling the solid is collected on a filter, washed with ethanol and dried. The yield of deep red crystals is 30% and they have a melting point of 282–286° C., with decomposition.

The above prepared dye is tested by the exact procedure described in above Example 1. The results in Table 1 hereinafter show densities of 2.04 and 0.04 in the unexposed and exposed areas, respectively, with maximum sensitivity at 550 mμ and a relative speed of 501, thereby indicating the dye of the above example is an excellent electron acceptor and spectral sensitizer for fogged direct positive photographic emulsions.

EXAMPLE 5

3-[(3-ethyl-6-nitro-2-benzothiazolinylidene)ethylidene]-2H-pyridol[1,2-a]pyrimidine-2,4(3H)-dione



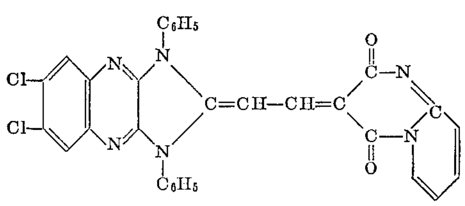
A mixture of 2.6 g. (1 mol.) of 3-anilinomethylene-2H-pyrido[1,2-a]pyrimidine-2,4(3H)-dione, 3.9 g. (1 mol.) of 3-ethyl-2-methyl-6-nitrobenzothiazolium p-toluenesulfonate, 1.1 g. (1 mol+10% excess) of triethylamine is refluxed for 5 minutes in 25 ml. of acetic anhydride. The reaction mixture is chilled, the solid is collected on a filter and it is washed with methanol. The crude dye is dissolved in a hot m-cresol, the solution is filtered and methanol plus 5 ml. of triethylamine are added. After chilling the solution, the dye is collected on a filter and washed with methanol. The yield of dark crystals with a shiny reflex is 64% and they have a melting point of 277–279° C., with decomposition.

The photographic testing of the above prepared dye containing the 3-ethyl-6-nitro-2-benzothiazole nucleus is carried out by the exact procedure described in above Example 1. The results, as shown in Table 1 hereinafter, of maximum densities of 1.82 and 0.04 in the unexposed and exposed areas, respectively, with maximum sensivity at 550 mμ and a relative speed of 436, indicate that the dye of the above example is an excellent electron acceptor and spectral sensitizer for fogged photographic reversal emulsions.

In place of the 3-ethyl-2-methyl-6-nitrobenzothiazolium p-toluene sulfonate 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 quaternary 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 quaternary 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 3-[(3-ethyl-6-nitro-2-benzoxazolinylidene) ethylidene] - 2H - pyrido[1,2-a]-pyrimidine-2,4(3H)-dione, the dye 3-[(3-ethyl-6-nitro-2-benzoselenazolinylidene)ethylidene] - 2H - pyrido[1,2-a] pyrimidine-2,4(3H)-dione, etc. The 3-anilinomethylene-2H-pyrido[1,2-a]pyrimidine-2,4(3H)-dione reactant can also be substituted in the above example by an equimolar amount of other related compounds coming under Formula III above such as, for example, 3-anilinomethylene-2H-pyrimido[2,1-b]benzothiazole - 2,4(3H)-dione, or 3-anilinomethylene - 2H-pyrimido[1,2 - a]-benzimidazole-2,4(3H)-dione, etc., to give the corresponding cyanine dyes having generally similar electron acceptor and spectral sensitizer properties.

EXAMPLE 6

3-[(6,7 - dichloro - 1,3 - diphenyl-2(1H)-imidazo[4,5-b] quinoxalinylidene)ethylidene] - 2H - pyrido[1,2 - a] pyrimidine-2,4(3H)-dione

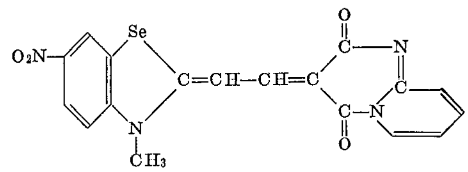


A mixture of 2.2 g. (1 mol.) of 3-anilinomethylene-2H-pyrido[1,2-a]pyrimidin - 2,4(3H) - dione and 5.3 g. (1 mol.) off 6,7-dichloro-2-methyl-1,3-diphenylimidazo[4,5-b]quinoxalinium iodide is refluxed in 50 ml. of acetate anhydride for 1 minute. The reaction mixture is filtered hot and the resulting solid is stirred in 300 ml. of ethanol containing 1.2 g. of DABCO (diazobicyclo-octane) for 2 hours. The crude dye is collected on a filter and washed with ethanol. The dye is purified by dissolving it in 25 ml. of m-cresol, filtering the solution, adding 350 ml. of methanol containing 2 g. of DABCO to the solution, chilling the whole for 4 hours and collecting the crystalline dye on a filter. The yield of shiny green crystals is 17% and they have a melting point 298–299° C., with decomposition.

The above prepared dye containing a desensitizing 6,7-dichloro-1,3-diphenyl-2(1H) - imidazo[4,5-b]quinoxaline nucleus is photographically tested by the exact procedure of above Example 1 and found, as shown in Table 1 hereinafter, to be an outstanding electron acceptor and spectral sensitizer for fogged direct positive photographic emulsions. Referring to Table 1, it will be noted that this dye indicates a relative speed of 1380, densities of 1.84 and 0.03 for the unexposed and exposed areas, respectively, and maximum sensitivity at 565 mμ.

EXAMPLE 7

3-[3-methyl-6-nitro-2-benzoselenazolinylidene)ethylidene]-2H-pyridol[1,2-a]pyrimidine-2,4(3H)-dione



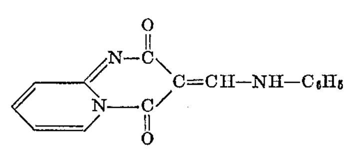
2,3-dimethyl - 6 - nitrobenzoselenazolium p-toluenesulfonate (1 mol., 2.13 g.) and 2,3-dimethylaminomethylene-2H-pyrido[1,2-a]pyrimidine - 2,4(3H) - dione hydrochloride (1 mol., 1.27 g.) are mixed in acetic anhydride (20 ml.) and the mixture heated under reflux for two minutes. The reaction mixture is chilled, crystalline dye as the hydrochloride salt collected on a filter, washed with acetone and dried. After two recrystallizations by dissolving the dye in m-cresol, turning into methyl alcohol and converting the dye to the free base by adding diazabicyclo-octane, the yield of pure dye is 38% and has a melting point of 301–302° C., with decomposition.

The above prepared dye containing a desensitizing nitrobenzoselenazole nucleus is photographically tested by the exact procedure of above Example 1 and found, as shown in Table 1 hereinafter, to be an excellent electron acceptor and spectral sensitizer for fogged direct positive photographic emulsions. Referring to Table 1, it will be noted that this dye indicates a relative speed of 795, densities of 1.82 and 0.17 for unexposed and exposed areas, respectively, and maximum sensitivity at 570 mμ.

The following Examples 8, 9 and 10 illustrate the preparation of a number of intermediate fused pyrimidinediones employed in the preceding cyanine dye examples.

EXAMPLE 8

3-anilinomethylene-2H-pyrido[1,2-a]pyrimidine-2,4(3H)-dione



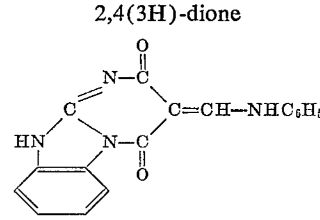
A mixture of 8.1. g. of 2H-pyrido[1,2-a]pyrimidine-2,4(3H)-dione and 100 ml. of m-cresol is heated to the refluxing temperature and then 8.3 g. (1 mol. +10% excess) of ethyl isoformanilide is added. The reaction mixture is then cooled and the product precipitated by the addition of methanol. After a recrystallization from pyridine (50 ml./g.) the yield of tan crystals was 40%.

EXAMPLE 9

In a like manner 3-anilinomethylene-2H-pyrimido[2,1-b]benzothiazole-2,4(3H)-dione is prepared from 3.6 g. (1 mol.) of 2H-pyrimido[2,1-b]benzothiazole-2,4(3H)-dione and 2.8 g. (1 mol. +10% excess) of ethyl isoformanilide. The yield of pale yellow crystals is 61%.

EXAMPLE 10

3-anilinomethylene-2H-pyrimido[1,2-a]benzimidazole-2,4(3H)-dione



A mixture of 10 g. (1 mol.) of 2H-pyrimido[1,2-a]-benzimidazole-2,4(3H)-dione and 100 ml. of 1-methyl pyrrolidinone is heated until solution is complete then 8.3 g. (1 mol. +10% excess) of ethyl isoformaniline is added. The reaction mixture is cooled and methanol is added, the whole is chilled and the solid is collected on a filter and washed with methanol. The yield of cream colored crystals is 64%.

The cyanine dyes prepared in accordance with above Examples 1 to 7 are photographically tested by the exact procedure described in Example 1 herein. The results are listed in Table 1 immediately below.

TABLE 1

Example No.	Dye Conc., g./mole silver	Relative clear speed	Density: Maximum in unexposed areas	Density: Minimum in exposed areas	Maximum sensitivity (mμ)
1	0.080	295	2.44	0.08	530
2	0.460	91	2.26	0.30	----------
3	0.450	1,000	2.38	0.04	550
4	0.650	501	2.04	0.04	550
5	0.650	436	1.82	0.04	550
6	0.650	1,380	1.84	0.03	565
7	0.750	795	1.82	0.17	570

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

EXAMPLE 11

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 3-[(1,3-diethyl-2(1H)-imidazo [4,5-b]-quinoxalinylidene)ethylidene]-2H - pyrido[1,2-a] pyrimidine-2,4-(3H)-dione (Example 3). 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 sufite, 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. Generally similar results are obtained when the dye of Example 6 is used in place of the above dye.

EXAMPLE 12

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 3 - [(3 - ethyl-6-nitro-2-benzothiazolinylidene)ethylidene]-2H-pyrido[1,2-a]-pyrimidine-2,4(3H)-dione is added (Example 5). The emulsion is coated on a support, and provides good direct positive images. Similar results are obtained when the dyes of Example 7 are substituted for the above dye.

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 incrasing 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.

We claim:

1. A direct positive photographic silver halide emulsion containing at least one cyanine dye selected from those comprising first and second 5- to 6-membered nitrogen containing heterocyclic nuclei joined by a linkage selected from the group consisting of a double bond and a dimethine bridge; the first of said nuclei being a complex fused pyrimidinedione nucleus joined at the 3-carbon atom thereof to said linkage; and, said second nucleus being a desensitizing nucleus joined at a carbon atom thereof to said linkage.

2. A direct positive emulsion in accordance with claim **1** wherein said cyanine dye contains a nitro substituted desensitizing nucleus.

3. A direct positive emulsion in accordance with claim **1** wherein said cyanine dye contains an imidazo[4,5-b]-quinoxaline desensitizing nucleus.

4. A direct positive emulsion in accordance with claim **1** in which the said silver halide is present in the form of fogged silver halide grains.

5. A direct positive emulsion in accordance with claim **1** in which the said silver halide is present in the form of reduction and gold fogged silver halide grains.

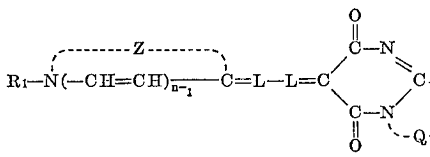
6. A direct positive emulsion in accordance with claim **1** containing a photographic color former.

7. A direct positive, photographic emulsion in accordance with claim **1** 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.

8. A direct positive, photographic emulsion in accordance with claim **1** 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.

9. A direct positive photographic silver halide emulsion containing at least one cyanine dye selected from those represented by the following general formula:



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

10. A direct positive emulsion in accordance with claim **9** wherein said Z represents the non-metallic atoms required to complete a nitrobenzothiazole nucleus.

11. A direct positive emulsion in accordance with claim **9** wherein said Z represents the non-metallic atoms required to complete a nitrobenzoxazole nucleus.

12. A direct positive emulsion in accordance with claim **9** wherein said Z represents the non-metallic atoms required to complete a nitrobenzoselenazole nucleus.

13. A direct positive emulsion in accordance with claim **9** wherein said Z represents the non-metallic atoms required to complete an imidazo[4,5-b]quinoxaline nucleus.

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

15. A direct positive emulsion in accordance with claim **9** in which the said silver halide is present in the form of reduction and gold fogged silver halide grains.

16. A direct positive emulsion in accordance with claim **9** containing a photographic color former.

17. A direct positive photographic emulsion in accordance with claim **9** 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.

18. A direct positive photographic emulsion in accordance with claim **9** 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.

19. A direct positive emulsion in accordance with claim **9** containing a cyanine dye selected from the group consisting of 3-[(1,3-diethyl-2(1H)-imidazo[4,5-b]quinoxalinylidene) ethylidene] - 2H - pyrimido[1,1 - b]benzothiazole-2,4(3H) - dione; 3-[(1,3-diethyl-2(1H) - imidazo[4,5-b]quinoxalinylidene) - ethylidene] - 2H - pyrimido[1,2-a]benzimidazole - 2,4(3H) - dione; 3 - [1,3 - diethyl-2(1H) - imidazo[4,5-b]quinoxalinylidene) - ethylidene]-2H - pyrido[1,2-a]pyrimidine - 2,4(3H) - dione; 3-[(6-chloro-1,3-diphenyl-2(1H) - imidazo[4,5-b]quinoxalinylidene) - ethylidene] - 2H - pyrido[1,2-a]pyrimidine - 2,4(3H) - dione; 3 - [(3 - ethyl - 6 - nitro - 2 - benzothiazolinylidene)ethylidene] - 2H - pyrido - [1,2-a]pyridimidine-2,4(3H) - dione; 3 - [6,7 - dichloro - 1,3 - diphenyl-2(1H) - imidazo[4,5 - b]quinoxalinylidene)ethylidene]-2H-pyrido[1,2 - a]pyrimidine - 2,4(3H) - dione; and 3-[(3 - methyl - 6 - nitro - 2 - benzoselenazolinylidene) ethylidene]-2H-pyrido[1,2-a]pyrimidine-2,4(3H)-dione.

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

21. A photographic element comprising a support having thereon at least one layer containing a direct positive emulsion of claim **7**.

22. A photographic element comprising a support having thereon at least one layer containing a direct positive emulsion of claim **8**.

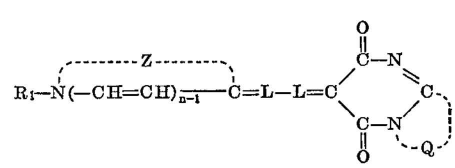
23. A photographic element comprising a support having thereon at least one layer containing a direct positive emulsion of claim **9**.

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

25. A photographic element comprising a support having thereon at least one layer containing a direct positive emulsion of claim **18**.

26. A light sensitive silver halide emulsion containing a cyanine dye comprising first and second 5- to 6-membered nitrogen containing heterocyclic nuclei joined by a linkage selected from the group consisting of a double bond and a dimethine bridge; the first of said nuclei being a complex fused pyrimidinedione nucleus joined at the 3-carbon atom thereof to said linkage; and, said second nucleus being a desensitizing nucleus joined at a carbon atom thereof to said linkage.

27. A light sensitive silver halide emulsion containing a cyanine dye selected from those represented by the following general 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; Z represents the non-metallic atoms necessary to complete a desensitizing nucleus containing 5 to 6 atoms; and, Q represents the non-metallic atoms required to complete a fused heterocyclic ring containing 5 to 6 atoms in said ring.

28. A light sensitive silver halide emulsion containing a cyanine dye selected from the group consisting of 3-[(1,3 - diethyl - 2(1H) - imidazo[4,5-b]quinoxalinylidene) - ethylidene] - 2H - pyrimido[2,1-b]benzothiazole-2,4(3H) - dione; 3 - [(1,3 - diethyl - 2(1H)-imidazo[4,5-b]quinoxalinylidene)ethylidene] - 2H - pyrimido[1,2-a]benzimidazole - 2,4(3H) - dione; 3 - [(1,3 - diethyl - 2(1H)-

imidazo]4,5-b]quinoxalinylidene)ethylidene] - 2H - pyrido[1,2-a]pyrimidine - 2,4(3H) - dione; 3 - [(6 - chloro-1,3 - diphenyl - 2(1H) - imidazo[4,5-b]quinoxalinylidene) ethylidene] - 2H - pyrido[1,2-a]pyrimidine - 2,4(3H)-dione; 3-[(3-ethyl - 6 - nitro - 2 - benzothiazolinylidene) ethylidene] - 2H - pyrido[1,2-a]pyrimidine - 2,4(3H)-dione; 3 - [(6,7 - dichloro - 1,3 - diphenyl - 2(1H) - imidazo - [4,5-b]quinoxalinylidene)ethylidene] - 2H - pyrido[1,2-a]pyrimidine - 2,4(3H) - dione; and 3-[(3-methyl - 6 - nitro - 2 - benzoselenazolinylidene)ethylidene]-2H-pyrido[1,2-a]pyrimidine-2,4(3H)-dione.

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U.S. Cl. X.R.

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