United States Patent Office 3,501,311 Patented Mar. 17, 1970

3,501,311

DIRECT POSITIVE SILVER HALIDE EMULSIONS CONTAINING CARBOCYANINE DYES HAVING A NITRO-SUBSTITUTED 3H-INDOLE NUCLEUS

Lewis L. Lincoln and Donald W. Heseltine, Rochester, N.Y., assignors to Eastman Kodak Company, Rochester, N.Y., a corporation of New Jersey

No Drawing. Filed Jan. 17, 1967, Ser. No. 609,793
Int. Cl. G03c 1/36, 1/10
U.S. Cl. 96—106 19 Claims

ABSTRACT OF THE DISCLOSURE

Direct positive silver halide emulsions contain carbocyanine dyes having a nitro-substituted 3H-indole nucleus.

This invention relates to novel photographic materials, and more particularly to new and improved direct positive photographic silver halide emulsions containing certain desensitizing cyanine dyes derived from 2,3,3-trialkyl-3H-nitroindoles, and to photographic elements prepared with such novel 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 highlight areas of the images obtained with these materials are substantially free from fog. However, known materials of this type have not exhibited the high speed required for many applications of photography. Also, such known materials have not shown the desired selective sensitivity, especially to radiation in the green-to-red region of the spectrum. It is evident, therefore, that there is need in the art for improved direct positive photographic materials having both good speed and desirable sensitivity to longer wavelength radiations.

We have now found that certain cyanine dyes containing certain 3,3-dialkyl-5 or 6-nitro-3H-indole nuclei are outstanding electron acceptors and spectral sensitizers in direct positive type photographic silver halide emulsions. They provide superior reversal systems, especially with fogged silver halide emulsions that are characterized by both good speed and desired sensitivity to radiation in the green-to-red region of the spectrum, with maximum sensitivity occurring in the region of about 560–625 mμ. The images produced with these new direct positive photographic emulsions are clear and sharp.

It is, accordingly, an object of this invention to provide new and improved direct positive photographic silver halide emulsions, and more particularly fogged emulsions of this type containing one or more of the desensitizing cyanine dyes of the invention. Another object of this invention is to provide novel light-sensitive photographic elements comprising a support material having thereon at least one layer of the novel direct positive photographic emulsions of this invention. Other objects will become apparent from the disclosure and the appended claims.

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, $(NH_4)_2PdCl_6$, 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 sulfonate	2.5
Sodium sulfite (anhydrous)	30.0
Hydroquinone	2.5
Sodium metaborate	10.0
Potassium bromide	0.5

Water to make 1.0 liter.

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. Patent 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 developable to metallic silver with conventional surface image developing compositions. The silver salt of the sheet 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 make 1.0 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 sliver, 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 Saubenoir 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 applications Ser. No. 609,794, filed Jan. 17, 1967, now abandoned, and continuation-in-part Ser. No. 619,936, filed Mar. 2, 1967, and titled "Photographic Reversal Materials III." 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 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—50.00 mg.
Acetic acid (glacial)—3.47 cc.
Sodium acetate—11.49 g.
Potassium bromide—119.00 mg.
Water to make 1.00 liter.

The grains of such emulsions will lose at least about 35% 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 applications Ser. No. 609,778, filed Jan. 17, 1967, now abandoned, and continuation-in-part, Ser. No. 619,909, filed Mar. 2, 1967, and titled, "Direct Positive Photographic Emulsions I." Such grains advantageously have a rather uniform diameter frequency distribution, as disclosed and claimed in Illingsworth U.S. patent applications Ser. No. 609,790, filed Jan. 17, 1967, now abandoned, and continuation-in-part Ser. No. 619,948, filed Mar. 2, 1967, and titled, "Photographic Reversal Emulsions II." 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, particlularly 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, reducing agents and metal compounds of the invention are advantageously incorporated in the washed, finished silver halide emulsion and should, of course, be uniformly distributed throughout the emulsion. The methods of incorporating dyes and other addenda in emulsions are relatively simple and well known to those skilled in the art of emulsion making. For example, it is convenient to add them from solutions in appropriate solvents, in which case the solvent selected should be completely free from any deleterious effect on the ultimate light-sensitive materials. Methanol, isopropanol, pyridine, water, etc., alone or in admixtures, have proven satisfactory as solvents for this purpose. The type of silver halide emulsions that can be sensitized with the new dyes include any of those prepared with hydrophilic colloids that are known to be satisfactory for dispersing silver halides, for example, emulsions comprising natural materials such as gelatin, albumin, agar-agar, gum arabic, alginic acid, etc., and hydrophilic synthetic resins such as polyvinyl alcohol, polyvinyl pyrrolidone, cellulose ethers, partially hydrolyzed cellulose acetate, 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 chloro bromoiodide, etc. Particularly useful for direct positive fogged emulsions in which the silver salt is a silver bromohalide comprising more than 50 mole percent bromide. As indicated previously, certain dyes of this invention are also useful in emulsions which contain color formers. This is unexpected since related prior art dyes cannot be used in emulsions containing a color former.

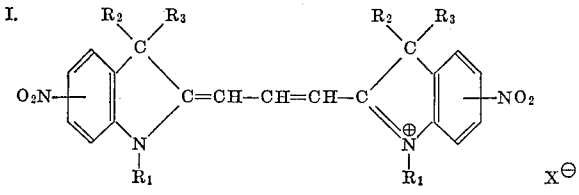
The novel emulsions of this invention may be coated on any suitable photographic support, such as glass, film base such as cellulose acetate, cellulose acetate butyrate, polyesters such as polyethylene terephthalate, paper, baryta coated paper, polyolefin coated paper, e.g., polyethylene or polypropylene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

produce the novel photographic elements of the invention.

Suitable desensitizing cyanine dyes for preparing the novel and improved direct positive photographic silver halide emulsions, and more particularly fogged emulsions of this type, include carbocyanine dyes in which at least one of the heterocyclic nuclei thereof is a nitro-substituted indole nucleus.

One highly useful class of carbocyanine dyes of the invention include the symmetrical dyes represented by the following general formula:

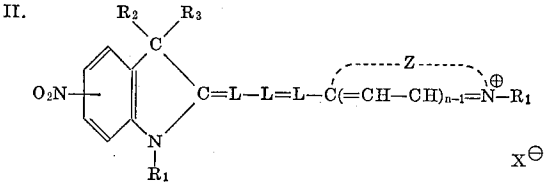
I.



wherein R_1 represents an alkyl group (including substituted alkyl), preferably, a lower alkyl group containing from 1 to 4 carbon atoms, e.g., methyl, ethyl, propyl, isopropyl, butyl, hexyl, cyclohexyl, decyl, dodecyl, etc., an alkoxyalkyl group, e.g. β-methoxyethyl, ω-butoxybutyl, etc., a hydroxyalkyl group, e.g., β-hydroxyethyl, ω-hydroxybutyl, etc., a carboxyalkyl group, e.g., β-carboxyethyl, ω-carboxybutyl, etc., a sulfoalkyl group, e.g., β-sulfoethyl, γ-sulfobutyl, ω-sulfobutyl, etc., a sulfatoalkyl group, e.g., β-sulfatoethyl, ω-sulfatobutyl, etc., an acyloxyalkyl group, e.g., β-acetoxyethyl, γ-propionyloxypropyl, ω-butyryloxybutyl, etc., an alkoxycarbonylalkyl, e.g., β-methoxycarbonylethyl, ω-methoxycarbonylbutyl, etc., and the like, or an alkenyl group, e.g., allyl, 1-propenyl, 2-butenyl, etc., or an aryl group, e.g., phenyl, tolyl, xylyl, chlorophenyl, methoxyphenyl, naphthyl, etc., and the like; R_2 and R_3 each represents an alkyl group, preferably a lower alkyl containing from 1 to 4 carbon atoms, e.g., methyl, ethyl, propyl isopropyl, butyl, hexyl, decyl, dodecyl, etc.; and X represents an acid anion, e.g., chloride, bromide, iodide, thiocyanate, sulfamate, perchlorate, p-toluenesulfonate, methyl sulfate, ethyl sulfate, etc., which acid anion may be incorporated in said R_1 group.

Another very useful class of carbocyanine dyes of the invention include the unsymmetrical dyes represented by the following general formula:

II.



wherein R_1, R_2, R_3 and X are as previously defined, *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., and Z represents the nonmetallic atoms required to complete a sensitizing or 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,
4-nitrothiazole,
benzothiazole,
4-chlorobenzothiazole,
5-nitrobenzothiazole,
5-chloro-6-5-chlorobenzothiazole,
nitrobenzothiazole,
6-nitrobenzothiazole,
5,6-dinitrobenzothiazole,
6-chlorobenzothiazole,
7-chlorobenzothiazole,
4-methylbenzothiazole,
5-methylbenzothiazole,
6-methylbenzothiazole,
5-bromobenzothiazole,
6-bromobenzothiazole,
5-phenylbenzothiazole,
6-phenylbenzothiazole,
4-methoxybenzothiazole,
5-methoxybenzothiazole,
6-methoxybenzothiazole,
5-bromobenzothiazole,
5-iodobenzothiazole,
6-iodobenzothiazole,
4-ethoxybenzothiazole,
5-ethoxybenzothiazole,
tetrahydrobenzothiazole,
5,6-dimethoxybenzothiazole,
5,6-dioxymethylenebenzothiazole,
5-hydroxybenzothiazole,
6-hydroxybenzothiazole,
α-naphthothiazole,
β-naphthothiazole,
5-methoxy-β-naphthothiazole,
5-ethoxy-β-naphthothiazole,
8-methoxy-α-naphthothiazole,
7-methoxy-α-naphthothiazole,
4'-methoxythianaphtheno-7', 6', 4, 5-thiazole, nitro group substituted naphthothiazoles, etc.; an oxazole nucleus, e.g.,

4-methyloxazole,
4-nitrooxazole,
5-methyloxazole,
4-phenyloxazole,
4,5-diphenyloxazole,
4-ethyloxazole,
4,5-dimethyloxazole,
5-phenyloxazole,
benzoxazole,
5-chlorobenzoxazole,
5-nitrobenzoxazole,
5-methylbenzoxazole,
5-phenylbenzoxazole,
6-nitrobenzoxazole,
6-methylbenzoxazole,
5,6-dinitrobenzoxazole,
5,6-dimethylbenzoxazole,
4,6-dimethylbenzoxazole,
5-methoxybenzoxazole,
5-ethoxybenzoxazole,
5-chlorobenzoxazole,
5-bromobenzoxazole,
5-iodobenzoxazole,
6-methoxybenzoxazole,
5-hydroxybenzoxazole,
6-hydroxybenzoxazole,
α-naphthoxazole,
β-naphthoxazole,

nitro group substituted naphthoxazoles, etc., a selenazole nucleus, e.g.,

4-methylselenazole,
4-phenylselenazole,
4-nitrobenzoselenazole,
6-nitrobenzoselenazole,
benzoselenazole,
5-chlorobenzoselenazole,

i-methoxybenzoselenazole,
i-hydroxybenzoselenazole,
i- or 6-nitrobenzoselenazole,
etrahydrobenzoselenazole,
:-naphthoselenazole,
i-naphthoselenazole,

iitro group substituted naphthoselenazoles, etc., a thiazoine nucleus, e.g., thiazoline, 4-methylthiazoline, 4-nitrohiazoline, etc.; a pyridine nucleus, e.g., 2-pyridine, i-methyl-2-pyridine, 4-pyridine, 3-methyl-4-pyridine, a iitro substituted pyridine, etc.; a quinoline nucleus, e.g.,

:-quinoline,
i-methyl-2-quinoline,
i-ethyl-2-quinoline,
i-chloro-2-quinoline,
i-chloro-2-quinoline,
i-methoxy-2-quinoline,
i-ethoxy-2-quinoline,
i-hydroxy-2-quinoline,
i-quinoline,
i-methoxy-4-quinoline,
'-methyl-4-quinoline,
i-chloro-4-quinoline,
:-isoquinoline,
i,4-dihydro-1-isoquinoline,
i-isoquinoline,

iitro group substituted quinolines, etc.; a 3,3-dialkylindolenine nucleus, e.g., 3,3-dimethyl-5 or 6-cyanoindolenine, 3,3-dimethyl-5-chloroindolenine, etc.; and, an imidazole nucleus, e.g.,

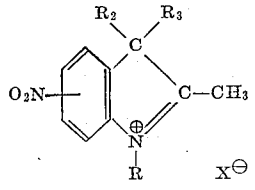
midazole,
.-alkylimidazole,
.-alkyl-4-phenylimidazole,
.-alkyl-4,5-dimethylimidazole,
)enzimidazole,
.-alkylbenzimidazole,
.-aryl-5,6-dichlorobenzimidazole,
.-alkyl-α-naphthimidazole,
.-aryl-β-naphthimidazole,
.-alkyl-5-methoxy-α-naphthimidazole, etc.

The nuclei wherein Z represents the atoms required to complete a nitro substituted heterocyclic nucleus form particularly efficacious desensitizing dyes for preparing the direct positive photographic emulsions and elements of the invention.

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

The symmetrical cyanine dyes are defined by Formula I above are conveniently prepared by condensing an indolium salt represented by the general formula:

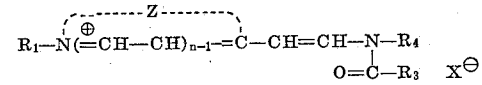
II.



wherein R_1, R_2, R_3 and X are as previously defined, with diethoxymethylacetate, at elevated temperatures, in an inert solvent medium such as γ-butyrolactone, acetic anhydride, and the like, in the proportions of approximately 2 moles of the compound of Formula III above to each mole, or more, of the diethoxymethylacetate. After chilling, the crude dye is separated and then purified by one or more recrystallizations from an appropriate solvent, e.g., methanol.

To prepare the unsymmetrical cyanine dyes as defined by Formula II above a heterocyclic salt represented by the general formula:

IV.



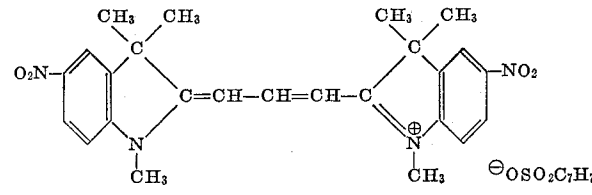
wherein *n*, R_1, X and Z are as previously defined, R_4 represents an aryl group, e.g. phenyl, tolyl, etc., and R_5 represents an alkyl group, e.g., methyl, ethyl, propyl, isopropyl, butyl, etc. is condensed with a compound of Formula III above by heating approximately equimolar proportions of these components with 2 or more moles of sodium acetate, in an inert solvent medium, e.g., acetic anhydride, followed by chilling separation of the crude dye, and purification by one or more recrystallizations from an appropriate solvent, e.g., methanol.

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 invention is further illustrated by the following examples.

EXAMPLE I

1,1',3,3,3',3'-hexamethyl-5,5'-dinitroindocarbocyanine-p-toluenesulfonate



1,2,3,3 - tetramethyl - 5 - nitro - 3H - indolium - p-toluenesulfonate (2 mols., 1.9 g.) and diethoxymethylacetate (1 mol.+100% excess, 1.6 g.) were mixed in γ-butyrolactone (7 ml.) contained in a large test tube and the mixture heated over a free flame for one minute. The mixture was chilled, stirred with an excess of ether and the dye crystallized from solution. The crystalline dye was collected on a Buchner funnel, washed with acetone and dried. After two recrystallizations from methyl alcohol the yield of pure dye was 0.4 g. (25%) M.P. 298–299° C. decomposes.

The above-prepared symmetrical cyanine dye of Formula I above containing two desensitizing nitro groups substituted indole nuclei was photographically tested as an electron acceptor and spectral sensitizer for fogged direct positive photographic silver halide emulsions as follows:

The above-prepared dye, 1,1',3,3,3',3'-hexamethyl-5,5'-dinitroindocarbocyanine-p-toluenesulfonate is then added to the above fogged emulsion in amount sufficient to give a concentration of 0.176 gram of the dye per mole of

silver. The resulting emulsion is then coated on a cellulose acetate film support at a coverage of 100 mg. of silver and 400 mg. of gelatin per square foot of support.

A sample of the coated support is then exposed on an Eastman Ib sensitometer using 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

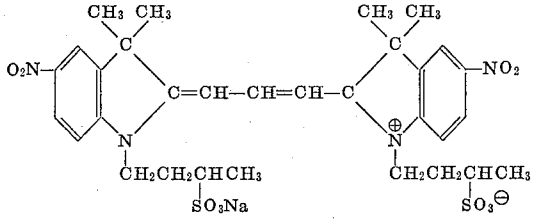
Water to make 1.0 liter.

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 relative speed of 1150, maximum density in the unexposed areas of 1.82, a minimum density in the exposed areas of 0.04, and maximum sensitizing at 620 mμ, whereas the related dye of Example 3 included herein for comparison purposes differing only by having a pentamethine linkage in place of the trimethine linkage of above Example I, has a relative speed of only 40, densities of 1.84 and 0.70, respectively, and no sensitization maximum. In another comparison, the styryl dyes containing the 1,3,3-trimethyl-5-nitro-3H-indolium salt nucleus as illustrated by Examples 5, 6 and 7 included herein for comparison purposes, show relative speeds of 209, 25 and 32, respectively, minimum densities in the exposed areas of 0.54, 1.22 and 0.26, respectively, indicating thereby very poor contrast and unsuitability as desensitizers for fogged direct positive photographic emulsions. The dyes of Examples 6 and 7 also show no sensitization maximum.

These results indicate clearly that the dye compound of above Example I of Formula I of the invention is especially well-suited to function as both an electron acceptor and spectral sensitizer. It thus provides excellent quality direct positive photographic silver halide emulsions. Excellent magenta images are obtained when the color former 1-(2,4,6-trichlorophenyl)-3,3′-(2″,4″-di-t-amylphenoxyacetamido)benzimidazo-5-pyrazolone is incorporated in the emulsion of this example, the emulsion is coated on a support, exposed to a tungsten source through Wratten filter No. 61 and No. 16, and reversal processed as described in Graham et al. U.S. Patent 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 II

Anhydro-3,3,3′,3′-tetramethyl-5,5′-dinitro-1,1′-di(3-sulfobutyl)indocarbocyanine hydroxide, monosodium salt

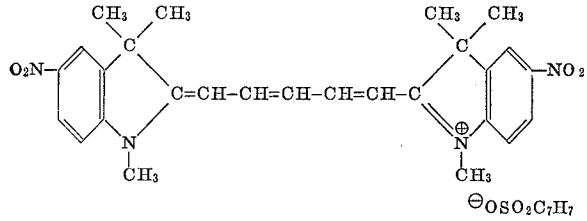


Anhydro - 2,3,3 - trimethyl - 5-nitro-1-(3-sulfobutyl)-3H-indolium hydroxide (2 mols., 3.4 g.) and diethoxymethylacetate (1 mol.+100% excess, 1.6 g.) were mixed in acetic anhydride (10 ml.) and the mixture heated under reflux for one minute. The mixture was chilled, crystalline dye collected on a Buchner funnel, washed with acetone and dried. For solubility purposes the dye was converted to the monosodium salt by dissolving in methyl alcohol and adding solid sodium iodide (1.5 g.) with stirring. The solid dye was collected on a Buchner funnel, washed with acetone and dried. After two recrystallizations from methyl alcohol, the yield of pure dye was 0.65 g. (19%), M.P. above 320° C.

The above-prepared symmetrical cyanine dye of Formula I above containing two desensitizing nitro-substituted indole nuclei was photographically tested by the exact procedure of Example I and, as shown in Table I hereinafter, had an indicated relative speed of 479, densities of 1.86 and 0.05, and sensitizing maximum at 620 mμ. These results clearly show that the dye of this example is an excellent electron acceptor and spectral sensitizer for fogged direct positive photographic emulsions. Comparison with the dye of Example III (symmetrical nitro-substituted indolium salt nuclei with pentamethine linkage) and Examples 5, 6 and 7 (styryl dyes containing a nitro-substituted indolium salt nucleus) indicate that the dye of this example is far superior over the above-mentioned comparison examples as to relative speed, contrast and sensitivity, and is eminently suited as an electron acceptor and spectral sensitizer for fogged direct positive photographic reversal emulsions. In place of the sodium, there can be substituted other alkali metal salts, e.g., potassium, lithium, etc.

EXAMPLE III

1,1′;3,3;3′,3′-hexamethyl-5,5′-dinitroindodicarbocyanine p-toluenesulfonate

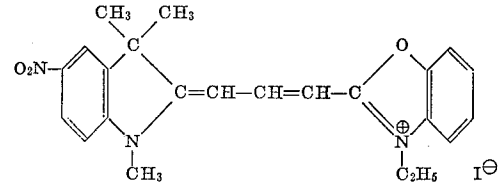


1,2,3,3-tetramethyl - 5 - nitro - 3H-indolium-p-toluenesulfonate (2 mols., 1.9 g.) and 1,3,3-trimethoxypropene (1 mol. + 100% excess, 1.6 g.) were mixed in γ-butyrolactone (7 ml.) contained in a large test tube and the mixture heated over a free flame for one minute. The mixture was chilled, stirred with an excess of ether and th dye crystallized from solution, the crystalline dye was collected on a Buchner funnel, washed with acetone and dried. After two recrystallizations from methyl alcohol the yield of pure dye was 0.2 g. (13%) M.P. 261–262° C. dec.

The above-prepared dye contains two desensitizing nitro-substituted indole nuclei joined together through a pentamethine linkage, but as set forth in the comments under above Examples 1 and 2, this dye was found to be unsuitable as an electron acceptor and spectral sensitizer for fogged direct positive photographic emulsions. The results as shown in Table I hereinafter indicate a relative speed of only 40, a minimum density in exposed areas of 0.70 indicating relatively poor contrast, and no sensitizing maximum.

EXAMPLE IV

3′-ethyl-1,3,3-trimethyl-5-nitroindo-oxacarbocyanine iodide



1,2,3,3 - tetramethyl - 5 - nitro-3H-indolium-p-toluenesulfonate (1 mol., 0.65 g.) and 2-acetanilidovinyl-3-ethylbenzoxazolium iodide (1 mol., 0.72 g.) were mixed in acetic anhydride (10 ml.), sodium acetate (2 mols., 0.28 g.) added and the mixture heated under reflux for

three minutes. The mixture was chilled, crystalline dye collected on a Buchner funnel, washed with acetone and dried. After two recrystallizations from methyl alcohol the yield of pure dye was 0.5 g. (58%) M.P. 284–285° C. dec.

The above-prepared dye illustrates the dyes of the invention coming under Formula II above. In this instance, the desensitizing nitro group substituted indole nucleus is attached through the trimethine linkage to a sensitizing benzoxazolium salt nucleus. This dye was photographically tested by the exact procedure described in Example I and found as shown in Table I hereinafter to be a moderately good electron acceptor and spectral sensitizer for fogged direct positive photographic emulsions.

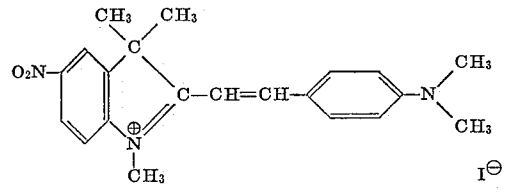
The relative speed thereof is 174, the densities 1.62 and 0.06 and the sensitizing maximum is 565 mμ, which results are somewhat below those of the dyes of Examples I and II, but markedly superior to the overall results indicated for the comparison of Examples III, V, VI and VII.

In place of the 2 - acetanilidovinyl-3-ethylbenzoxazolium iodide in the above example, there can be substituted by an equal molar amount of other intermediates of Formula IV such as, for example, a 2-acetanilidovinyl-3-alkyl (e.g. methyl, ethyl, propyl, butyl, etc.) benzothiazolium salt, e.g., the chloride, bromide iodide, perchlorate, p-toluenesulfonate, etc. salt, or a 2-acetanilidovinyl-3-alkyl (e.g., methyl, ethyl, propyl, butyl, etc.) benzoselenazolium salt, e.g., the chloride, bromide, iodide, perchlorate, p-toluenesulfonate, etc., salt and the like to give the corresponding desensitizing cyanine dyes having generally similar electron acceptor and sensitizer properties, for example, the dye 3' - ethyl - 1,3,3-trimethyl-5-nitroindothiacarbocyanine iodide, the dye 3'-ethyl-1,3,3-trimethyl-5-nitroindo-selenacarbocyanine iodide, etc.

It will also be apparent from the definition of Formula IV that other intermediates having a nitro substituent such as 2-acetanilidovinyl-3-alkyl-5, or 6-nitrobenzoxazolium salts, or 2-acetanilidovinyl-3-alkyl-5 or 6-nitrobenzothiazolium salts, or 2-acetanilidovinyl-3-alkyl-5 or 6-nitrobenzoselenazolium salts can also be substituted in the above example for the specified 2-acetanilidovinyl-3-ethylbenzoxazolium iodide to give the corresponding desensitizing carbocyanine dyes having generally similar electron acceptor and spectral sensitizer properties and useful for preparing direct positive photographic silver halide emulsions, for example, the dye 3'-ethyl-5'-nitro-1,3,3-trimethyl - 5 - nitroindo-oxacarbocyanine iodide, the dye 3'-ethyl-5'-nitro-1,3,3-trimethyl-5-nitroindo-thiacarbocyanine iodide, the dye 3'-ethyl-5'-nitro-1,3,3-trimethyl-5-nitroindo - selenacarbocyanine iodide, etc.

EXAMPLE V

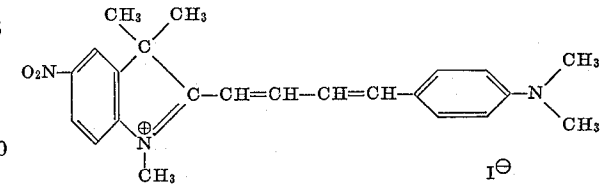
2-p-dimethylaminostyryl-1,3,3-trimethyl-5-nitro-3H-indolium iodide



1,2,3,3-tetramethyl-5-nitro-3H-indolium iodide (1 mol., 1.15 g.) and p-dimethylaminobenzaldehyde (1 mol. +100% excess, 1 g.) were mixed in acetic anhydride (20 ml.) and the mixture heated under reflux for two minutes. The mixture was chilled, crystalline dye collected on a Buchner funnel, washed with acetone and dried. After two recrystallizations from methanol the yield of pure dye was 1.1 g. (69%) M.P. 282–283° C. dec.

EXAMPLE VI

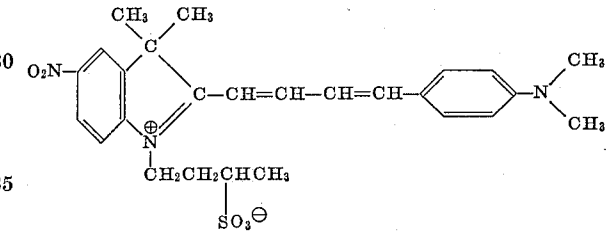
Anhydro-2-(4-p-dimethylaminophenyl-1,3-butadienyl)-1,3,3-trimethyl-5-nitro-3H-indolium iodide



1,2,3,3-tetramethyl-5-nitro-3H-indolium iodide (1 mol., 1.15 g.) and p-dimethylaminocinnamaldehyde (1 mol. +100% excess, 1.2 g.) were mixed in acetic anhydride (20 ml.) and the mixture heated under reflux for one minute. The mixture was chilled, crystalline dye collected on a Buchner funnel, washed with acetone and dried. After two recrystallizations from methyl alcohol the yield of pure dye was 1 g. (60%) M.P. 226–227° C. dec.

EXAMPLE VII

Anhydro - 2-(4-p-dimethylaminophenyl-1,3,-butadienyl)-3,3-dimethyl-5-nitro-1-(3-sulfobutyl)-3H-indolium hydroxide



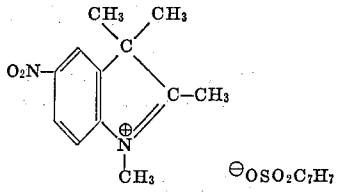
Anhydro-2,3,3-trimethyl-5-nitro-3-(3 - sulfobutyl)-3H-indolium hydroxide (1 mol., 1.1 g.) and p-dimethylaminocinnamaldehyde (1 mol. +100% excess, 1.2 g.) were mixed in acetic anhydride (20 ml.) and the mixture heated under reflux for one minute. The mixture was chilled, crystalline dye collected on a Buchner funnel, washed with acetone and dried. After two recrystallizations from methyl alcohol the yield of pure dye was 0.2 g. (12%) M.P. above 320° C.

As indicated in the comments in the preceding examples, the above styryl type dyes of Examples V, VI and VII are included herein for purpose of comparison with the dyes of the invention. These dyes were also photographically treated by the exact procedure of Example I and found, as shown in Table I hereinafter, to be unsuitable as electron acceptors and spectral sensitizers for fogged direct positive photographic emulsions as compared with the dyes of the invention illustrated by Examples I, II and IV herein. Referring more specifically to Table I, it will be seen that Examples I, II and IV had relative speeds of 1150, 479 and 174, respectively, densities of 1.82 and 0.04, 1.86 and 0.05, and 1.62 and 0.06, respectively, and sensitizing maximum at 620, 620 and 565 mμ, respectively, whereas Examples V, VI and VII had relative speeds of 209, 25 and 32, respectively, densities of 1.88 and 0.54, 1.90 and 1.22, and 1.84 and 0.26, respectively, indicating thereby very poor contrast, and only Example V showed a sensitizing maximum at 675 mμ. Accordingly, the dyes of the invention as illustrated by preceding Examples I, II and IV are markedly superior electron acceptors and spectral sensitizers for fogged direct positive photographic emulsions.

The following examples illustrate the preparation of indolium salt intermediates employed in the preceding examples for the preparation of the cyanine dyes of Examples I to V.

EXAMPLE VIII

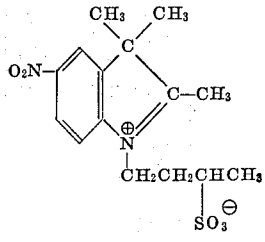
1,2,3,3-tetramethyl-5-nitro-3H-indolium p-toluene-sulfonate



2,3,3-trimethyl-5-nitro-3H-indole (1 mol., 10.2 g.) and methyl-p-toluenesulfonate (1 mol.+10% excess, 10.2 g.) and the mixture heated on a steam bath. The formed pink cake was ground under acetone, collected on a Buchner funnel, washed with more acetone and dried. After two recrystallizations from a one to one mixture of ethanol and ether the yield of pure salt was 12 g. (68%), M.P. 186–188° C. dec.

EXAMPLE IX

Anhydro-2,3,3-trimethyl-5-nitro-1-(3-sulfobutyl)-3H-indolium hydroxide



2,3,3-trimethyl-5-nitro-3H-indole (1 mol., 10.2 g.) was mixed with 2,4-butanesultone (1 mol.+10% excess, 7.5 g.) in acetonitrile (50 ml.) and the mixture heated under reflux for sixteen hours. The yellow solid that had precipitated from solution was collected on a filter funnel, washed with acetone and dried. The yield of crude salt was 14 g. (82%). The salt was used without further purification to prepare dyes. The 5-nitro-2,3,3-trimethyl-3H-indole reactant employed in the above example is described in Chem. Zentr. 1936 II, page 1437.

The effectiveness of the dyes of Examples I to VII as electron acceptors and spectral sensitizers for fogged direct positive photographic materials was determined by the exact test procedure described in above Example I. The results are listed in the following table.

TABLE I

Dye of Ex. No.	Dye conc., g./mole silver	Relative Clear Speed	Density: Max., Unexposed Areas	Density: Min., Exposed Areas	Sensitizing Max. (mμ)
I	0.45	1,150	1.82	0.04	620
II	0.45	479	1.86	0.05	620
III	0.21	40	1.84	*0.70*	no sens.
IV	0.50	174	1.62	0.06	565
V	0.85	209	1.88	*0.54*	675
VI	0.20	25	1.90	*1.22*	no sens.
VII	0.19	32	1.84	*0.26*	no sens.

The following examples illustrate the preparation of photographic elements and images with the novel direct positive emulsions of the invention.

EXAMPLE X

To 9.0 pounds of a silver chloride gelatin emulsion containing an equivalent of 100 grams of silver nitrate is added 0.017 gram of 1,1',3,3,3',3'-hexamethyl-5,5'-dinitroindocarbocyanine p-toluenesulfonate (Example I). The emulsion is coated on a nonglossy 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 water:

	Grams
N-methyl-p-aminophenol sulfate	3.1
Sodium sulfite, des.	45.0
Hydroquinone	12.0
Sodium carbonate, des.	67.5
Potassium bromide	1.9
Water to 1.0 liter.	

The light-fogged material can be exposed to an image with light modulated by a Wratten No. 15 filter to give a direct positive image. Similar results are obtained when the dye of Example II is substituted for the 1,1',3,3,3',3'-hexamethyl-5,5'-dinitroindocarbocyanine p-toluenesulfonate.

EXAMPLE XI

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'-ethyl-1,3,3-trimethyl-5-nitroindo-oxacarbocyanine iodide (Example IV). The emulsion is coated on a support, and provides good direct positive images. Similar results are obtained when the dye 3'-ethyl-1,3,3-trimethyl-5-nitroindo-thia-carbocyanine iodide or the 3'-ethyl-1,3,3-trimethyl-5-nitroindo-selenacarbocyanine iodide is substituted for the dye of Example IV.

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

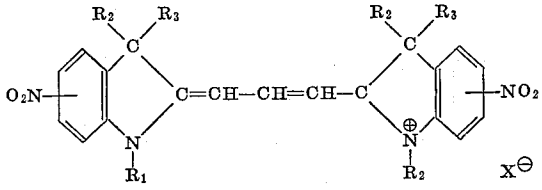
The photographic silver halide emulsion and other layers present in the photographic elements made accordingly to the invention can be hardened with any suitable hardener, including aldehyde hardeners such as formaldehyde, and mucochloric acid, aziridine hardeners, hardeners which are derivatives of 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. Patent 2,322,027, issued June 15, 1943, Fierke et al. U.S. Patent 2,801,171, issued July 30, 1957, Fisher U.S. Patents 1,055,155 and 1,102,028, issued Mar. 4, 1913, and June 30, 1914, respectively, and Wilmanns U.S. Patent 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:

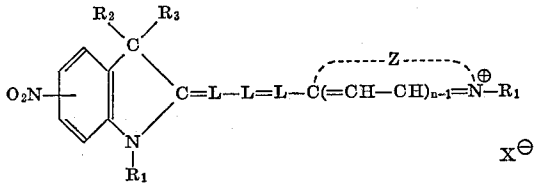
1. A fogged direct positive photographic silver halide emulsion comprising a carbocyanine dye in which at least one of the heterocyclic nuclei thereof is a nitro substituted indole nucleus.

2. A direct positive silver halide emulsion of claim 1 wherein said carbocyanine dye is selected from those represented by the following general formula:



wherein 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 an alkyl group and X represents an acid anion.

3. A direct positive silver halide emulsion of claim 1 wherein said carbocyanine dye is 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, R_2 and R_3 each represents an alkyl group, X represents an acid anion, and Z represents the nonmetallic atoms required to complete a nucleus selected from the class consisting of a thiazole nucleus, an oxazole, nucleus, a selenazole nucleus, a thiazoline nucleus, a pyridine nucleus, a quinoline nucleus, and an imidazole nucleus.

4. A direct positive silver halide emulsion of claim 3 wherein said Z represents the atoms required to complete a nucleus selected from the class consisting of a benzothiazole nucleus, a benzoxazole nucleus, a benzoselenazole nucleus, a 3,3-dialkylindolenine nucleus, and a benzimidazole nucleus.

5. A direct positive silver halide emulsion of claim 3 wherein said Z represents the atoms required to complete a densensitizing nucleus.

6. A direct positive silver halide emulsion of claim 1 wherein said carbocyanine dye is a 1,1',3,3,3',3'-hexamethyl-5,5'-dinitroindocarbocyanine salt.

7. A direct positive silver halide emulsion of claim 1 wherein said carbocyanine dye is an anhydro 3,3,3',3'-tetramethyl-5,5'-dinitro-1,1'-di-(3-sulfobutyl) indocarbocyanine hydroxide, monalkali metal salt.

8. A direct positive silver halide emulsion of claim 1 wherein said carbocyanine dye is a 3'-ethyl-1,3,3-trimethyl-5-nitroindo-oxacarbocyanine salt.

9. A direct positive silver halide emulsion in accordance with claim 1 containing a photographic color coupler.

10. A direct positive silver halide emulsion in accordance with claim 2 containing a photographic color coupler.

11. A photographic element comprising a support coated with at least one layer containing a direct positive silver halide emulsion of claim 1.

12. A photographic element comprising a support coated with at least one layer containing a direct positive silver halide emulsion of claim 2.

13. A photographic element comprising a support coated with at least one layer containing a direct positive silver halide emulsion of claim 3.

14. 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.

15. 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 size which is within about 40% of the average grain size.

16. A direct-positive, photographic emulsion in accordance with claim 2 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.

17. A direct-positive, photographic emulsion in accordance with claim 2 which comprises fogged silver halide grains, at least 95%, by weight, of said grains having a size which is within about 40% of the average grain size.

18. A direct-positive, photographic emulsion in accordance with claim 3 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.

19. A direct-positive, photographic emulsion in accordance with claim 3 which comprises fogged silver halide grains, at least 95%, by weight, of said graints having a size which is within about 40% of the average grain size.

References Cited

UNITED STATES PATENTS

2,953,561	9/1960	Doorenbos et al.	96—101 X
3,367,779	2/1968	Nakazawa et al.	96—101

NORMAN G. TORCHIN, Primary Examiner

R. E. FICHTER, Assistant Examiner

U.S. Cl. X.R.

96—101, 107