

United States Patent

Haefner et al.

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[54] **PHOTOGRAPHIC MATERIALS AND PROCESSES**

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[51] Int. Cl.G03c 1/62, G03c 5/24

[58] Field of Search96/48, 63, 64, 88

[56] **References Cited**

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[57]

ABSTRACT

This invention relates to a direct positive light sensitive photographic material comprising non-silver halide physically developable nuclei having adsorbed thereto an organic dye which is an electron acceptor and a process for preparing a positive metallic image comprising physically developing the same.

14 Claims, No Drawings

PHOTOGRAPHIC MATERIALS AND PROCESSES

This invention relates to light sensitive photographic materials and processes, and more particularly to photographic materials and processes which employ physically developable nuclei.

It is known that direct positive images can be obtained by exposing non-silver halide photosensitive materials comprising physically developable nuclei associated with a photosensitive substance which, on exposure to actinic radiation, forms a desensitizing agent that renders the exposed nuclei inert. A direct positive image is obtained at the non-exposed nuclei by physical development. For example, Hanson, Jr. et al., U.S. Pat. No. 3,320,064, issued May 16, 1967, describe a photosensitive composition comprising a light sensitive organic azide compound, silver nuclei and a thioether photographic coupler. When exposed to light, the organic azide reacts with the thioether coupler to release a composition which deactivates the silver nuclei in exposed areas. On physical development a direct positive image is obtained. While this system has proven quite useful in providing direct positive images by physical development, a simpler and more efficient physical development system would be desirable.

As noted by Hanson, Jr. et al., in U.S. Pat. No. 3,320,064, it is sometimes desirable to employ non-silver halide physically developable nuclei, such as in materials where high image resolution is desired.

It is, accordingly, an object of this invention to provide direct positive light sensitive photographic compositions.

Another object of this invention is to provide photographic elements comprising direct positive photosensitive compositions.

A further object of this invention is to provide photographic materials and processes which yield high image resolution.

Still another object of this invention is to provide a novel direct positive photographic physical development process.

Other objects will be apparent from this disclosure and the appended claims.

We have now made the important and valuable discovery that novel direct positive light sensitive photographic materials are provided by adsorbing an organic dye which is an electron acceptor onto physically developable nuclei.

In accordance with one embodiment of this invention, non-silver halide direct positive photographic materials are provided which comprise physically developable nuclei having adsorbed thereto an organic dye which is an electron acceptor. On imagewise exposure, such materials provide good direct positive images by physical development.

In accordance with another embodiment of this invention, photographic elements are provided comprising a support having coated thereon a photosensitive material comprising physically developable nuclei having an electron accepting organic dye adsorbed thereto.

In still another embodiment of this invention, a novel photographic process is provided which comprises physically developing an exposed photographic material comprising physically developable nuclei having adsorbed thereto an organic dye which is an electron acceptor.

The photographic materials and processes of this invention employ physically developable nuclei. Physically developable nuclei are well known in the art, and frequently consist of dispersed particulate matter which function as centers for physical development. The term "physically developable nuclei" is a word of art, and refers to materials which are active sites for the deposition of metal ions, e.g., a metal complex such as a silver complex. In the practice of the present invention, the organic electron accepting dye apparently destroys the ability of the nuclei to promote physical development in just those areas where the dye has been exposed to actinic radiation.

Any of the physically developable nuclei known to the art can be employed in the processes and materials of this invention. Such nucleating agents can consist of particles of any of the heavier metals, such as gold, palladium, platinum and

silver, including colloidal sulfides and selenides of the metals of Groups I-B, II-B, IV-B, VIII of the Periodic Table, such as zinc, cadmium, nickel and so forth. Metallic particles such as titanium particles, for example in the form of titanium dioxide, palladium particles, and silver particles such as Carey Lea silver particles provide particularly good results in the practice of the present invention.

The physically developable nuclei typically have an average particle size in the range up to 0.5 micron and preferably from about 0.001 micron to about 0.25 micron. The physical development nuclei in accordance with the invention can be coated on a support in extremely thin layers. Concentrations of physically developable nuclei of about 10^{-4} moles per square foot provide highly useful results. Ranges of about 0.005 to 10 mg. per square foot, and preferably from about 0.02 to 0.5 mg. per square foot, physically developable nuclei can be used.

The electron accepting organic dyes which are employed in this invention include cyanine, merocyanine and benzylidene dyes which contain a desensitizing nucleus; and desensitizing dyes such as pyrylium, thiapyrylium, and selenapyrylium. These dyes when incorporated in a test negative gelatin silver bromoiodide emulsion, the halide consisting of 99.35 mole percent bromide and 0.65 mole percent iodide, at a concentration of 0.2 millimole of dye per mole of silver halide, desensitize the emulsion more than 0.4 log E when the test emulsion is coated on a support, exposed through a step wedge in a sensitometer (to obtain D_{max}) to light having a wavelength of 365 nm., processed for three minutes at 20° C. in Kodak developer D-19, and is fixed, washed and dried. As used herein the "test" negative silver bromoiodide emulsions are prepared as follows:

In a container with temperature control is put a solution with the following composition:

(A)	Potassium bromide	165 g.
	Potassium iodide	5 g.
	Gelatin	65 g.
	Water	1,700 cc.

And in another container is put a filtered solution consisting of:

(b)	Silver nitrate	200 g.
	Water	2,000 cc.

Solution A is kept at a temperature of 54° C. during precipitation and ripening, while solution B is put in a separating funnel at a temperature of 54° C. The silver nitrate solution runs from the separating funnel through a calibrated nozzle into the container, the contents of which are kept in constant motion during precipitation and ripening, and later during finishing, by a mechanical stirrer. The precipitation is conducted over a period of 10 minutes.

The developer employed in the test referred to above is Kodak developer D-19 which has the following composition:

N-Methyl-p-aminophenol sulfate	2.0 g.
Sodium sulfite, desiccated	90.0 g.
Hydroquinone	8.0 g.
Sodium carbonate, monohydrated	52.5 g.
Potassium bromide	5.0 g.
Water to make	1.0 liter

As noted above, the dyes employed in this invention desensitize conventional negative silver halide emulsions. Such emulsions are inherently sensitive to blue radiation. The present dyes reduce that sensitivity. In addition, these dyes fail

to provide practical spectral sensitization for such emulsions. Therefore, it was quite unexpected to find that they spectrally sensitized photonucleating coatings.

The dyes useful herein are electron accepting dyes. They have an anodic polarographic half-wave potential and a cathodic half-wave polarographic potential which, when added together algebraically, give a positive sum. As used herein and in the appended claims, polarographic measurements are made in accordance with the following procedure. Cathodic polarographic half-wave values are obtained against an aqueous silver-silver chloride reference electrode for the electrochemical reduction of the test dye using controlled-potential polarographic techniques. A 1×10^{-4} M methanol solution of the test dye is prepared. The solvent is 100 percent methanol, if the dye is soluble therein. In some instances, it is necessary to use mixtures of methanol and another solvent, e.g., acetone, to prepare the 1×10^{-4} M solution of dye. There is present in the test solution, as supporting electrolyte, 0.1 M lithium chloride. Only the most positive (least negative) half-wave potential value observed is considered, and it is designated herein as E_c . Voltammetric electropositive (anodic) half-wave values are determined against an aqueous silver-silver chloride reference electrode for the electrochemical oxidation of the dyes at a pyrolytic graphite electrode, and are obtained by controlled-potential voltammetry using solutions identical to those used to determine the cathodic polarographic values. Only the most negative (least positive) half-wave potential observed is utilized, and it is designated herein as E_a . In both measurements, the reference electrode (aqueous silver-silver chloride) is maintained at 20° C. Signs are given according to the recommendation of IUPAC at the Stockholm Convention, 1953. The well known general principles of polarographic measurements are used. See Kolthoff and Lingane, "Polarography" second edition, Interscience Publishers, New York (1952). The principles of controlled-potential electrochemical instrumentation which allows precise measurements in solvents of low conductivity is described by Kelly, Jones and Fisher, *Anal. Chem.*, 31, 1475 (1959). The theory of potential sweep voltammetry such as that employed in obtaining the anodic determinations is described by Delahay, "New Instrumental Methods in Electrochemistry" Interscience Publishers, New York (1954) and Nicholson and Shain, *Anal. Chem.*, 36, 706 (1964). Information concerning the utility and characteristics of the pyrolytic graphite electrode is described by Chuang, Fried and Elving, *Anal. Chem.*, 36, (1964). It should be noted that the spectral sensitizing dyes operable in this invention include those dyes which contain oxidizable ions, such as iodide. For example, many dyes which are iodide salts are useful herein. However, the polarographic measurements referred to above cannot be determined in the presence of oxidizable ions. Therefore, such dyes are converted, just for purposes of making polarographic determinations, to an anion such as chloride or p-toluenesulfonate, which do not interfere in making accurate polarographic measurements. Hence, dyes containing oxidizable ions are included within the scope of the useful dyes defined herein and in the appended claims.

As noted above, this invention is applicable to spectral sensitization of photonuclear coatings or layers with certain cyanine, merocyanine, benzylidene and pyrylium type dyes which also function as electron acceptors. The term "cyanine dye," as used herein, is to be construed broadly as inclusive of simple cyanines, carbocyanines, dicarbocyanines, tricarbocyanines, etc. containing a desensitizing nucleus. The term includes symmetrical and unsymmetrical cyanine dyes, as well as chain-methine-substituted dyes. Also included are the reaction products of bromine and certain simple cyanine sensitizing dyes. Cyanine dyes useful herein feature the amidinium chromophoric system. See Mees and James, "The Theory of the Photographic Process" published by the MacMillan Company (1966) page 201. The term "merocyanine" is also used broadly, and includes dyes which are characterized by the amidic chromophoric system. See Mees and James, *supra*, pages 201 and 218. The term "pyrylium type" dye in the above text refers broadly to pyrylium salts, thiapyrylium salts

and selenapyrylium salts.

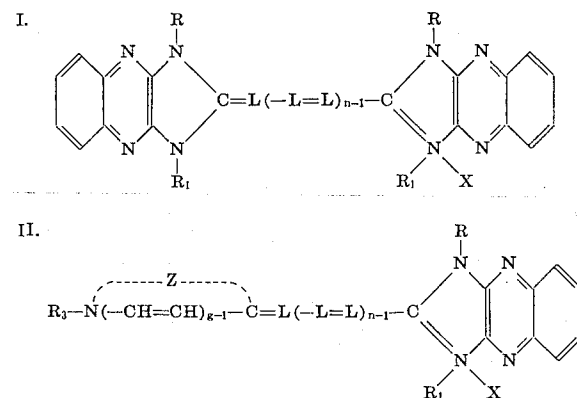
As used herein and in the appended claims, "desensitizing nucleus" refers to those nuclei which, when converted to a symmetrical cyanine dye and added to a gelatin silver chlorobromide emulsion containing 40 mole percent chloride and 60 mole percent bromide, at a concentration of from about 0.01 to 0.2 g. dye per mole of silver, cause at least an 80 percent loss in the blue speed of the test emulsion when it is sensitometrically exposed and developed three minutes at 20° C. in Kodak developer D-19, the composition of which is given above. Preferably, the desensitizing nuclei are those which, when converted to a symmetrical carbocyanine dye and tested as described above, essentially completely desensitize the test emulsion to blue radiation. Substantially complete desensitization, as used herein, results in at least a 90 percent, and preferably a 95 percent loss of speed to blue radiation. Desensitizing nuclei which are especially effective herein include 5- to 6-membered nitrogen containing heterocyclic nuclei of the type used in cyanine dyes having a nitro substituent; imidazo[4,5-b]quinoxaline nuclei; and 2-aromatic substituted indole nuclei. Other desensitizing nuclei are the nitro substituted aryl nuclei used in the benzylidene type dyes of this invention.

One highly useful class of dyes which may be used in this invention includes cyanine and merocyanine dyes which contain the desensitizing imidazo[4,5-b]quinoxaline nucleus. Typical useful cyanine dye salts of this class comprise two nuclei joined together by methine linkage, one of the nuclei being an imidazo[4,5-b]quinoxaline nucleus which is joined through the 2-carbon atom thereof to the methine linkage, and a second nucleus to complete the cyanine dye. Advantageously, the second nucleus of such dyes contains a heterocyclic nitrogen atom and the methine linkage is part of a polyene chain containing an equal number of alternating single and double bonds, one terminal carbon atom of the polyene chain being the 2-carbon atom of an imidazo[4,5-b]quinoxaline nucleus, the other terminal carbon atom of the polyene chain being in the second nucleus and attached to a heterocyclic nitrogen atom. Preferably, the second nucleus in these dyes is also a desensitizing nucleus.

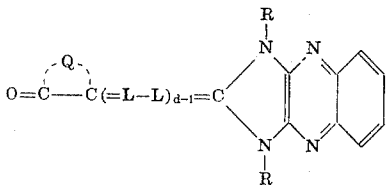
Also useful herein are merocyanine dyes comprising two nuclei joined together through an acyclic methine group which is part of a polyene chain containing an equal number of alternating single and double bonds, one of the terminal atoms of the polyene chain being the 2-carbon atom of an imidazo[4,5-b]quinoxaline nucleus, the other terminal carbon atom of the polyene chain being in a heterocyclic ring of a second nucleus and attached to an extracyclic carbonylic oxygen atom.

Also useful herein are cyanine dyes comprising two imidazo[4,5-b]quinoxaline nuclei joined together through a polyene chain containing an equal number of alternating single and double bonds, the terminal carbon atoms of the polyene chain being the 2-carbon atoms, respectively, of the imidazo[4,5-b]quinoxaline nuclei. Preferably, the polyene chain of these dyes is composed of five carbon atoms.

Preferred classes of dyes featuring an imidazo[4,5-b]quinoxaline nucleus include those represented by the following general formulas:



III.



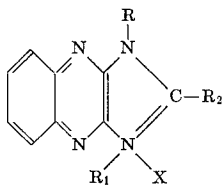
wherein n represents a positive integer of from 1 to 4, g represents a positive integer of from 1 to 2, d represents a positive integer of from 1 to 3, each L represents a methine linkage, such as $=CH-$, $=C(CH_3)-$ or $=C(C_6H_5)-$; each R and R_1 represents a substituent independently selected from the group consisting of an organic substituent, such as an alkyl group (including substituted alkyl), preferably containing from 1 to 18 carbon atoms, e.g., methyl, ethyl, propyl, isopropyl, butyl, sec-butyl, hexyl, cyclohexyl, dodecyl, octadecyl, hydroxyalkyl, (e.g., 2-hydroxyethyl, 3-hydroxypropyl, etc.) and alkenyl substituents, such as allyl, 1-propenyl, 2-propenyl, 1-butenyl, 2-butenyl and 3-butenyl, etc., and alkaryl substituents such as benzyl and 2-phenylethyl; and, aryl substituents, e.g., phenyl, *p*-tolyl, *o*-tolyl, 3,4-dichlorophenyl, etc., groups; R_2 represents an alkyl substituent, (preferably having from 1-4 carbon atoms), e.g., methyl, 3-sulfopropyl, isopropyl, butyl, sec-butyl, 4-sulfobutyl, dodecyl, 2-hydroxyethyl, 3-hydroxypropyl, 2-methoxyethyl, 2-ethoxyethyl, 2-phenylethyl, 2-carboxyethyl, carboxymethyl, 3-carboxypropyl, 2-acetoxyethyl, 3-acetoxypropyl, carbomethoxymethyl, carboxyethoxyethyl, etc., groups, aryl such as phenyl, or alkenyl such as allyl or 2-butenyl; X represents an acid anion, which may be part of R_3 , e.g., chloride, bromide, iodide, perchlorate, sulfamate, *p*-toluenesulfonate, methyl sulfate, etc.; Z represents the non-metallic atoms necessary to complete a 5- to 6-membered nitrogen containing heterocyclic nucleus of the type used in cyanine dyes, which nucleus may contain a second hetero atom such as, oxygen, sulfur, selenium or nitrogen such as the following nuclei: a thiazole nucleus, e.g., thiazole, 4-methylthiazole, 4-phenylthiazole, 5-methylthiazole, 5-phenylthiazole, 4,5-dimethylthiazole, 4,5-diphenylthiazole, 4-(2-thienyl)thiazole, benzothiazole, 4-chlorobenzothiazole, 5-chlorobenzothiazole, 6-chlorobenzothiazole, 7-chlorobenzothiazole, 4-methylbenzothiazole, 5-methylbenzothiazole, 6-methylbenzothiazole, 5-bromobenzothiazole, 6-bromobenzothiazole, 5-phenylbenzothiazole, 5-phenylbenzothiazole, 4-methoxybenzothiazole, 5-methoxybenzothiazole, 6-methoxybenzothiazole, 5-iodobenzothiazole, 4-ethoxybenzothiazole, 5-ethoxybenzothiazole, tetrahydrobenzothiazole, 5,6-dimethoxybenzothiazole, 5,6-dioxymethylenebenzothiazole, 5-hydroxybenzothiazole, 6-hydroxybenzothiazole, naphtho[2,1-d]thiazole, naphtho[1,2-d]thiazole, 5-methoxynaphtho[2,3-d]thiazole, 5-ethoxynaphtho[2,3-d]thiazole, 8-methoxynaphtho[2,3-d]thiazole, 7-methoxynaphtho[2,3-d]thiazole, 4'-methoxythianaphtho-7',6', 4,5-thiazole, etc.; an oxazole nucleus, e.g., 4-methylloxazole, 5-methylloxazole, 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-chlorobenzoxazole, 6-methoxybenzoxazole, 5-hydroxybenzoxazole, 6-hydroxybenzoxazole, naphtho[2,1-d]oxazole, naphtho[1,2-d]oxazole, etc.; a selenazole nucleus, e.g., 4-methylselenazole, 4-phenylselenazole, benzoselenazole, 5-chlorobenzoselenazole, 5-methoxybenzoselenazole, 5-hydroxybenzoselenazole, tetrahydrobenzoselenazole, naphtho[2,1-d]selenazole, naphtho[1,2-d]selenazole, etc.; a thiazoline nucleus, e.g., thiazoline, 4-methylthiazoline, etc.; a pyridine nucleus, e.g., 2-pyridine, 5-methyl-2-pyridine, 4-pyridine, 3-methyl-4-pyridine, etc.; a quinoline nucleus, e.g., 2-quinoline,

3-methyl-2-quinoline, 5-ethyl-2-quinoline, 6-chloro-2-quinoline, 8-chloro-2-quinoline, 6-methoxy-2-quinoline, 8-ethoxy-2-quinoline, 8-hydroxy-2-quinoline, 4-quinoline, 6-methoxy-4-quinoline, 7-methyl-4-quinoline, 8-chloro-4-quinoline, 1-isoquinoline, 3,4-dihydro-1-isoquinoline, 3-isoquinoline, etc.; a 3,3-dialkylindolenine nucleus, e.g., 3,3-dimethylindolenine, 3,3,5-trimethylindolenine, etc.; and, an imidazole nucleus, e.g., imidazole, 1-alkylimidazole, 1-alkyl-4-phenylimidazole, 1-alkyl-4,5-dimethylimidazole, benzimidazole, 1-alkylbenzimidazole, 1-aryl-5,6-dichlorobenzimidazole, 1-alkyl-1H-naphth[1,2-d]imidazole, 1-aryl-3-H-naphth[1,2-d]imidazole, 1-alkyl-5-methoxy-1H-naphth[1,2-d]imidazole, etc.; and, Q represents the non-metallic atoms required to complete a 5 to 6 membered heterocyclic ketomethylene nucleus, of the type used in merocyanine dyes, typically containing a nitrogen atom and a second hetero atom selected from nitrogen, sulfur and oxygen, such as a pyrazolin-5-one nucleus (e.g., 3-methyl-1-phenyl-2-pyrazolin-5-one, 1-phenyl-2-pyrazolin-5-one, 1-(2-benzothiazolyl)-3-methyl-2-pyrazolin-5-one, etc.); an isoxazolone nucleus (e.g., 3-phenyl-5(4H)-isoxazolone, 3-methyl-5-(4H)-isoxazolone, etc.); an oxindole nucleus (e.g., 1-alkyl-2,3-dihydro-2-oxindoles, etc.), a 2,4,6-triketohexahydropyrimidine nucleus (e.g., barbituric acid or 2-thiobarbituric acid as well as their 1-alkyl (e.g., 1-methyl-1-ethyl, 1-propyl, 1-heptyl, etc.) or 1,3-dialkyl (e.g., 1,3-dimethyl, 1,3-diethyl, 1,3-dipropyl, 1,3-diisopropyl, 1,3-dicyclohexyl, 1,3-di(β -methoxyethyl), etc., or 1,3-diaryl (e.g., 1,3-diphenyl, 1,3-di(*p*-chlorophenyl), 1,3-di(*p*-ethoxycarbonylphenyl), etc.), or 1-aryl (e.g., 1-phenyl, 1-*p*-chlorophenyl, 1-*p*-ethoxycarbonylphenyl), etc.) or 1-alkyl-3-aryl (e.g., 1-ethyl-3-phenyl, 1-n-heptyl-3-phenyl, etc.) derivatives; a rhodanine nucleus (i.e., 2-thio-2,4-thiazolidinedione series), such as rhodanine, 3-alkylrhodanines (e.g., 3-ethylrhodanine, 3-allylrhodanine, etc.), 3-carboxyalkylrhodanines (e.g., 3-(2-carboxyethyl) rhodanine, 3-(4-carboxybutyl)rhodanine, etc.), 3-sulfoalkylrhodanines (e.g., 3-(2-sulfoethyl)rhodanine, 3-(3-sulfopropyl) rhodanine, 3-(4-sulfobutyl)rhodanine, etc.), or 3-arylrhodanines (e.g., 3-phenylrhodanine, etc.) etc.; a 2(3H)-imidazo[1,2-a]pyridone nucleus; a 5,7-dioxo-6,7-dihydro-5-thiazolo[3,2-a]pyrimidine nucleus (e.g., 5,7-dioxo-3-phenyl-6,7-dihydro-5-thiazolo[3,2-a]pyrimidine, etc.); a 2-thio-2,4-oxazolinedione nucleus (i.e., those of the 2-thio-2,4(3H,5H)-oxazolinedione series, e.g., 3-ethyl-2-thio-2,4-oxazolinedione, 3-(2-sulfoethyl)-2-thio-2,4-oxazolinedione, 3-(4-sulfobutyl)-2-thio-2,4-oxazolinedione, 3-(3-carboxypropyl)-2-thio-2,4-oxazolinedione, etc.); a thianaphthenone nucleus (e.g., 3-(2H)-thianaphthenone, etc.); a 2-thio-2,5-thiazolidinedione nucleus (i.e., the 2-thio-2,5(3H,4H)-thiazolidinedione series, e.g., 3-ethyl-2-thio-2,5-thiazolidinedione, etc.); a 2,4-thiazolidinedione nucleus (e.g., 2,4-thiazolidinedione, 3-ethyl-2,4-thiazolidinedione, 3-phenyl-2,4-thiazolidinedione, 3- α -naphthyl-2,4-thiazolidinedione, etc.); a thiazolidinone nucleus (e.g., 4-thiazolidinone, 3-ethyl-4-thiazolidinone, 3-phenyl-4-thiazolidinone, 3- α -naphthyl-4-thiazolidinone, etc.); a 2-thiazolin-4-one series (e.g., 2-ethylmercapto-2-thiazolin-4-one, 2-alkylphenylamino-2-thiazolin-4-one, 2-diphenylamino-2-thiazolin-4-one, etc.); a 2-imino-4-oxazolidinone (i.e., pseudohydantoin) nucleus; a 2,4-imidazolinedione (hydantoin) series (e.g., 2,4-imidazolinedione, 3-ethyl-2,4-imidazolinedione, 3-phenyl-2,4-imidazolinedione, 3- α -naphthyl-2,4-imidazolinedione, 1,3-diethyl-2,4-imidazolinedione, 1-ethyl-3-phenyl-2,4-imidazolinedione, 1-ethyl-3- α -naphthyl-2,4-imidazolinedione, 1,3-diphenyl-2,4-imidazolinedione, etc.); a 2-thio-2,4-imidazolinedione (i.e., 2-thiohydantoin) nucleus (e.g., 2-thio-2,4-imidazolinedione, 3-ethyl-2-thio-2,4-imidazolinedione, 3-(4-sulfobutyl)-2-thio-2,4-imidazolinedione, 3-(2-carboxyethyl)-2-thio-2,4-imidazolinedione, 3-phenyl-2-thio-2,4-imidazolinedione, 3- α -naphthyl-2-thio-2,4-imidazolinedione, 1,3-diethyl-2-thio-2,4-imidazolinedione, 1-ethyl-3-phenyl-2-thio-2,4-imidazolinedione, 1-ethyl-3- α -naphthyl-2-thio-2,4-imidazolinedione, 1,3-diphenyl-2-thio-2,4-

imidazolidinedione, etc.); a 2-imidazolin-5-one nucleus (e.g., 2-propylmercapto-2-imidazolin-5-one, etc.), etc. Especially useful are nuclei wherein Q represents the atoms required to complete a heterocyclic nucleus containing 5 atoms in the heterocyclic ring, 3 of said atoms being carbon atoms, 1 of said atoms being a nitrogen atom, and 1 of said atoms being selected from the group consisting of a nitrogen atom, an oxygen atom, and a sulfur atom.

Dyes containing an imidazo[4,5-b]quinoxalinium salt can be prepared from intermediates represented by the formula:

IV.

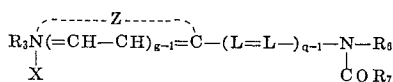


wherein R, R₁ and X are as previously defined and R₂ represents a member selected from an alkyl group of from 1-4 carbon atoms, e.g., methyl, ethyl, propyl, isopropyl, butyl, sec-butyl, etc., or benzyl, phenylethyl. In general, such dyes are produced by heating a mixture of a quaternary salt of above Formula IV with the appropriate intermediate. The reaction mixtures are heated to advantage in any of the suitable solvents used in dye synthesis including solvents such as ethanol, propanol, dioxane, pyridine, quinoline, and the like, at temperatures up to the reflux temperature of the mixture. Advantageously, the reaction is carried out in the presence of a basic condensing agent such as a pyridine or a tertiary amine, e.g., trimethylamine, triethylamine, tri-n-propylamine, tri-n-butylamine, N-methylpiperidine, N-ethylpiperidine, N,N-dimethylaniline, N,N-diethylaniline, etc.

The symmetrical cyanine dyes of Formula I are prepared to advantage by heating a mixture of a compound of Formula IV (in which R₂ is methyl) with diethoxymethyl acetate (forms carbocyanine), trimethoxypropene (forms dicarbocyanine), 1-anilino-5-phenylimino-1,3-pentadiene hydrochloride (forms tricarbocyanine), etc., preferably in a solvent and in the presence of a basic condensing agent such as mentioned above, if desired.

The unsymmetrical cyanine dyes of Formula II are prepared advantageously by heating a mixture of a compound of Formula IV (in which R₂ is methyl) with a compound of the formula:

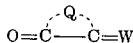
V.



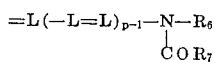
wherein R₃, L, X and Z are as previously defined, g and q each represents a positive integer of from 1 to 2, R₆ represents an aryl group of from 6-7 carbon atoms, e.g., phenyl, p-tolyl, etc., and R₇ represents an alkyl group of from 1-12 carbon atoms. This is preferably carried out in a suitable solvent and in the presence of a basic condensing agent.

Merocyanine dyes, such as those of Formula III, are made to advantage by heating a mixture of a compound of Formula IV (in which R₂ is methyl) with a compound of the formula:

VI.



wherein Q is as defined previously and W represents the group



wherein p represents a positive integer of from 1 to 2 and L, R₆ and R₇ are as previously defined.

Typical specific useful dyes containing the imidazo-[4,5-b]quinoxalinium nucleus include 1,1',3,3'-tetraethylimidazo[4,5-b]quinoxalinocarbocyanine chloride; 1,1',3,3'-tetraethyl-imidazo[4,5-b]quinoxalinodicarbocyanine chloride; 1,3,3'-triethylimidazo[4,5-b]quinoxalinooxacarbocyanine iodide; 1,3,3'-triethylimidazo[4,5-b]quinoxalinothiacarbocyanine iodide; 1,3-diethyl-1',3',3'-trimethylimidazo[4,5-b]quinoxalinoindocarbocyanine iodide; 1,3-diethyl-3'-methylimidazo[4,5-b]-quinoxalinothiazolinocarbocyanine iodide; 1,1',3-triethylimidazo[4,5-b]quinoxalino-2'-carbocyanine iodide; 5-[(1,3-diethylimidazo[4,5-b]quinoxalin-2-ylidene)-ethylidene]-3-ethylrhodanine; 5-[(1,3-diethylimidazo[4,5-b]quinoxalin-2-ylidene)ethylidene]-1,3-diethyl-2-thiobarbituric acid; 1,1',3,3'-tetra(2-hydroxy-ethyl)imidazo[4,5-b]quinoxalino-carbocyanine iodide; 1,3-di(2-hydroxyethyl)-1',3',3'-trimethylimidazo[4,5-b]quinoxalinoindocarbocyanine iodide; 1,1',3,3'-tetraallylimidazo[4,5-b]-quinoxalinocarbocyanine p-toluenesulfonate; 1,3-diallyl-3'-ethylimidazo[4,5-b]quinoxalinooxacarbocyanine iodide; 1,3-diallyl-3'-ethylimidazo[4,5-b]quinoxalinothiacarbocyanine iodide; 1,3-diallyl-1',3',3'-trimethylimidazo[4,5-b]quinoxalinoindocarbocyanine iodide; 1,3-diallyl-3'-ethyl-4',5'-benzoimidazo-[4,5-b]quinoxalinothiacarbocyanine p-toluenesulfonate; 1,3-diallyl-1'-ethylimidazo[4,5b]quinoxalino-2'-carbocyanine iodide; 5-[(1,3-diallylimidazo[4,5-b]quinoxalin-2(3H)-ylidene)-ethylidene]-3-ethylrhodanine; 1,1',3,3'-tetraphenylimidazo[4,5-b]quinoxalinocarbocyanine p-toluenesulfonate; 3'-ethyl-1,3-diphenylimidazo[4,5]quinoxalinothiacyanine iodide; 3'-ethyl-1,3-diphenylimidazo[4,5-b]quinoxalinooxacarbocyanine iodide; 3'-ethyl-1,3-diphenylimidazo[4,5-b]quinoxalinothiacarbocyanine iodide; 1',3',3'-trimethyl-1,3-diphenylimidazo[4,5-b]quinoxalinoindocarbocyanine iodide; 1'-ethyl-1,3-diphenylimidazo[4,5-b]-quinoxalino-2'-carbocyanine iodide; 5-[(1,3-diphenylimidazo-[4,5-b]quinoxalin-2(3H)-ylidene)ethylidene]-3-ethylrhodanine, 6-chloro-2-[(1-methyl-2-phenyl-3-indolyl)vinyl]-1,3-diphenylimidazo[4,5-b]quinoxalinium p-toluenesulfonate, 6,6'-dinitro-1,1',3,3'-tetraphenylimidazo[4,5-b]quinoxalino p-toluenesulfonate, and 9-[2-(1-methyl-2-phenyl-3-indolyl)vinyl]-8,10-diphenyl-8H-benzof[j]imidazo[4,5-b]quinoxalinium bromide.

A more detailed description for the preparation of dyes of the type described above is contained in Brooker and Van Lare Belgian Pat. No. 660,253, issued Mar. 15, 1965, and Brooker and Van Lare Belgian Pat. No. 695,368 granted Sept. 11, 1967, and U.S. Application Ser. No. 609,791 filed Jan. 17, 1967, which is a continuation-in-part of Brooker and VanLare U.S. Application Ser. No. 573,183, filed Aug. 18, 1966, and Brooker and Van Lare U.S. Application Ser. No. 286,469, filed June 10, 1963.

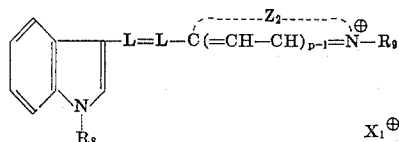
It will be noted that in the dyes described above, the imidazo[4,5-b]quinoxaline nucleus can be substituted, for example, with halogen (such as mono- or dichloro, mono- or dibromo) nitro, or with a fused ring.

Another class of dyes which may be used in accordance with the invention to spectrally sensitize organic photoconductors are cyanine dyes which feature a 2-aromatically substituted indole nucleus attached to the methine chain of the cyanine dye by the 3-carbon atom of the indole nucleus. Dyes of this type are described by Coenen et al. U.S. Pat. No. 2,930,694 issued Mar. 29, 1960; British Pat. No. 970,601 and Litzerman et al. Belgian Pat. No. 695,365 granted Sept. 11, 1967, and U.S. Pat. application Ser. No. 609,764, filed Jan. 17, 1967. These dyes include trimethine cyanine dyes which feature two 2-aromatically substituted indole nuclei each joined by the 3-carbon atom thereof to the respective terminal carbon atoms of the trimethine chain. Such dyes include, for example, bis-(1-methyl-2-phenyl-indole-3)-trimethine cyanine bromide. Also useful are unsymmetrical dyes having first and second nuclei joined by methine linkage, one nucleus being a 2-aromatically substituted indole nucleus, and the second nucleus being a heterocyclic nucleus to complete the dye. The indole nucleus of such dyes is attached to the methine chain of the dye through the 3-carbon atom of the in-

dole nucleus. Advantageously, the second nucleus of these dyes is a desensitizing nucleus. An especially useful class of such dyes may be represented by the following general formula:

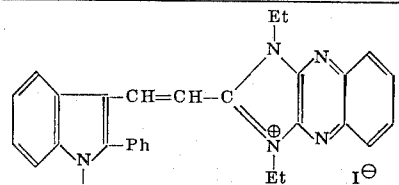
VII. D-L=L-Y

wherein D represents a 2-aromatically substituted indole nucleus attached to the methine chain through the 3-carbon atom of the indole nucleus; L represents a methine linkage; and, Y represents a desensitizing nucleus. For example, a preferred desensitizing nucleus is an imidazo[4,5-b]quinoxaline nucleus attached, through the 2-carbon atom thereof, to the methine chain. Spectral sensitizing dyes of this type can be prepared using any of the methods generally used for preparing such dyes. One convenient method involves refluxing, in a suitable solvent, a carboxaldehyde derivative of a 2-aromatically substituted indole with an alkyl substituted quaternary salt of a compound containing the desired desensitizing nuclei. For example, a 2-aromatically substituted indole-3-carboxaldehyde can be refluxed in a solvent such as acetic anhydride with a 2-alkylimidazo[4,5-b]quinoxalinium salt or a 2-alkylene pyrrolo-[2,3-b]pyridine compound to provide the desired dye. The substituent in the 2-position of the indole nucleus may be any suitable aromatic group, such as a phenyl nucleus, which can contain various groups such as alkyl (e.g., methyl, ethyl, propyl, butyl, etc.) alkoxy (e.g., methoxy, ethoxy, propoxy, butoxy, etc.) halogens such as bromine, fluorine, or chlorine, as well as aryl such as naphthyl or phenyl. Among the useful dyes of this class are those having the following formula:

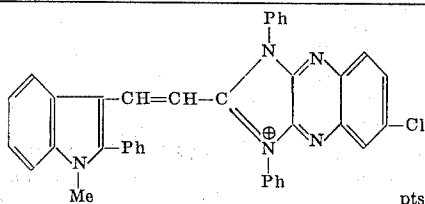


wherein L represents a methine group and R_8 and R_9 each represents a value selected from those given for R_3 above; Z_2 is selected from the values given for Z above; p represents an integer of from 1 to 2; and, Ar represents an aromatic substituent such as phenyl or those referred to above. Some specific useful dyes of this class include:

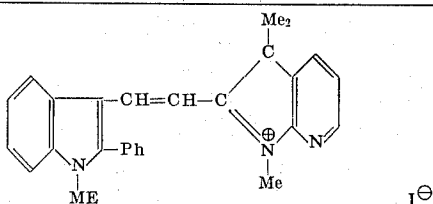
1,3-diethyl-1'-methyl-2'-phenylimidazo[4,5-b]quinoxalino-3'-indolocarbo-cyanine iodide



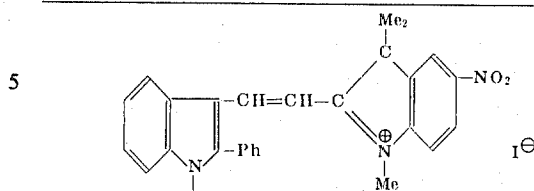
6-chloro-1'-methyl-1,2',3-triphenylimidazo[4,5-b]quinoxalino-3'-indolocarbo-cyanine p-toluenesulfonate



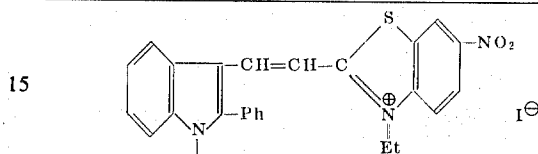
1,1',3',3'-tetramethyl-2-phenyl-3-indolopyrrolo[2,3-b]pyridocarbo-cyanine iodide



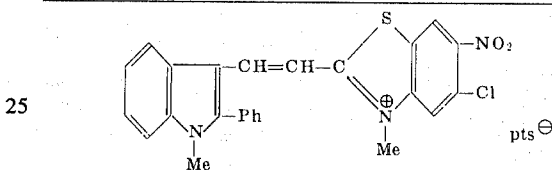
1,1',3,3-tetramethyl-5-nitro-2'-phenylimido-3'-indolocarbo-cyanine iodide



3'-ethyl-1-methyl-2-phenyl-6'-nitro-3-indolothiacarbo-cyanine iodide

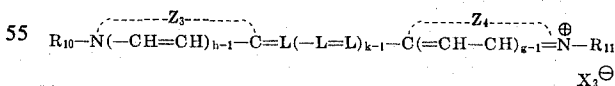


5'-chloro-1,3'-dimethyl-2-phenyl-6'-nitro-3-indolothiacarbo-cyanine p-toluenesulfonate

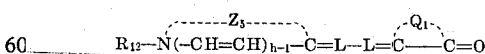


Still another class of useful dyes in accordance with this invention are the cyanine and merocyanine dyes in which at least one nucleus, and preferably two nuclei thereof, contains a desensitizing substituent such as nitro. Such dyes of the cyanine salt type (Formula IX below) comprise first and second 5- to 6-membered nitrogen containing heterocyclic nuclei of the type used in cyanine dyes joined together by methine linkage at the 2-carbon atoms thereof, at least one of said nuclei being substituted by a nitro group. The merocyanine dyes (Formula X below) comprise first and second 5- to 6-membered nitrogen containing heterocyclic nuclei joined together by methine linkage; the first of said nuclei being a ketomethylene nucleus of the type used in merocyanine dyes joined at a carbon atom thereof to said linkage; and said second nucleus being of the type used in cyanine dyes having a nitro substituent thereon and joined at a carbon atom thereof to said linkage, to complete said dye. Typical dyes of this class are represented by the formulas:

IX.



X.



wherein R_{10} , R_{11} , R_{12} , each is independently selected from a value given for R_3 above; Z_3 , Z_4 and Z_5 each represents a value given for Z above; at least one of Z_3 and Z_4 and at least one of Z_5 and Q_1 contains a nitro group; Q_1 has a value given for Q above; g , j and h each represents a positive integer of from 1 to 2, k represents a positive integer of from 1 to 3; X_2 represents an acid anion; and, L represents a methine group. A typical dye of this class is 3,3'-diethyl-6,6'-dinitrothiacarbo-cyanine salt.

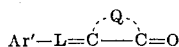
Another useful class of dyes which can be employed in the practice of this invention are the cyanine dyes which feature a trifluoromethyl group either in the nucleus or the chain. Representative dyes of this class can be represented by Formula IX above wherein an "L" group represents the substituent:



The most useful dyes of this class are those wherein a hydrogen atom in the methine chain of the cyanine dye is replaced with a trifluoromethyl group. The cyanine dye can be a simple cyanine, a dicarbocyanine or a tricarbocyanine. Especially useful dyes are the meso-trifluoromethyl substituted carbocyanines. Dyes of this class preferably contain a nucleus such as those derived from benzimidazole, benzoxazole, benzothiazole, benzoselenazole or indole.

Also useful herein are the benzylidene dyes in which one nucleus is a ketomethylene nucleus of the type used in merocyanine dyes joined by a methine group to a nitro substituted aryl nucleus. Typical dyes of this class are represented by the formula:

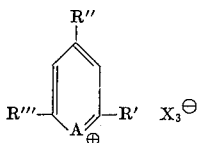
XI,



wherein L represents a methine group; Q has the previously defined value; and Ar' represents a nitro substituted aryl group, e.g., m-nitrophenyl, p-nitrophenyl, a nitronaphthyl, etc.

Another useful class of dyes which can be employed in this invention are the electron accepting cyanine dyes having at least one methine group wherein the hydrogen atom thereof is replaced with a chlorine, bromine or iodine atom, such as the dyes described in Belgian Pat. No. 695,354 of Sept. 11, 1967, and Gilman et al. U.S. Pat. Application Ser. No. 607,734 filed Jan. 17, 1967. Best results are obtained with the monomethine cyanine dyes, such as the reaction product of bromine with a 1,1'-diethyl-2,2'-cyanine dye salt or a 1',3-diethylthia-2'-cyanine dye salt.

Still another class of dyes useful in the practice of this invention include pyrylium, thiapyrylium and selenapyrylium compounds and more particularly those represented by the following formula:



wherein A represents an oxygen, sulfur or selenium atom, X_3 represents an acid anion which has no adverse effects on the emulsion, e.g., chloride, bromide, iodide, thiocyanate, sulfamate, perchlorate, p-toluenesulfonate, methyl sulfate, ethyl sulfate, fluoroborate, sulfoacetate, borofluoride, trifluoroacetate, etc., and R', R'', and R''' each represents an alkyl group including substituted alkyl (preferably a lower alkyl containing from 1-4 carbon atoms), e.g., methyl, ethyl, propyl, isopropyl, butyl, hexyl, cyclohexyl, decyl, dodecyl, benzyl, phenethyl, a styryl group such as styryl, o-, p- and m-methoxy-styryl, o-, p- and m-styrylstyryl, N-phenylacridanylidene-methyl groups, etc., etc.; an alkoxy group, preferably a lower alkoxy, e.g., methoxy, ethoxy, propoxy, isopropoxy, butoxy, etc.; an aryl group (including substituted aryl), e.g., phenyl, o-, p- and m-tolyl, o-, p- and m-ethylphenyl, etc., an alkoxyphenyl group, e.g., o-, p- and m-anisyl, o-, p- and m-ethoxyphenyl, etc., a hydroxyalkoxyphenyl group such as β -hydroxyethoxyphenyl, ω -hydroxyamyloxyphenyl, ω -hydroxybutoxyphenyl, etc., a carboxyalkoxyphenyl group such as carboxymethoxyphenyl, β -carboxyethoxyphenyl, ω -carboxybutoxyphenyl, etc., a biphenyl group, an azidophenyl such as o-, p- and m-azidophenyl, etc., an acylamidophenyl group such as o-, p- and m-acetamidophenyl, p-propionamidophenyl, etc., an alkoxy-carbonylphenyl group such as methoxycarbonylphenyl, ω -butoxycarbonylphenyl, chloromethoxycarbonylphenyl, bromomethoxycarbonylphenyl, etc., a naphthyl group such as 1- or 2-naphthyl; etc., an arylalkenyl group typi-

cally having 1-20 carbon atoms such as 4-phenylbutadienyl, 3-methyl-4-phenylbutadienyl, etc., and the like. The dye compounds wherein R', R'' and R''' each represents an aryl group are especially efficacious in this invention and are the preferred species of this class of dyes.

Typical dyes coming under the definition of Formula XII above include, for example, 2,6-di-p-methoxyphenyl-4-phenylpyrylium fluoroborate; 2,6-bis-(p-anisyl)-4-(p-n-amyloxyphenyl)pyrylium perchlorate; 2-(p-n-amyloxyphenyl) 4,6-diphenylpyrylium fluoroborate;

2-(4-Phenylbutadienyl)-4,6-diphenylpyrylium perchlorate

6-(4-Phenylbutadienyl)-2,4-diphenylthiapyrylium perchlorate

2,6-Bis-(p-ethylphenyl)-4-(p-anisyl)pyrylium perchlorate

2,6-Bis-(p-ethylphenyl)-4-(p-anisyl)thiapyrylium perchlorate

2,6-Diphenyl-4-(p-anisyl)-thiapyrylium chloride

2,6-Bis-(p-ethylphenyl)-4-(p-n-amyloxyphenyl)pyrylium fluoroborate

2,6-Bis-(p-anisyl)-4-(p-n-amyloxyphenyl)thiapyrylium perchlorate

2,4-Diphenyl-6-styrylpyrylium perchlorate

2,6-Bis-(p-anisyl)-4-phenylthiapyrylium fluoroborate

2,6-Bis-(p-ethylphenyl)-4-(p-n-amyloxyphenyl)pyrylium perchlorate

2,4,6-Tris(p-anisyl)pyrylium fluoroborate

2-[p-(β -hydroxyethoxy)phenyl]-4,6-diphenylpyrylium perchlorate

2,4,6-Triphenylselenapyrylium fluoroborate

2,4,6-Tris-(p-anisyl)thiapyrylium p-toluenesulfonate

2,4,6-Tris-(p-anisyl)thiapyrylium sulfoacetate

2,6-Bis-(p-chloromethoxycarbonylphenyl)-4-phenylpyrylium fluoroborate

2,6-Bis-(p-ethylphenyl)-4-

(p-n-amyloxyphenyl)thiapyrylium fluoroborate

2,4,6-Tris(p-anisyl)pyrylium perchlorate

2,4,6-Tris-(p-anisyl)thiapyrylium perchlorate

2,6-Diphenyl-4-(p-acetaminophenyl)pyrylium perchlorate

2-[p-(β -hydroxyethoxy)-phenyl]-4-phenyl-6-(p-anisyl)pyrylium perchlorate

2-(2-naphthyl)-4,6-diphenylthiapyrylium perchlorate

2,6-Bis-(p-tolyl)-4-(p-

2,4,6-Tris-(p-anisyl)thiapyrylium trifluoroacetate

2-Methyl-4,6-bis-(p-anisyl)

2,6-Bis-(p-anisyl)-4-(p-n-amyloxyphenyl)thiapyrylium fluoroborate; and the like.

The organic electron accepting dyes can be adsorbed onto the physically developable nuclei in any convenient manner. For example, a dispersion can be formed of the physically developable nuclei in a suitable hydrophilic colloid, the organic dye can be mixed therewith and the resulting composition can be coated onto a suitable support and dried. If desired, a dispersion of physically developable nuclei can be dispersed in a hydrophilic colloid and coated on a suitable support and the resulting coating can be dipped in a suitable solution of the dye, or a solution of the dye can be swabbed, brushed or sprayed over the coating. When binderless vacuum

deposited coatings of physically developable nuclei are utilized, it is convenient to dip the support having the physical developable nuclei thereon into a suitable solution of the dye, or by swabbing, brushing or spraying the dye solution onto the binderless coating of physically developable nuclei.

The term "physical developer" is used herein as a word of art. It refers to materials which contain a source of reducible metal and a reducing agent which causes the reducible metal to be deposited on a particular site.

Physical development may be conducted in accordance with the practice of this invention with any suitable metal. Silver is highly useful in preparing images in the physical development process. However, other metals are known for use in physical development and can be used in place of silver. Metals which are members of electromotive scale below hydrogen are used most commonly for physical development and they include copper, arsenic, antimony, platinum, gold, mercury, silver and the like.

Various physical development processes can be utilized. For example, an imagewise exposed element can be contacted with the emulsion side of a conventional negative photographic silver halide emulsion previously wetted with a conventional photographic developer modified by the inclusion therein of a silver halide solvent, such as sodium thiosulfate. After contacting for a brief time, the two layers are separated and a positive silver image is produced in the unexposed regions of the layer containing the physically developable nuclei. Exposed regions of the layer are essentially free from any silver image.

In another physical development technique, the exposed material comprising physically developable nuclei is immersed in a physical developer solution comprising silver halide, a conventional silver halide developing agent, and silver halide solvent. At the time required to obtain sufficient density, usually several minutes, the element is removed to obtain a direct positive silver image.

The binder for the above photonucleating coating compositions is not critical since practically any water permeable colloid known for use in silver halide photography can be used such as gelatin, carboxymethylcellulose, zein, albumin, various synthetic resins such as polyvinyl alcohol, polyvinyl pyrrolidone, acrylic resins, and the like. Although the concentration of the binder can vary over a wide range, it has been found that quite useful coating compositions are prepared wherein the binder is present in the range up to about 10 percent by weight of the total coating melt.

The wet thickness of the coatings can be in the range of about from 0.001 to about 0.01-inch with a preferred wet thickness in the range from about 0.003 to about 0.006-inch. Thicker coatings can also be employed without detracting from the invention.

Suitable support materials for preparing the light sensitive photographic elements of the invention include cellulose acetate, cellulose acetate propionate, cellulose nitrate, polyethylene, polypropylene, polystyrene, polyvinyl chloride, polyethylene terephthalate, paper, metal, glass, and the like.

When diffusion transfer physical development is employed, any of the known silver halide emulsions may be used in contact with the light sensitive, exposed, silver-dye complex emulsion, such as silver chlorobromide, silver chloroiodide, silver chlorobromiodide, silver bromide, and silver bromoiodide.

In developing the exposed layers of the invention any of the usual developing agents can be used in the developer compositions such as N-monomethyl-p-aminophenol sulfate; dihydroxybenzene; hydroquinone, p-phenylenediamine developers; hydroquinone compounds (e.g., chlorohydroquinone, dichlorohydroquinone, bromohydroquinone, etc.); 1-phenyl-3-pyrazolidone and its derivatives; triaminophenols; and the like.

Silver halide solvents for use in the physical developing process of the invention include alkali metal thiosulfates, ammonium thiosulfate, alkali metal thiocyanate, ammonium thiocyanate, sodium sulfite, etc.

The following examples are included for a further understanding of the invention.

EXAMPLE 1

A direct positive silver image is formed in a diffusion transfer physically developable system as follows:

A photonucleating coating is prepared as follows:

To 100 ml. of 5 percent gelatin add:

a. 4 ml. of 7 1/2 percent saponin solution

b. 3 ml. of 10 percent formaldehyde solution

To 10 ml. of the above solution is added 0.10 ml. of 0.10 Molar silver nitrate solution.

Coatings of above dispersion having a 0.004-inch wet thickness are made on a cellulose triacetate film support to give a coverage of approximately 2.6 mg. Ag NO₃ per square foot, 400 mg. of gelatin per square foot, and 0.065 mg. of dye per square foot.

A step tablet exposure is given by exposing the coating 15 seconds to a 100-watt Tungsten lamp at a distance of 3 feet. The coating is then immersed for 2 minutes in a solution of the dye-1,1'-diethyl-2,2'-cyanine sulfate which had been reacted with bromine-pyrrolidone complex to produce a light sensitive blue colored solution. The dyed coating is then dried and given a stepped exposure perpendicular to the first exposure and processed by contacting with an unexposed fine grain silver chlorobromide film previously soaked for 3 seconds in a developer solution of the composition:

Developer 1

Methylaminoethanol-sulfur dioxide (18.9% sulfur dioxide)	190 g.
Hydroquinone	11.6 g.
1-Phenyl-4,4-dimethyl pyrazolidone	1 g.
Sodium thiosulfate · 5H ₂ O	60 g.
Potassium iodide	0.42 g.
Water to	1 liter
1% methanol solution of 5-methyl-3-piperidinylmethyl- 2-thioxazolidine	10ml.

The wet fine grain silver chlorobromide film is rolled in contact with the dyed and re-exposed coating. After 2 minutes contact (at about 20°) the two layers are peeled apart. The second exposure removed the effect of the first exposure in a manner proportional to the intensity of the second exposure.

The above process is repeated except that a line image is employed in a prior stepwedge exposure. Good reversal line images are obtained.

By giving the photonucleating coating a uniform fogging exposure of 4 seconds to a 100-watt lamp at a distance of 3 feet and then immersing the layer in the blue dye solution, it is found that a second image exposure produces a high density direct positive line image after using the diffusion transfer physical development described above. The quality of the reversed silver image is excellent.

PREPARATION OF DYE SOLUTION

To 40 ml. of solution of ethyl alcohol containing 5×10^{-6} grams of the sensitizing dye, 1,1'-diethyl-2,2'-cyanine sulfate, is added 20 ml. of an aqueous solution containing 2×10^{-4} grams of a bromine-pyrrolidone complex sold by the General Aniline and Film Corp.

The mixture of the above two solutions results in the conversion of the previously red colored solution of the dye (absorption max = 540 μ) to a blue colored solution (absorption

max — 590 μ). The blue form of the dye is light-sensitive and should be prepared and used only in total darkness to prevent spontaneous decomposition.

EXAMPLE 2

The process of above Example 1 is repeated, except that the dye solution in this instance is the reaction product of 1', 3-diethylthia-2'-cyanine iodide and bromine-pyrrolidone complex. The results are generally similar to those of Example 1, e.g., a high density direct positive line image of excellent quality is likewise obtained.

EXAMPLE 3

This example illustrates the production of a direct positive silver image by performing metallic nuclei latent images in a titanium dioxide layer and incorporating an electron acceptor such as a brominated dye into the system, followed by exposure and development in a solution physical developer. The following coating was prepared in the light.

A dispersion of finely divided titanium dioxide in 50 ml. of water is stirred with 50 ml. of 10 percent gelatin solution at 40° C. To 10 ml. of the dispersion is added 0.1 ml. of 0.1 N AgNO₃, 5 ml. of water and 0.3 ml. of 10 percent formaldehyde solution and a coating made at 0.002 in. wet thickness on polyethylene-coated paper. A metallic nuclei latent image is formed in the titanium dioxide by the action of light in preparing the coating.

The above prepared coating layer comprised:

Silver (AgNO ₃)	3 mg./square foot
Gelatin	150 mg./square foot
TiO ₂	300 mg./square foot

The coated paper is then dipped in a brominated dye under red safelights, the brominated dye being prepared by adding 98 mg. of N-bromosuccinimide in 50 ml. of methanol to 100 mg. 1,1'-diethyl-2,2'-cyanine chloride in 50 ml. of methanol. The dyed light sensitive element is then dried in the dark, exposed for 5-10 seconds to a photoflood lamp through a negative line image and immersed directly for 2 minutes in a physical developer solution (20° C.) of the following composition:

Developer 2	
Part A	
Water	800 cc.
Sodium sulfite	20 g.
Sodium isoascorbate	26 g.
Sodium carbonate (monohydrate)	50 g.
** Wetting Agent	20 cc. (1% in H ₂ O)
Water to pH = 11.0	1 liter
Part B	
Water	800 cc.
Sodium thiosulfate	
5 H ₂ O	30 g.
* Silver chloride	5 × 10 ⁻² moles (2 bottles)
Water to	960 cc.
5-Methylbenzotriazole	40 cc. (1% in dilute KOH)
For use:	Mix parts A and B 1:1

* For making silver chloride:

1) 42.4 g. AgNO₃ in 900 cc. of water

2) 42.4 g. KCl in 900 cc. of water

3) Mix 90 cc. of (1) and 90 cc. of (2) in a 6 ounce bottle

4) Let stand overnight, then pour off liquid for use Each bottle contains 2.5 × 10⁻² moles, therefore, two bottles are required to make 5 × 10⁻² molar

** octyl phenoxy ethoxy ethyl dimethyl-p-chlorobenzyl ammonium chloride

After development, the element is rinsed in water. A direct positive silver image is obtained with the image appearing after 20 seconds in the developer. It was clear and sharp. The titanium dioxide in the above procedure can be replaced with zinc oxide to give a generally similar direct positive silver image.

EXAMPLE 4

In this example, the sensitizing dye is incorporated into the nuclei containing composition and the mixture coated onto a suitable support material. This element is then exposed and developed to a positive image by solution physical development. All operations are carried out under red safelights.

To 15.0 of finely divided titanium dioxide dispersed in 200 ml. of water in a 40° C. bath is added 150 ml. of 10 percent gelatin and 30 ml. of 1.0 percent silver nitrate. The pH is adjusted to 9.0, the temperature raised to 55° C. and 6.0 ml. of 5 percent formaldehyde solution is added. The stirred mixture is held 16 minutes at 55° C. after which the pH is lowered to 5.8. A 20 ml. aliquot of this melt is mixed with 13 ml. of brominated dye solution, (same as that described in above Example 3) and the mixture is coated at 4.7 ml./ft.² on polyethylene-coated paper to give a coverage of 1.6 mg./ft.² of silver, 2.7 mg./ft.² of dye (as the dibromide) and 110 mg./ft.² of titanium dioxide.

A sample of the above prepared dyed light sensitive element is given a spectrograph exposure of 2 minutes at a slit width of 10 mm. on a monochrometer and then developed 2 minutes in Developer 2 (composition of which is shown in Example 3 herein) at room temperature. Excellent direct positive spectral response is shown.

EXAMPLE 5

This example is generally similar to that of preceding Example 4, except that the titanium dioxide is omitted. All operations in this example are carried out under red safelights.

A dispersion is prepared with 30 ml. of aqueous 1.0 percent silver nitrate and 350 ml. of aqueous 4.3 percent gelatin in a 40° C. bath. The melt temperature of this dispersion is raised from 40° C. to 55° C. at a rate of 1.7° C. per minute and then held 2 minutes at 55° C. before lowering the pH to 4.75, and lowering the temperature to 40° C. A 20 ml. aliquot of this melt is mixed with 13 ml. of the brominated dye solution described in above Example 3 and the mixture is coated 4.7 ml. per square foot on polyethylene coated paper to give a coverage of 1.6 mg. of silver per square foot and 2.7 mg. per square foot of the brominated dye.

A sample of the above prepared light sensitive element is given a spectrograph exposure of 2 minutes at a slit width of 10 mm. on a monochrometer and then developed in Developer 2 (composition of which is given in above Example 3) at room temperature. An excellent direct positive spectral response is obtained.

EXAMPLE 6

This example illustrates the use of evaporated silver nuclei physical development sites.

Under red safelights a sample containing 0.15 mg. per square foot, of particle size 20 A. or less, of evaporated silver on polyethylene paper is immersed in the previously described brominated dye solution of above Example 3 and then drained and dried. The sample (in contact with a line negative) is given a 30-second photoflood exposure at a distance of 1 foot and then developed for 3 minutes in Developer 2 (composition of which is given in above Example 3) at room temperature. An excellent direct positive image is obtained.

EXAMPLE 7

By the same procedure (Example 6 above) a direct positive image is obtained on a polyethylene coated paper containing

evaporated palladium in place of evaporated silver. The coating coverage in this example is approximately 0.15 mg. of palladium per square foot having an average particle diameter size of about 20 A. or less.

EXAMPLE 8

The procedure of above Example 7 is repeated, except that a coating of palladium nuclei, prepared by reducing palladium chlorate with hypophosphite, in a terpolymer of acrylic acid, acrylonitrile and vinylidene chloride in gelatin (25 percent of monomer in gelatin) is applied on a polyethylene-coated paper using a 4-minute photoflood exposure at a distance of 6 inches, followed by developing (at 20° C.) in Developer 2 (composition of which is given in above Example 3) for 1 minute. An excellent direct positive image is obtained. The coating coverage in that example is approximately 0.04 mg. palladium per square foot of average particle diameter size of about 50 A. or less.

In place of the brominated dye solution employed in above Examples 4 to 9, there can be substituted a like amount of a solution of other dyes such as, for example, 5-m-nitrobenzylidene rhodanine; 1,3-diethyl-1'-methyl-2'-phenylimidazo[4,5-b]quinoxolino-3'-indolocarboyanine iodide; 3'-ethyl-1-methyl-2-phenyl-6'-nitro-3-indolothiacarboyanine iodide; and the like. It will be understood that the above carboyanine dyes can be used in any of the mentioned salt forms, e.g., the chloride, bromide, perchlorate, p-toluenesulfonate, etc. salts, which likewise function effectively as electron acceptors and spectral sensitizers in the systems of the above examples. It will also be understood that the nuclei can be combined with the electron accepting dye either by mixing solutions of the two and coating them or by coating the nuclei alone and then imbibing the dye.

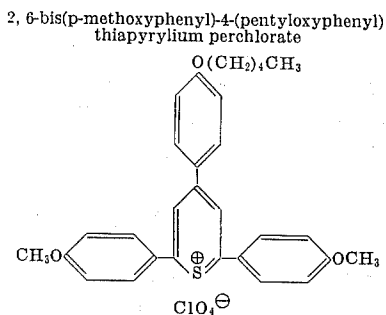
EXAMPLE 9

In this example a pyrylium type dye such as defined in Formula VIII above is employed as an electron acceptor and spectral sensitizer for preparing a Carey Lea Silver (CLS) for diffraction transfer physical development.

Colloidal silver having an average diameter of from 50 to 70 A. is prepared by a modified CLS technique (M. Carey Lea, Kall. Zeitschrift, 13, 180 (1913)).

A gelatin coating of above CLS is prepared. This is applied over a gelatin pad (which contains 475 mg. of gelatin per square foot) in such thickness as to give a coverage of 25 mg. of gel and approximately 0.4 mg. of silver per square foot.

The above CLS coating is sensitized by bathing it for 30 seconds in a solution which contains 0.1 g. per liter of the thiapyrylium dye.



The dye is dissolved in a 1 percent potassium bromide solution with the solvent composed of equal parts of water, acetone and dimethylformamide.

After immersing the CLS coating in this dye bath for 30 seconds, it is dried without washing, then exposed through a line image to a No. 2 photoflood lamp for 10 seconds at a distance of 24 inches.

When the exposed CLS coating is immersed in a physical developer such as Developer 2 (composition of which is given in above Example 3) for one minute at 20° C., a direct positive image is obtained with silver physically developed in the unexposed areas while the light exposed areas remained relatively clear.

It will be apparent from all of the foregoing description and the examples of the invention that any other of the sensitizing dyes defined in Formulas I to III and VII to XII above can be substituted into the preceding examples in place of the specified dyes to give generally similar good quality direct positive images.

In the above examples, the images formed by physical development are silver or palladium-silver. However, other metals are known for use in physical development and can be used for the same purposes as silver by the appropriate substitution of metallic salts. Metals which are members of the electromotive scale below hydrogen are those which are most commonly employed for this purpose and include copper, mercury, platinum, gold, and the like. The use of these metals to form images is within the scope of this invention.

The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.

We claim:

1. A non-silver halide direct positive photographic material comprising non-silver halide physically developable nuclei having adsorbed thereto an organic dye which is an electron acceptor.

2. A non-silver halide direct positive photographic material comprising non-silver halide physically developable nuclei having an average diameter of up to about 0.5 micron, said nuclei having adsorbed thereto an organic dye which is an electron acceptor having an anodic polarographic halfwave potential and a cathodic polarographic half halfwave potential which, when added together, give a positive sum.

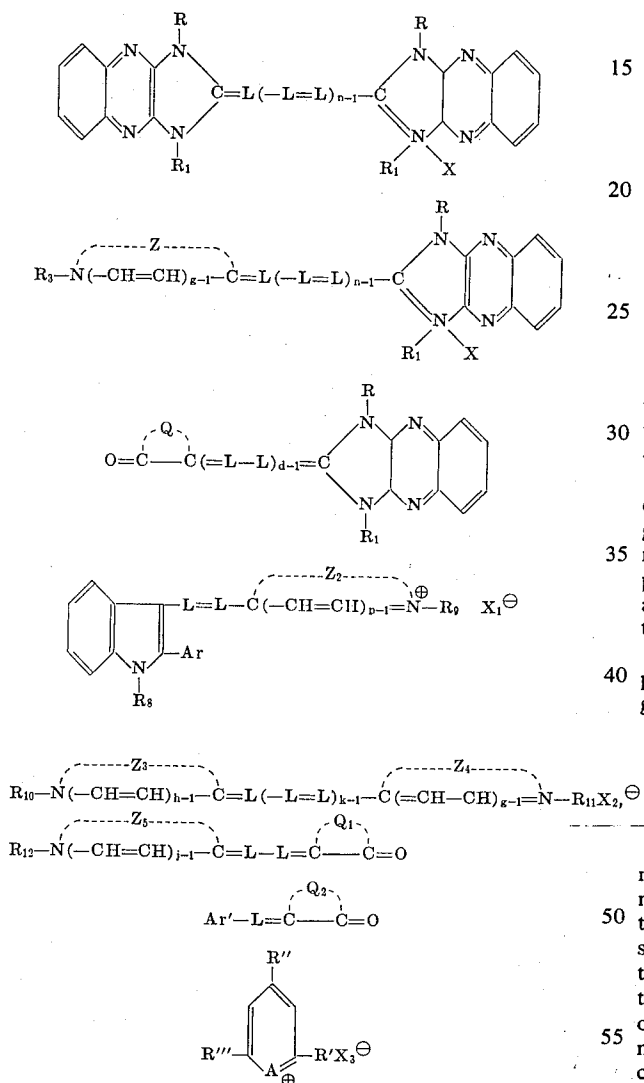
3. A photographic material as defined in claim 2 wherein said nuclei have an average diameter of from 0.001 to 0.25 micron.

4. A non-silver halide direct positive photographic material comprising non-silver halide physically developable nuclei having adsorbed thereto an electron accepting dye selected from the group consisting of (1) a methine dye containing a desensitizing nucleus selected from the group consisting of (a) a 5- to 6-membered nitrogen containing heterocyclic nucleus of the type used in cyanine dyes having a nitro group substituted on a carbon atom thereof (b) an imidazo[4,5-b]quinoxaline nucleus and (c) a 2-arylindole nucleus; (2) a benzylidene dye comprising a ketomethylene nucleus of the type used in merocyanine dyes joined by methine linkage to a nitro substituted aryl group; (3) a cyanine dye having at least one methine group wherein the hydrogen atom thereof is replaced with a halogen atom selected from the group consisting of chlorine, bromine and iodine atoms; and (4) a dye selected from the group consisting of a pyrylium dye, a thiapyrylium dye, and a selenapyrylium dye.

5. A non-silver halide direct positive photographic material comprising non-silver halide physically developable nuclei selected from the group consisting of silver, titanium and palladium nuclei, said nuclei having adsorbed thereto an electron accepting dye selected from the group consisting of (1) a methine dye containing a desensitizing nucleus selected from the group consisting of (a) a 5- to 6-membered nitrogen containing heterocyclic nucleus of the type used in cyanine dyes having a nitro group substituent on a carbon atom thereof; (b) an imidazo[4,5-b]quinoxaline nucleus and (c) a 2-arylindole nucleus; (2) a benzylidene dye comprising a ketomethylene nucleus of the type used in merocyanine dyes joined by methine linkage to a nitro substituted aryl group; (3) a cyanine dye having at least one methine group wherein the hydrogen atom thereof is replaced with a halogen atom selected from the group consisting of chlorine, bromine and

iodine atoms; and (4) a dye selected from the group consisting of a pyrylium dye, a thiapyrylium dye, and a selenapyrylium dye.

6. A non-silver halide direct positive light sensitive photographic material comprising non-silver halide physical development sites of heavy metal nuclei having an average particle diameter less than about 0.25 having adsorbed thereto a dye selected from the group consisting of the reaction product of bromine and a monomethine cyanine dye salt, and a dye selected from those having one of the following formulas:



wherein n represents a positive integer of from 1 to 4; d and k each represents a positive integer of from 1 to 3; g , h , j and p each represents a positive integer of from 1 to 2; L represents a methine linkage; each R , R_1 , R_3 , R_8 , R_9 , R_{10} , R_{11} and R_{12} represents a member independently selected from the group consisting of an alkyl group, an alkenyl group and an aryl group; A represents an atom selected from the group consisting of oxygen, sulfur and selenium; R' , R'' , and R''' each represents a member selected from the group consisting of an alkyl group, an alkoxy group, an alkenyl group and an aryl group; Ar represents an aryl group; Ar' represents a nitro substituted aryl group; X , X_1 , X_2 and X_3 each represents an acid anion; Z , Z_2 , Z_3 , Z_4 and Z_5 each represents the non-metallic atoms required to complete a heterocyclic nucleus of the type used in cyanine dyes containing from 5 to 6 atoms in the heterocyclic ring; and Q , Q_1 and Q_2 each represents the non-metallic atoms required to complete a ketomethylene nucleus of the type used in merocyanine dyes, at least one of Z_3 and Z_4 , and at least one of Z_5 and Q_1 being nitro-substituted.

7. A direct positive material in accordance with claim 6 wherein said nuclei is selected from the group consisting of silver, titanium and palladium nuclei.

8. A photographic element comprising a support having coated thereon a non-silver halide direct positive photographic material comprising non-silver halide physically developable nuclei having adsorbed thereto an organic dye which is an electron acceptor.

9. A photographic element comprising a support having coated thereon a non-silver halide direct positive photographic material comprising non-silver halide physically developable nuclei having adsorbed thereto an electron accepting dye selected from the group consisting of (1) a methine dye containing a desensitizing nucleus selected from the group consisting of (a) a 5- to 6-membered nitrogen containing heterocyclic nucleus of the type used in cyanine dyes having a nitro group substituted on a carbon atom thereof; (b) an imidazo[4,5-b]quinoxaline nucleus and (c) a 2-arylidole nucleus; (2) a benzylidene dye comprising a ketomethylene nucleus of the type used in cyanine dyes joined by methine linkage to a nitro substituted aryl group; (3) a cyanine dye having at least one methine group wherein the hydrogen atom thereof is replaced with a halogen atom selected from the group consisting of chlorine, bromine and iodine atoms; and (4) a dye selected from the group consisting of a pyrylium dye, a thiapyrylium dye and a selenapyrylium dye.

10. A direct positive photographic material comprising physically developable Carey Lea silver having adsorbed thereto the electron accepting dye 2,6-Bis(p-methoxyphenyl)-4-(p-pentylloxyphenyl)thiapyrylium perchlorate.

11. A process for preparing a positive metallic image which comprises physically developing an imagewise exposed photographic element comprising a support having coated thereon a non-silver halide direct positive photographic material comprising non-silver halide physically developable nuclei having adsorbed thereto an organic dye which is an electron acceptor.

12. A process for preparing metallic images which comprises physically developing an imagewise exposed photographic element comprising a non-silver halide photographic

material comprising non-silver halide physically developable nuclei having adsorbed thereto an organic dye selected from the group consisting of (1) a methine dye containing a desensitizing nucleus selected from the group consisting of (a) a 5- to 6-membered nitrogen containing heterocyclic nucleus of the type used in cyanine dyes having a nitro group substituted on a carbon atom thereof; (b) an imidazo[4,5-b]quinoxaline nucleus; and (c) a 2-arylidole nucleus (2) a benzylidene dye comprising a ketomethylene nucleus of the type used in merocyanine dyes joined by methine linkage to a nitro substituted aryl group; (3) a cyanine dye having at least one methine group wherein the hydrogen atom thereof is replaced with a halogen atom selected from the group consisting of chlorine, bromine and iodine atoms; and (4) a dye selected from the group consisting of a pyrylium dye, a thiapyrylium dye and a selenapyrylium dye.

13. A process as defined in claim 12 wherein said nuclei is selected from the group consisting of silver, titanium and palladium nuclei, and said physical development is conducted with a composition comprising silver halide developing agent and silver halide solvent.

14. The process of forming direct positive images wherein an imagewise exposed photographic element comprising a support having coated thereon physically developable Carey Lea silver having adsorbed thereto the electron accepting dye 2,6-Bis(p-methoxyphenyl)-4-(p-pentylloxyphenyl)thiapyrylium perchlorate is physically developed with a composition comprising silver chloride and sodium thiosulfate.