United States Patent Office

3,597,196
Patented Aug. 3, 1971

3,597,196

SENSITIZATION OF ORGANIC PHOTOCONDUCTORS WITH CYANINE MEROCYANINE, AND AZOCYANINE DYES

Jean E. Jones and Charles J. Fox, Rochester, N.Y., assignors to Eastman Kodak Company, Rochester, N.Y.

No Drawing. Continuation-in-part of applications Ser. No. 633,421, Apr. 25, 1967, and Ser. No. 716,000, Mar. 26, 1968. This application July 22, 1968, Ser. No. 746,256
Int. Cl. G03g *5/00, 7/00*
U.S. Cl. 96—1.6 **38 Claims**

ABSTRACT OF THE DISCLOSURE

Organic photoconductors are sensitized with cyanine, merocyanine or azacyanine dyes which (1) have a cathodic polarographic half-wave potential more positive than −1.0 volt; (2) have an anodic polarographic half-wave potential and a cathodic polarographic half-wave potential which, when added together, give a sum more positive than −0.10 volt; and (3) desensitive negative silver bromoiodide emulsions, containing 99.35 mole percent bromide, more than 0.4 log E at radiation of 365 nm. when incorporated therein at a concentration of 0.2 millimole of dye per mole of silver halide.

This application is a continuation-in-part of our copending U.S. patent applications Ser. No. 633,421 filed Apr. 25, 1967, now abandoned and Ser. No. 716,000 filed Mar. 26, 1968, now abandoned, both entitled "The Electrophotographic Processes and Materials."

This invention relates to electrophotography, and more particularly to materials and elements useful in the electrophotographic process.

Elements useful in the electrophotographic process commonly comprise an electrically conductive support bearing a stratum including a photoconductive insulating layer which has a resistivity substantially greater in the dark than in light actinic thereto. Such elements can be used in electrophotographic processes, for example, by first adapting the element in the dark to obtain a uniformly high resistivity in the photoconductive insulating layer, and electrostatically charging the element in the dark to obtain a relatively high potential which may be either negative or positive in polarity. The element can then be exposed to a light pattern which lowers the resistivity and thereby the charge density of the illuminated areas imagewise in proportion to the intensity of illumination incident upon each point of the illuminated areas. A latent electrostatic image is obtained. Visible images can be formed from the latent electrostatic image in any convenient manner, such as by dusting with a finely divided, fusible pigment the particles of which bear an electrostatic charge opposite that remaining on the surface of the photoconductive insulating layer. Thereafter, the pigment particles can be fused to the surface to provide a permanent image.

Various photoconductive substances have been employed in photographic elements and processes of the type described above. Typical inorganic photoconductive materials include selenium and zinc oxide. Such inorganic photoconductive materials have inherent disadvantages, such as an inability to be readily adapted to reflex copying systems, or to produce images on transparent supports except by indirect means. Organic photoconductors avoid such disadvantages, but, generally have relatively poor sensitivity to visible radiation. It has been proposed to increase the spectral sensitivity of organic photoconductors with certain cyanine or merocyanine dyes. The spectral sensitivity imparted by such dyes has been very weak. It therefore appears highly desirable to provide effective spectral sensitizers for organic photoconductors.

One object of this invention is to provide novel sensitized organic photoconductors.

Another object of this invention is to provide novel spectrally sensitized organic photoconductor materials.

Still another object of this invention is to provide novel compositions of matter comprising organic photoconductors and certain spectral sensitizers.

A further object of this invention is to provide novel compositions of matter comprising organic photoconductor, binder and certain spectral sensitizers for the organic photoconductor.

Still another object of this invention is to provide a novel electrophotographic material including a conductive support having coated thereon an insulating layer containing spectrally sensitized organic photoconductor.

A further object of this invention is to provide methods for spectrally sensitizing organic photoconductors.

Still other objects of this invention will be apparent from the following disclosure and the appended claims.

In accordance with one embodiment of this invention, novel compositions of matter are provided comprising organic photoconductor spectrally sensitized with the dyes defined more fully below. These compositions can be incorporated in a suitable binder and coated on a conductive support for use in electrophotography.

In another embodiment of this invention, compositions of matter are provided comprising organic photoconductor spectrally sensitized with the dyes described below, dispersed in an insulating binder. These compositions of matter can be coated on a conductive support and used in electrophotographic processes.

In still another embodiment of this invention, electrophotographic materials are provided comprising a conductive support having coated thereon a layer comprising an insulating binder, organic photoconductor and a spectral sensitizing quantity of a dye defined more fully below.

In another embodiment of this invention. a method is provided for spectrally sensitizing organic photoconductors which comprises mixing a dye of the type described below with an organic photoconductor, in a concentration sufficient to effectively spectrally sensitize the organic photoconductor. Preferably, the dye and organic photoconductor are mixed in a suitable solvent.

The spectral sensitizing dyes which are employed in this invention are the cypanine, merocyanine and azacyanine dyes which, when incorporated in a test negative gelatin silver bromoiodide emulsion consisting of 99.35 mole percent bromide and .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 and in the appended claims, 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—1700 cc.

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

(B)

Silver nitrate—200 g.
Water—2000 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:

	G.
N-methyl-p-aminophenol sulfate	2.0
Sodium sulfite, desicated	90.0
Hydroquinone	8.0
Sodium carbonate, monohydrated	52.5
Potassium bromide	5.0

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 organic photoconductors.

Another characteristic of the dyes of this invention is that they are substantially non-photoconductive. The term "substantially non-photoconductive" as used herein means that no image is formed when a solution of 0.002 g. of the dye and 0.5 g. of polyester binder (described in Examples 1-18 below) are dissolved in 5.0 ml. of methylene chloride, and is coated and tested (in the absence of any photoconductor) as described in Examples 1-18 below.

The dyes of this invention increase the speed of organic photoconductors by extending or increasing the response of the photoconductor to visible radiation (i.e., radiation in the range of about 400 nm. to 700 nm.). In the concentrations used, the dyes herein appear to function as spectral sensitizers when employed with efficient organic photoconductors. When the organic photoconductor used is poor or inefficient, the dyes seem to function as speed increasing compounds as well as spectral sensitizers.

The dyes useful herein are further distinguished by having a cathodic polarographic half-wave potential more positive than −1.0 volt, and an anodic polarographic half-wave potential and a cathodic half-wave polarographic potential which, when added together algebraically, produce a value more positive than −.10 volt. 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% 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 reefrence 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 Kenny, Jones and Fisher, Anal. Chem., 31, 1475 (1959). The theory of potential sweep voltammeary such ts 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 organic photoconductors with certain cyanine, merocyanine and azacyanine dyes. The term "cyanine dye," as used herein, is to be construed broadly as inclusive of simple cyanines, carbocyanines, dicarbocyanines, tricarbocyanines, etc. The term includes symmetrical and unsymmetrical cyanine dyes, as well as chain-methine-substituted dyes. Cyanine dyes useful herein feature the amidinium-ion 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 "azacyanines" is used to refer to cyanine dyes in which a methine (e.g., a =CH—) group, linking two nuclei of the dye, is replaced by an aza (=N—) group. See Mees and James, supra, at page 227. A number of classes of dyes which are typical of those that may be used in this invention are described below.

Highly useful dyes of the type described above which provide effective spectral sensitization for organic photoconductors include azacyanine, cyanine and merocyanine dyes containing a nitro group or a trifluoromethyl group; or, a heterocyclic nucleus such as a 1,2,4,5-cyclohexanetetrone nucleus; an indolizine nucleus; an imidazo[4,5-b]quinoxaline nucleus; or a 2-aromatically substituted indole nucleus.

One highly useful class of dyes which may be used in this invention includes cyanine and merocyanine dyes which contain an 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 a desensitizing nucleus.

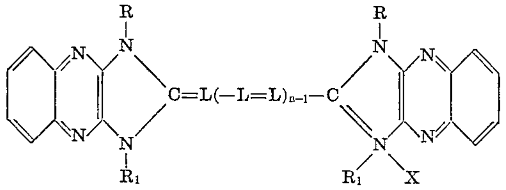
As used herein and in the appended claims, "desensitizing nucleus" refers to those nuclei which, when converted to a symmetrical cyanine dye and added to a gelatin silver chlorobromide emulsion containing 40 mole percent chloride and 60 mole percent bromide, at a concentration of from about 0.01 to 0.2 g. dye per mole of silver, cause at least an 80% 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.

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.

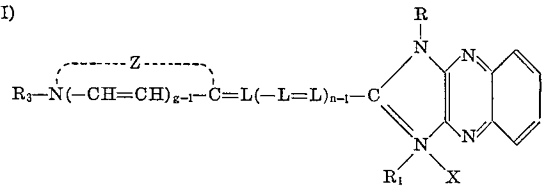
Also useful herein are cyanine dyes comprising two imidazo[4,5-b]quinoxaline nuclei joined together through a polyene chain containing an equal number of alternating single and double bonds, the terminal carbon atoms of the polyene chain being the 2-carbon atoms, respectively, of the imidazo[4,5-b]quinoxaline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

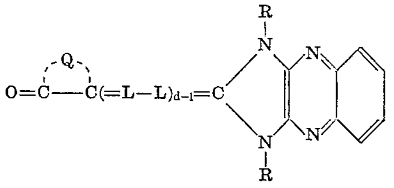
(I)



(II)



(III)

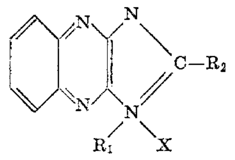


wherein n represents a positive integer of from 1 to 4, g. represents a positive integer of from 1 to 2, d represents a positive integer of from 1 to 3, each L represents a methine linkage, such as $=CH-$, $=C(CH_3)-$ or $=C(C_6H_5)-$; each R and R_1 represents a substituent independently selected from 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_3 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 ion, which may be part of R_3, e.g., chloride, bromide, iodide, thiocyanate, sulfamate, methyl sulfate, ethyl sulfate, perchlorate, p-toluenesulfonate, etc., Z represents the non-metallic atoms required to complete a heterocyclic nucleus containing from 5 to 6 atoms in the heterocyclic ring, which may also include, in addition to the hetero nitrogen atom, a second hetero atom such as an oxygen atom, a sulfur atom, a selenium atom, or a second nitrogen atom, such as the atoms required, to complete a thiazole nucleus (e.g., thiazole, 4-methylthiazole, 4-phenylthiazole, 5-methylthiazole, 5-phenylthiazole, 4,5-dimethylthiazole, 4,5 - diphenylthiazole, 4-(2-thienyl(thiazole, etc.); a benzothiazole nucleus (e.g., benzothiazole, 4-chlorobenzothiazole, 5-chlorobenzothiazole, 6-chlorobenzothiazole, 7-chlorobenzothiazole, 4-methylbenzothiazole, 5-methylbenzothiazole, 6-methylbenzothiazole, 5-bromobenzothiazole, 6-bromobenzothiazole, 4-phenylbenzothiazole, 5-phenylbenzothiazole, 4-methoxybenzothiazole, 5-methoxybenzothiazole, 6-methoxybenzothiazole, 5-iodobenzothiazole, 6-iodobenzothiazole, 4-ethoxybenzothiazole, 5-ethoxybenzothiazole, tetrahydrobenzothiazole, 5,6 - dimethoxybenzothiazole, 5,6 - dioxymethylenebenzothiazole, 5-hydroxybenzothiazole, 6-hydroxybenzothiazole, etc.); a naphthothiazole nucleus (e.g., α-naphthothiazole, β-naphthothiazole, 5-methoxy-β-naphthothiazole, 5 - ethoxy - β-naphthothiazole, 8-methoxy-α-naphthothiazole, 7-methoxy-α-naphthothiazole, etc.); a thianaphtheno-7',6',4,5,-thiazole nucleus (e.g., 4'-methoxythianaphtheno-7',6',4,5-thiazole, etc.); an oxazole nucleus (e.g., 4-methyloxazole, 5-methyloxazole, 4-phenyloxazole, 4,5-diphenyloxazole, 4-ethyloxazole, 4,5-dimethoxazole, 5-phenyloxazole, etc.); a benzoxazole nucleus (e.g., benzoxazole, 5-chlorobenzoxazole, 5-methylbenzoxazole, 5-phenylbenzoxazole, 6-methylbenzoxazole, 5,6 - dimethylbenzoxazole, 4,6-dimethylbenzoxazole, 5-methoxybenzoxazole, 5-ethoxybenzoxazole, 6-chlorobenzoxazole, 6-methoxybenzoxazole, 5 - hydroxybenzoxazole, 6 - hydroxybenzoxazole, etc.); a naphthoxazole nucleus (e.g., α-naphthoxazole, β-naphthoxazole, etc.); a selenazole nucleus (e.g., 4-methylselenazole, 4-phenylselenazole, etc.); a benzoselenazole nucleus (e.g., benzoselenazole, 5-chlorobenzoselenazole, 5 - methoxybenzoselenazole, 5 - hydroxybenzoselenazole, tetrahydrobenzoselenazole, etc.); a naphthoselenazole nucleus (e.g., α-naphthoselenazole, β-naphthoselenazole, etc.); a thiazoline nucleus (e.g., thiazoline, 4-methylthiazoline, etc.); a 2-quinoline nucleus (e.g., quinoline, 3-methylquinoline, 5-methylquinoline, 7-methylquinoline, 8-methylquinoline, 6-chloroquinoline, 8-chloroquinoline, 6-methoxyquinoline, 6-ethoxyquinoline, 6-hydroxyquinoline, 8-hydroxyquinoline, etc.); a 4-quinoline nucleus (e.g., quinoline, 6-methoxyquinoline, 7-methylquinoline, 8-methylquinoline, etc.); a 1-isoquinoline nucleus (e.g., isoquinoline, 3,4-dihydroisoquinoline, etc.); a 3-isoquinoline nucleus (e.g., isoquinoline, etc.); a 3,3-dialkylindolenine nucleus (e.g., 3,3 - dimethylindolenine, 3,3,5 - trimethyl lindolenine, 3,3,7-trimethylindolenine, etc.), a 2-pyridine nucleus (e.g., pyridine, 3-methylpyridine, 4-methylpyridine, 5-methylpyridine, 3,4-dimethylpyridine, 4-chloropyridine, 3-hydroxypyridine, 3-phenylpyridine, etc.); a 4-pyridine nucleus (e.g., 2-methylpyridine, 3-methylpyridine, 3-chloropyridine, 2,6-di-methylpyridine, 3-hydroxypyridine, etc.); a 1-alkylimidazole nucleus (e.g., 1-methylimidazole, 1-ethyl-4-phenylimidazole, 1-butyl-4,5-dimethylimidazole, etc.); a 1-alkylbenzimidazole nucleus (e.g., 1-

methylbenzimidazole, 1 - butyl - 4 - methylbenzimidazole, 1 - ethyl - 5,6 - dichlorobenzimidazole, etc.), and, a 1-alkylnaphthimidazole nucleus (e.g., 1-ethyl-α-naphthimidazole, 1-methyl-β-naphthimidazole, etc.); and, Q represents the non-metallic atoms required to complete a 5 to 6 membered heretocyclic nucleus, typically containing a hetero atom selected from nitrogen, sulfur, selenium, and oxygen, such as a 2-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-oxazolidinedione nucleus (i.e., those of the 2-thio-2,4(3H,5H)-oxazoledione series, e.g., 3-ethyl-2-thio-2,4-oxazolidinedione, 3-(2-sulfoethyl)-2 - thio - 2,4 - oxazolidinedione, 3-(4-sulfobutyl)-2-thio 2,4 - oxazolidinedione, 3 - (3-carboxypropyl)-2-thio-2-,4-oxazolidinedione, 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)-thiazoledione 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., pseudohydantoi)nucleus; a 2,4-imidazolidinedione (hydantoin) series (e.g., 2,4-imidazolidinedione, 3 - ethyl - 2,4 - imidazolidinedione, 3-phenyl-2,4-imidazolidinedione, 3-α-naphthyl-2,4-imidazolidinedione, 1,3-diethyl-2,4-imidazolidinedione, 1-ethyl-3-phenyl-2,4-imidazolidinedione, 1-ethyl-3-α-naphthyl - 2,4 - imidazolidinedione, 1,3 - diphenyl-2,4-imidazolidinedione, etc.); a 2-thio-2,4-imidazolidinedione (i.e., 2-thiohydantoin) nucleus (e.g., 2-thio-2,4-imidazolidinedione, 3 - ethyl - 2 - thio - 2,4-imidazolidinedione, 3-(4 - sulfobutyl) - 2 - thio - 2,4 - imidazolidinedione, 3-(2 - carboxyethyl) - 2 - thio - 2,4 - imidazolidinedione, 3 - phenyl - 2 - thio - 2,4-imidazolidinedione, 3-α-naphthyl - 2 - thio - 2,4 - imidazolidinedione, 1,3-diethyl-2-thio-2,4 - imidazolidinedione, 1 - ethyl - 3 - phenyl-2-thio-2,4-imidazolidinedione, 1 - ethyl - 3 - α - naphthyl-2-thio-2,4 - imidazolidinedione, 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)

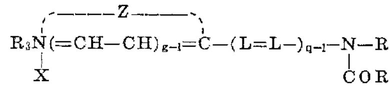


wherein R, R_1 and X are as previously defined and R_2 represents a member selected from an alkyl group of from 1–4 carbon atoms, e.g., methyl, ethyl, propyl, isopropyl, butyl, sec-butyl, etc., or benzyl, phenylethyl. In general such dyes are produced by heating a mixture of a quaternary salt of above 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 R_2 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 R_2 is methyl) with a compound of the formula:

(V)

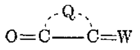


$$\overbrace{R_3\underset{\displaystyle X}{\underset{|}{N}}(=CH-CH)_{g-1}=C}^{Z}-(L=L-)_{q-1}-\underset{\displaystyle COR_7}{\underset{|}{N}}-R_6$$

wherein R_3, L, X and Z are as previously defined, *g* and *q* each represents a positive integer of from 1 to 2, R_6 represents an aryl group of from 6–6 carbon atoms, e.g., phenyl, p-tolyl, etc., and R_7 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.

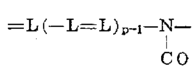
Merocyanine dyes, such as those of Formula III, are made to advantage by heating a mixture of a compound of Formula IV (in which R_2 is methyl) with a compound of the formula:

(VI)



$$O=\overbrace{C-\!\!-\!\!-C}^{Q}=W$$

wherein Q is as defined previously and W represents the group



$$=L(-L=L)_{p-1}-\underset{\displaystyle COR_7}{\underset{|}{N}}-R_6$$

wherein *p* represents a positive integer of from 1 to 2 and L, R_6 and R_7 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′-tetraethylimidazo[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-hydroxyethyl)imidazo[4,5-b]quinoxalinocarbocyanine 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[4,5-b]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-b]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-benzo[f]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. 660,253, issued Mar. 15, 1965, and Brooker and Van Lare Belgian Pat. 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 Van Lare 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.

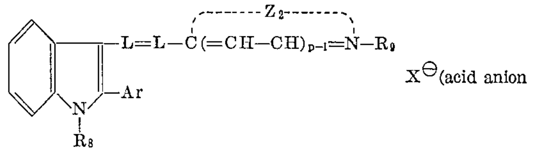
It will be noted that in the dyes described above, the imidazo[4,5-b]quinoxaline nucleus can be substituted, for example, with halogen (such as mono- or dichloro, mono- or dibromo) nitro, or with a fused ring.

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 of the indole nucleus. Dyes of this type are described by Coenen et al U.S. Pat. 2,930,694 issued Mar. 29, 1960; British Pat. 970,601 and Litzerman et al. Belgian Pat. 695,365 granted Sept. 11, 1967, and U.S. patent 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 indole nucleus. Advantageously, the second nucleus of these dyes is a densitizing nucleus. An especially useful class of such dyes may be represented by the following general formula:

$$\text{(VII)}\quad D{-}L{=}L{-}Y$$

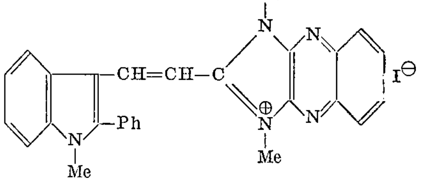
wherein D represents a 2-aromatically substituted indole nucleus attached to the methine chain through the 3-carbon atom of the indole nucleus; L represents a methine linkage; and, Y represents a desensitizing nucleus. For example, a preferred desensitizing nucleus is an imidazo[4,5-b]quinoxaline nucleus 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:

VII)

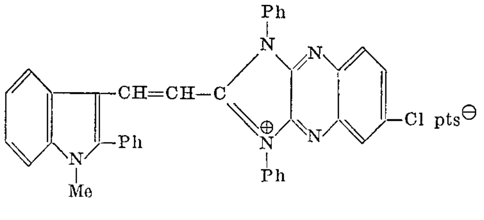


wherein L represents a methine group and R_8 represents an alkyl group; R_9 represents a value selected from those given for R_3 above; Z_2 is selected from the values given for Z above; *p* represents an integer of from 1 to 2; and, Ar represents an aromatic substituent such as phenyl or those referred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

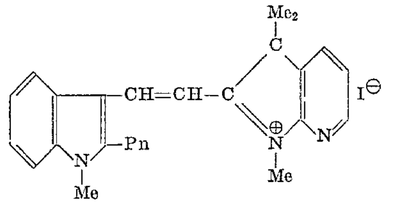
1,3-diethyl-1′-ethyl-2′-phenylimidazo[4,5-b]quinoxalino-3′-indolecarbocyanine iodide



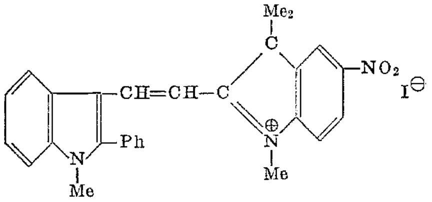
6-chloro-1′-methyl-1,2′,3-triphenylimidazo[4,5-b]quinoxalino-3′-indolocarbocyanine p-toluenesulfonate



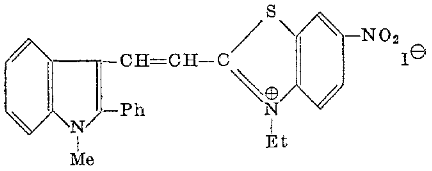
1,1′,3′,3′-tetramethyl-2-phenyl-3-indolopyrrolo[2,3-b]pyridocarbocyanine iodide



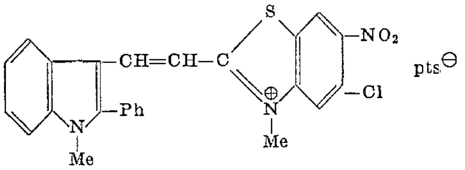
1,1′,3,3-tetramethyl-5-nitro-2′-phenylindo-3′-indolocarbocyanine iodide



3′-ethyl-1-methyl-2-phenyl-6′-nitro-3-indolothiacarbocyanine iodide

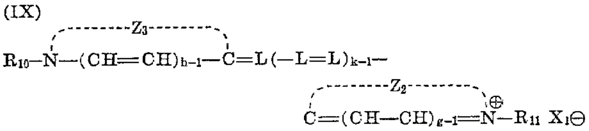


5′-chloro-1,3′-dimethyl-2-phenyl-6′-nitro-3-indolothiacarbocyanine p-toluenesulfonate



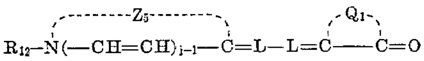
Still another class of useful dyes in accordance with this invention are the cyanine and merocyanine dyes in which at least one nucleus, and preferably two nuclei thereof, contains a desensitizing substituent such as nitro. Typical dyes of this class are represented by the formulas:

(IX)



$$R_{10}-\overbrace{N-(CH=CH)_{h-1}-C}^{Z_3}=L(-L=L)_{k-1}-\overbrace{C=(CH-CH)_{g-1}=\overset{\oplus}{N}}^{Z_2}-R_{11}\ X_1^{\ominus}$$

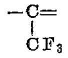
(X)



$$R_{12}-\overbrace{N(-CH=CH)_{j-1}-C}^{Z_5}=L-L=\overbrace{C-C}^{Q_1}=O$$

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_1 represents an acid anion; and, L represents a methine group. A typical dye of this class is 3,3′-diethyl-6,6′-dinitrothiacarbocyanine salt.

Another useful class of dyes which can be employed in the practice of this invention are the cyanine dyes which features 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:

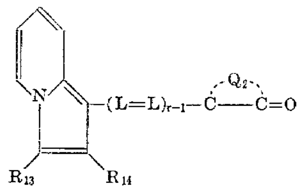


$$-\underset{CF_3}{\underset{|}{C}}=$$

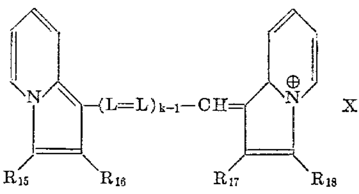
The most useful dyes of this class are those wherein a hydrogen atom in the methine chain of the cyanine dye is replaced with a trifluoromethyl group. The cyanine dye can be a simple cyanine, a dicarbocyanine or a tricarbocyanine. Expecially useful dyes are the meso-trifluoromethyl substituted carbocyanines.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

Also useful herein are cyanine and merocyanine dyes which have first and second heterocyclic nuclei joined by methine linkage, one of said nuclei being an indolizine nucleus joined, by the 1-carbon atom thereof, to the methine linkage. Some typical useful dyes of this type have the following formulas:

(XI)



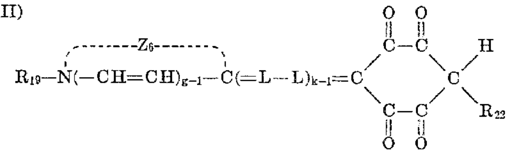
XII



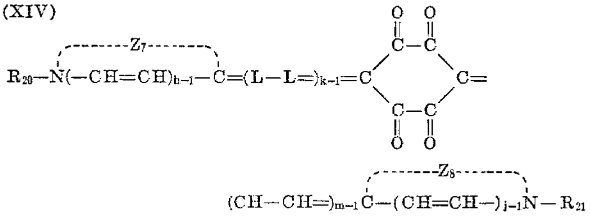
wherein R_{13}, R_{14}, R_{15} and R_{16} each are selected from the values given for R_1 above; Q_2 is selected from the values given for Q above, *k* represents an integer of from 1 to 3; and *r* represents an integer of from 2 to 3.

Another class of dyes useful in the practice of this invention includes cyanine and merocyanine dyes containing a 1,2,4,5-cyclohexanetetrone nucleus. Typical of such dyes are those having the following formulas:

(XIII)



(XIV)



wherein L represents a methine group; *k* and *m* each represents a positive integer of from 1 to 3; *h*, *g* and *j* each represents an integer of from 1 to 2; R_{19}, R_{20} and R_{21} each are selected from the values given for R_3; and R_{22} represents an alkyl group, e.g., methyl, ethyl or propyl; and, Z_6, Z_7 and Z_8 each are independently selected from the values given for Z, above. These dyes may be prepared by the procedure described by Heseltine and Brooker in U.S. Pat. 3,140,951. Specific types of dyes in this class are

3,6-di-(3-ethyl-2-benzothiazolinylidene)-1,2,4,5-cyclohexanetetrone;

3,6-di[(3-ethyl-2-benzothiazolinylidene)ethylidene]-1,2,4,5-cyclohexanetetrone;

3,6-di[(3-ethyl-2-benzoxazolinylidene)ethylidene]-1,2,4,5-cyclohexanetetrone;

3-[(3-ethyl-2-benzothiazolinylidene)ethylidene]-6-[(3-ethyl-2-benzoxazolinylidene)ethylidene]-1,2,4,5-cyclohexanetetrone;

3-(3-ethyl-2-benzothiazolinylidene)-6-[(3-ethyl-2-benzothiazolinylidene)ethylidene]-1,2,4,5-cyclohexanetetrone;

3-[4-(3-ethyl-2-benzothiazolinylidene)-2-butenylidene]-6-[(3-ethyl-2-benzothiazolinylidene)ethylidene]-1,2,4,5-cyclohexanetetrone;

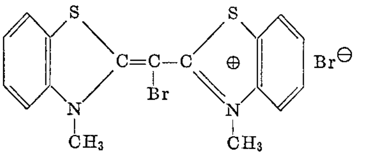
3,6-di-[4-(3-ethyl-2-benzothiazolinylidene)-2-butenylidene]-1,2,4,5-cyclohexanetetrone;

3,6-di-[(1-ethyl-3,3-dimethyl-2-indolinylidene)ethylidene]-1,2,4,5-cyclohexanetetrone;

3,6-di[(1-ethyl-2(1H)-quinolylidene)ethylidene]-1,2,4,5-cyclohexanetetrone; and

3,6-di[1-ethyl-4(1H)-quinolylidene)ethylidene]1,2,4,5-cyclohexanetetrone.

Cyanine dyes in which a methine linkage contains a halogen atom are also useful in this invention. Typical of such dyes are those wherein a hydrogen atom of one of the methine groups is replaced with a halogen atom such as chlorine or bromine, e.g., a dye having the formula:



Still other useful sensitizers are the merocyanine dyes having a 3-arylamino or 3-lower fatty acid amido substituted 2-pyrazolin-5-one nucleus, as described in Webster U.S. patent application 666,512 filed Sept. 8, 1967; the azacyanines derived from 1,2-disubstituted 3-nitrosoindoles, as described in Brooker and Mee U.S. patent application Ser. No. 660,173 filed Aug. 14, 1967; and, merocyanine dyes derived from 5-alkoxycarbonyl-2,4-dioxo-1-aryl-6-thioxopiperidine as described in Mee U.S. patent application Ser. No. 686,787 filed Nov. 30, 1967.

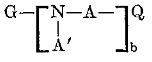
The dyes above can be used alone, or a combination of one or more of the above described dyes can be used to impart the desired spectral sensitivity.

The cyanine, merocyanine and azacyanine dyes referred to above are all spectral sensitizers for organic protoconductors. Organic photoconductors which are effectively spectrally sensitized by such dyes include both monomeric and polymeric organic photoconductors. The invention is particularly useful in increasing the speed of organic photoconductors which are substantially insensitive, or which have low sensitivity (e.g., a speed less than 25 when tested as described in Examples 1–18 below) to radiation of 400 to 700 nm.

The organic photoconductors which can be sensitized in accordance with this invention include p-type and n-type photoconductors, such as any of the n-type photoconductors described by Hoegl, The Journal of Physical Chemistry, vol. 69, No. 3, March 1965, e.g., 2,4,7-trinitrofluorenone.

An especially useful class of organic photoconductors is referred to herein as "organic amine" photoconductors. Such organic photoconductors have as a common structural feature at least one amino group. Useful organic photoconductors which can be spectrally sensitized in accordance with this invention include, therefore, arylamine compounds comprising (1) diarylamines such as diphenylamine, dinaphthylamine, N,N'-diphenylbenzidine, N-phenyl - 1 - naphthylamine; N-phenyl - 2 - naphthylamine; N,N'-diphenyl - p - phenylenediamine; 2-carboxy-5-chloro - 4' - methoxydiphenylamine; p-anilinophenol; N,N'-di - 2 - naphthyl - p - phenylene diamine; 4,4'-benzylidene-bis-(N,N-dimethyl - m - toluidine), those described in Fox U.S. Pat. 3,240,597 issued Mar. 15, 1966, and the like, and (2) triarylamines including (a) nonpolymeric triarylamines, such as triphenylamine, N,N,N',N'-tetraphenyl - m - phenylenediamine; 4-acetyltriphenylamine, 4 - hexanoyltriphenylamine; 4 - lauroyltriphenylamine; 4-hexyltriphenylamine, 4-dodecyltriphenylamine, 4,4'-bis(diphenylamino)benzil, 4,4' - bis(diphenylamino)-benzophenone, and the like, and (b) polymeric triarylamines such as poly[N,4''-(N,N',N'-triphenylbenzidine)]; polyadipyltriphenylamine, polysebacyltriphenylamine; polydecamethylenetriphenylamine; poly - N - (4 - vinylphenyl)diphenylamine, poly - N - (vinylphenyl)-α,α'-dinaphthylamine and the like. Other useful amine-type photoconductors are disclosed in U.S. Pat. 3,180,730, issued Apr. 27, 1965.

Useful photoconductive substances capable of being spectrally sensitized in accordance with this invention are disclosed in Fox U.S. Pat. 3,265,496 issued Aug. 9, 1966, and include those represented by the following general formula:

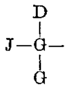


$$G-\left[\begin{matrix}N-A-\\ |\quad\quad\\ A'\quad\quad\end{matrix}\right]_b Q$$

wherein A represents a mononuclear or polynuclear divalent aromatic radical, either fused or linear, (e.g., phenylene, naphthylene, biphenylene, binaphthylene, etc.), or a substituted divalent aromatic radical of these types wherein said substituent can comprise a member such as an acyl group having from 1 to about 6 carbon atoms (e.g., acetyl, propionyl, butyryl, etc.), an alkyl group having from 1 to about 6 carbon atoms (e.g., methyl, ethyl, propyl, butyl, etc.), an alkoxy group having from 1 to about 6 carbon atoms (e.g., methoxy, ethoxy, propoxy, pentoxy, etc.), or a nitro group; A' represents a mononuclear or polynuclear monovalent aromatic radical, either fused or linear (e.g., phenyl, naphthyl, biphenyl, etc.); or a substituted monovalent aromatic radical wherein said substituent can comprise a member, such as an acyl group having from 1 to about 6 carbon atoms (e.g., acetyl, propionyl, butyryl, etc.), an alkyl group having from 1 to about 6 carbon atoms (e.g., methyl, ethyl, propyl, butyl, etc.), an alkoxy group having from 1 to about 6 carbon atoms (e.g., methoxy, propoxy, pentoxy, etc.), or a nitro group; Q can represent a hydrogen atom, a halogen atom or an aromatic amino group, such as A'NH—; *b* represents an integer from 1 to about 12, and G represents a hydrogen atom, a mononuclear or polynuclear aromatic radical, either fused or linear (e.g., phenyl, naphthyl, biphenyl, etc.), a substituted aromatic radical wherein said substituent comprises an alkyl group, an alkoxy group, an acyl group, or a nitro group, or a poly (4'-vinylphenyl) group which is bonded to the nitrogen atom by a carbon atom of the phenyl group.

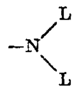
Polyarylalkane photoconductors are particularly useful in producing the present invention. Such photoconductors are described in U.S. Pat. 3,274,000; French Pat. 1,383,-461 and Seus and Goldman Belgian Pat. 696,114, granted Sept. 25, 1967. These photoconductors include leucobases of diaryl or triaryl methane dye salts, 1,1,1-triarylalkanes wherein the alkane moiety has at least two carbon atoms and tetraarylmethanes, there being substituted an amine group on at least one of the aryl groups attached to the alkane and methane moieties of the latter two classes of photoconductors which are non-leuco base material.

Preferred polyaryl alkane photoconductors can be represented by the formula:



$$\begin{matrix} & D & \\ & | & \\ J- & G & -E\\ & | & \\ & G & \end{matrix}$$

wherein each of D, E and G is an aryl group and J is a hydrogen atom, an alkyl group, or an aryl group, at least one of D, E and G containing an amino substituent. The aryl groups attached to the central carbon atom are preferably phenyl groups, although naphthyl groups can also be used. Such aryl groups can contain such substituents as alkyl and alkoxy typically having 1 to 8 carbon atoms, hydroxy, halogen etc. in the ortho, meta or para positions, ortho-substituted phenyl being preferred. The aryl groups can also be joined together or cyclized to form a fluorene moiety, for example. The amino substituent can be represented by the formula



wherein each L can be an alkyl group typically having 1 to 8 carbon atoms, a hydrogen atom, an aryl group, or together the necessary atoms to form a heterocyclic amino group typically having 5 to 6 atoms in the ring such as morpholino, pyridyl, pyrryl, etc. At least one of D, E and G is peferably p-dialkylaminophenyl group. When J is an alkyl group, such an alkyl group more generally has 1 to 7 carbon atoms.

Representative useful polyarylalkane photoconductors include the compounds listed below:

TABLE A

Compound No.
- (1)—4′,4″-bis(diethylamino)-2′,2″-dimethyltriphenylmethane
- (2)—4′,4″-diamino-4-dimethylamino-2′,2″-dimethyltriphenylmethane
- (3)—4′,4″-bis(diethylamino)-2,6-dichloro-2′,2″-dimethyltriphenylmethane
- (4)—4′,4″-bis(diethylamino)-2′,2″-dimethyldiphenylnaphthylmethane
- (5)—2′,2″-dimethyl-4,4′,4″-tris(dimethylamino) triphenylmethane
- (6)—4′,4″-bis(diethylamino)-4-dimethylamino-2′,2″-dimethyltriphenylmethane
- (7)—4′,4″-bis(diethylamino)-2-chloro-2′,2″-dimethyl-4-dimethylaminotriphenylmethane
- (8)—4′,5″-bis(diethylamino)-4-dimethylamino-2,2′,2″-trimethyltriphenylmethane
- (9)—4′,4″-bis(dimethylamino)-2-chloro-2′,2″-dimethyltriphenylmethane
- (10)—4′,4″-bis(dimethylamino)-2′,2″-dimethyl-4-methoxytriphenylmethane
- (11)—4′,4″-bis(benzylethylamino)-2′,2″-dimethyltriphenylmethane
- (12)—4′,4″-bis(diethylamino)-2′,2″-diethoxytriphenylmethane
- (13)—4,4′-bis(dimethylamino)-1,1,1-triphenylethane
- (14)—1-(4-N,N-dimethylaminophenyl)-1,1-diphenylethane
- (15)—4-dimethylaminotetraphenylmethane
- (16)—4-diethylaminotetraphenylmethane

As described herein a wide variety of photoconductor compounds can be spectrally sensitized with the dyes referred to above. Some organic photoconductors will, of course, be preferred to others; but in general useful results may be obtained from substantially all of the presently known organic photoconductors.

The following comprises a partial listing of such organic photoconductors and compositions which can be used in place of those more particularly described herein.

TABLE B

Issued	Patent numbers	Inventor
2/25, 1964	3,122,435	Noe et al.
3/31, 1964	3,127,266	Sus et al.
4/21, 1964	3,130,046	Schlesinger
4/28, 1964	3,131,060	Cassiers
6/30, 1964	3,139,338	Schlesinger
6/30, 1964	3,139,339	Schlesinger
7/14, 1964	3,140,946	Cassiers
9/15, 1964	3,148,982	Ghys
11/3, 1964	3,155,503	Cassiers
11/24, 1964	3,158,475	Cassiers
12/15, 1964	3,161,505	Tomanek
12/29, 1964	3,163,530	Schlesinger
12/29, 1964	3,163,531	Schlesinger
12/29, 1964	3,163,532	Schlesinger
2/9, 1965	3,169,060	Hoegl
3/23, 1965	3,174,854	Stumpf
4/27, 1965	3,180,729	Klupfel et al.
4/27, 1965	3,180,730	Klupfel et al.
6/15, 1965	3,189,447	Neugebauer
9/14, 1965	3,206,306	Neugebauer
7/21, 1964	3,141,770	Davis et al.
6/5, 1962	3,037,861	Hoegl et al.
6/26, 1962	3,041,165	Sus et al.
11/27, 1962	3,066,023	Schlesinger
1/8, 1963	3,072,479	Bethe
7/9, 1963	3,047,095	Klupfel et al.
11/26, 1963	3,112,197	Neugebauer et al.
12/3, 1963	3,113,022	Cassiers et al.
12/17, 1963	3,114,633	Schlesinger

The spectrally sensitized organic photoconductor compositions of this invention can, in certain arrangements, be employed in electrophotographic elements in the absence of binder. For example, the photoconductor itself is sometimes capable of film formation, and therefore requires no separate binder. An example of such film-forming photoconductor is poly(vinylcarbazole). However, the more common arrangement is to provide a binder for the spectrally sensitized organic photoconductive materials. Any suitable binder material may be utilized for the spectrally sensitized organic photoconductors of the invention. Such binders should possess high dielectric strength, and have good insulating properties (at least in the absence of actinic radiation) as well as good film forming properties. Preferred binder materials are polymers such as polystyrene, poly(methylstyrene), styrene-butadiene polymers, poly(vinyl chloride), poly(vinylidene chloride), poly(vinyl acetate), vinyl acetate-vinyl chloride polymers, poly(vinyl acetals), polyacrylic and methacrylic acid esters, polyesters such as poly(ethylene alkaryloxy-alkylene terephthalates), phenol-formaldehyde resins, polyamides, polycarbonates and the like.

Electrically conductive supports useful in the practice of our invention may be selected from any of those which are useful in electrophotographic processes, such as metal plates or foils, metal foils laminated to paper or plastic films, electrically conductive papers and films, papers and films coated with transparent electrically conductive resins, and the like. Whether a transparent, translucent or opaque support material is used will be determined by the method of exposure to be employed, e.g., by reflex or by transmission through the original, and by the end use to which the reproduction is to be put. Exposure by reflex, for example, requires that the support transmit light while no such requirement is necessary for exposures by projection. Similarly transparent supports are required if the reproduction is to be used for projection purposes; translucent supports are preferred for reflex prints; and opaque supports are adequate if the image is subsequently transferred by any means to another support, the reproduction is satisfactory as obtained, or the reproduction is to be used as a printing plate for preparing multiple copies of the original.

The quantity of the above-described dye required to spectrally sensitize an organic photoconductor varies with the results desired, the particular dye used, and the particular organic photoconductor used. Generally speaking, good results are obtained with about .01 to 10 parts by weight dye and about 1 to 75 parts by weight of the organic photoconductor. Binder can be employed in such compositions, when desired, at preferred ranges of 25 to 99 parts by weight. In addition, the composition can contain other sensitizers, either spectral sensitizers or speed increasing compounds, or both.

As used herein and in the appended claims, the terms "insulating" and "electrically conductive" have reference to materials the surface resistivities of which are greater than 10^{12} ohms per square unit (e.g., per square foot) and less than 10^{10} ohms per square unit (e.g., per square foot) respectively.

Coating thicknesses of the photoconductive compositions of the invention on a support can vary widely. As a general guide, a dry coating in the range from about 1 to 200 microns is useful for the invention. The preferred range of dry coating thickness is in the range from about 3 to 50 microns.

To produce a reproduction of an image utilizing the electrophotographic elements of our invention, the photoconductive layer is preferably dark adapted, and then is charged either negatively or positively by means of, for example, a corona discharge device maintained at a potential of from 6000–7000 volts. The charged element is then exposed to light through a master, or by reflex in contact with a master, to obtain an electrostatic image corresponding to the master. This invisible image may then be rendered visible by being developed by contact with a developer including a carrier and toner. The carrier can be, for example, small glass or plastic balls, or iron powder. The toner can be, for example, a pigmented thermoplastic resin having a grain size of from about 1–100μ which may be fused to render the image permanent. Alternatively, the developer may contain a pigment or pigmented resin suspended in an insulating liquid which optionally may contain a resin in solution. If the polarity of the charge on the toner particles is opposite to that of the electrostatic latent image on the photoconductive element, a reproduction corresponding to the original is obtained. If, however, the polarity of the toner charge is the same as that of the electrostatic latent image, a reversal or negative of the original is obtained.

Although the development techniques described hereinabove produce a visible image directly on the electrophotographic element, it is also possible to transfer either the electrostatic latent image, or the developed image to a second support which may then be processed to obtain the final print. All of these development techniques are well known in the art and have been described in a number of U.S. and foreign patents.

This invention will be further illustrated by the following examples. Examples 1 through 18 show the great increase in speed of organic photoconductors when the dyes employed in this invention are added thereto. This increase in speed is due to the spectral sensitivity imparted to the photoconductor by the dyes described herein.

EXAMPLES 1–18

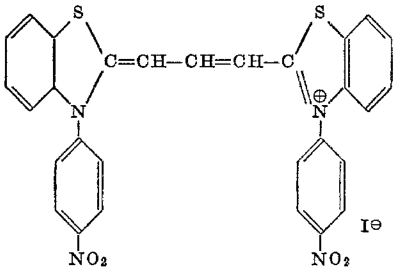
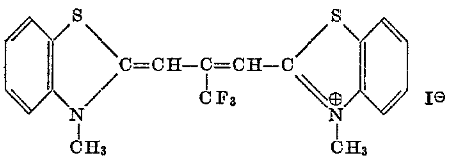
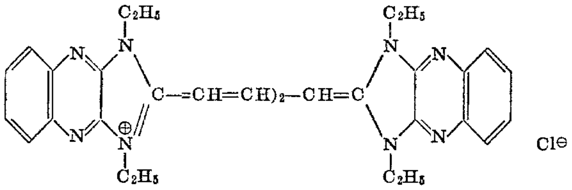
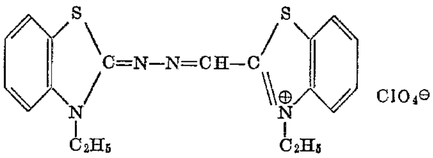
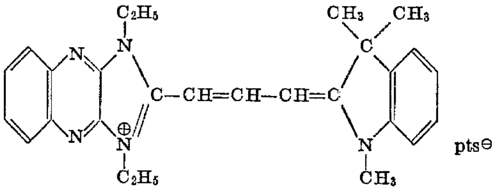
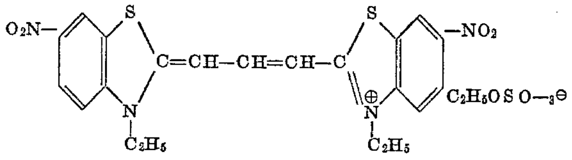
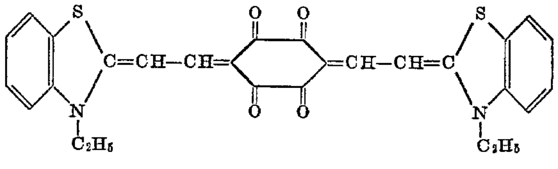
A series of solutions are prepared consisting of 5.0 ml. methylene chloride (solvent); 0.15 g. 4,4'-bis-(diethylamino) - 2,2' - dimethyltriphenylmethane (organic photoconductor); 0.50 g. polyester composed of terephthalic acid and a glycol mixture comprising a 9:1 weight ratio of 2,2-bis-[4-(2-hydroxyethoxy)phenyl]-propane and ethylene glycol (binder, which can be prepared by the method described in British Pat. 857,933 at page 3, lines 43–72) and 0.002 g. of the spectral sensitizing dye indicated by identifying number from Table C below. Each solution is coated on an aluminum surface maintained at 25° C., and dried. All operations are carried out in a darkened room. A sample of each coating is uniformly charged by means of a corona to a potential of about 600 volts and exposed through a transparent member bearing a pattern of varying optical density to a 3000° K. tungsten source. The resultant electrostatic image pattern is then rendered visible by cascading a developer composition comprising finely divided colored thermoplastic electrostatically responsive toner particles carried on glass beads over the surface of the element. The image is then developed by deposition of the toner in an imagewise manner on the element. (Other development techniques such as those described in U.S. 2,786,439; 2,786,440; 2,786,441; 2,811,465; 2,874,063; 2,984,163; 3,040,704; 3,117,884; re 25,779; 2,297,691; 2,551,582; and in "RCA Review," vol. 15 (1954) pp. 469–484, can be used with similar results.) An image is formed on each sample, as indicated in Table I. Another sample of each coating is tested to determine its electrical speed. This is accomplished by giving each element a positive or negative charge (as indicated in Table I) with a corona source until the surface potential, as measured by an electrometer probe, reaches 600 volts. It is then exposed to light from a 3000° K. tungsten source of 20-foot-candle illuminance at the exposure surface. The exposure is made through a stepped density gray scale. The exposure causes reduction of the surface potential of the element under each step of the gray scale from its initial potential, V_0, to some lower potential, V, whose exact value depends on the actual amount of exposure in meter-candle-seconds received by the area. The results of these measurements are plotted on a graph of surface potential V vs log exposure for each step. The actual speed of each element is expressed in terms of the reciprocal of the exposure required to reduce the surface potential by 100 volts. Hence, the speeds given in Table I are the numerical expression of 10^4 divided by the exposure in meter-candle-seconds required to reduce the 600 volts charged surface potential by 100 volts. The dyes employed in these examples are identified below in Table C. The results are shown in Table I below.

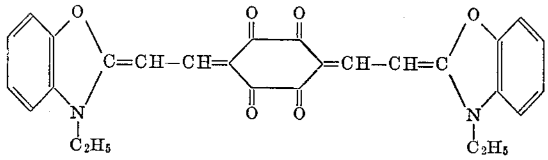
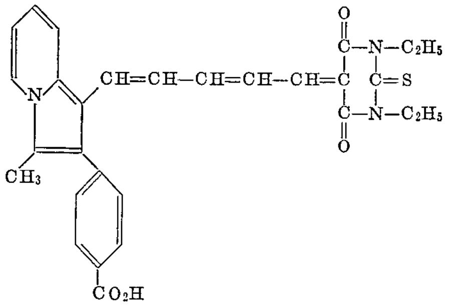
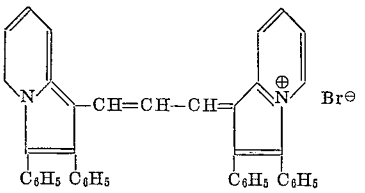
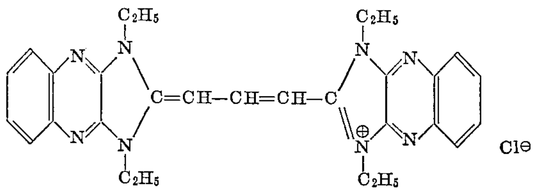
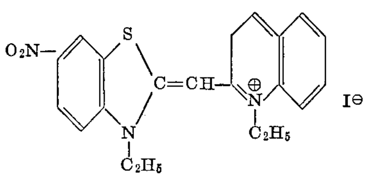
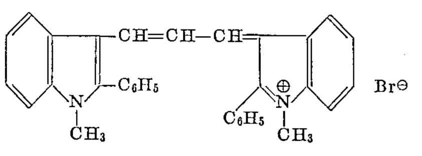
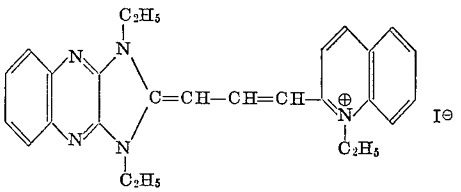
TABLE I

Example Number	Dye	Image formed	Speed	Polarity of surface potential
1	None (control)	Yes	5	− or +
2	I	Yes	98	−
3	II	Yes	98	−
4	III	Yes	60	+
5	IV	Yes	25	−
6	V	Yes	800	+
7	V	Yes	800	−
8	VI	Yes	160	−
9	VII	Yes	320	+
10	VII	Yes	320	−
11	VIII	Yes	550	+
12	IX	Yes	50	+
13	IX	Yes	50	−
14	X	Yes	500	+
15	XI	Yes	900	−
16	XII	Yes	50	−
17	XIII	Yes	320	−
18	XIV	Yes	500	−

The data in the above table establish that the dyes of this invention provide substantial increases in speed of organic photoconductors. This increase in speed is due primarily to the spectral sensitivity provided by the dyes employed herein. Good increases in speed, similar to those obtained in Examples 1–18, are obtained when the binder is replaced with an equivalent amount of a binder such as a styrene-butadiene copolymer, polystyrene or a polycarbonate resin, and when the organic photoconductor employed in those examples is replaced with an equivalent amount of 4',4'' - diamino - 4 - dimethylamino - 2',2''-dimethyltriphenylmethane; 4',5'' - bis(diethylamino) - 4-dimethylamino - 2,2',2'' - trimethyltriphenylmethane; 2,4,7 - trinitrofluoroenone or, triphenylamine. The specific dyes in the foregoing examples are defined in the following table.

TABLE C

Dye To.	Name
I	3,3′-di-p-nitrophenylthiocarbocyanine iodide 
II	3,3′-dimethyl-9-trifluoromethylthiacarbocyanine iodide 
III	1,1′,3,3′-Tetraethylimidazo[4,5-a]quinoxalinodicarbocyanine chloride 
IV	3,3′-diethyl-8,9-diazathiacarbocyanine perchlorate 
V	1,3-diethyl-1′,3′,3′-trimethylimidazo[4,5-a]-quinoxalinoindocarbocyanine p-toluenesulfonate 
VI	3,3′-diethyl-6,6′-dinitrothiacarbocyanine ethylsulfate 
VII	3,6-Bis[(3-ethyl-2-benzothiazolinylidene)ethylidene]-1,2,4,5-cyclohexanetetrone 
VIII	3,6-Bis[(3-ethyl-2-benzoxazolinylidene)ethylidene]-1,2,4,5-cyclohexanetetrone

Dye To.	Name
	
IX	5-[5-(2-p-carboxyphenyl-3-methyl-1-indolizinyl)-2,4-pentadienylidene]-1,3-diethyl-2-thiobarbituric acid 
X	2,2′,3,3′-tetraphenyl-1,1′-indolizinocarbocyanine bromide 
XI	1,1′,3,3′-tetraethylimidazo[4,5-b]quinoxalinocarbocyanine chloride 
XII	1′,3-diethyl-6-nitrothia-2′-cyanine iodide 
XIII	1,1′-dimethyl-2,2′-diphenyl-3,3′-indolocarbocyanine bromide 
XIV	1,1′,3-triethylimidazo[4,5-b]quinoxalino-2′-carbocyanine iodide 

The dyes described in Table C can be prepared by conventional methods. Dyes III, V, XI and XIV can be prepared as described in Brooker French Pat. 1,401,594 or Brooker and VanLare U.S. patent application Ser. No. 609,791, filed Jan. 17, 1967, and Belgian Pat. 695,368. Dye IV can be prepared by the method shown in Fuchs and Grauaug, Ber., 61, 57 (1928). Dye V can be prepared by the method of Brooker, Keyes and Williams, J. Am. Chem. Soc., 64, 199 (1942). A method for preparing Dyes VII and VIII is shown in U.S. Pat. 3,140,951. A procedure for preparing Dye IV is shown in Example 5 of U.S. Pat. 2,622,082. Dye X can be described in Example 1 of U.S. Pat. 2,571,775. A method for preparing Dye XII is disclosed in J. Am. Chem. Soc., 57, 2488 (1935). Dye XIII can be prepared by the procedure shown in U.S. Pat. 2,930,694.

Examples 19–24 demonstrate the increase in sensitivity when dyes are added to organic photoconductors in accordance with this invention.

EXAMPLES 19–24

Coating solutions are made consisting of 0.002 g. Dye XIII (dye sensitizer); 0.15 g. of the photoconductor indicated in Table II and identified in Table D; 0.5 g. of the copolyester binder described and employed in Examples 1–18; and, 5.0 ml. of methylene chloride (solvent). These solutions are coated and tested (using both negative and positive charging) by the same procedure described in Examples 1–18. The results are shown in Table II.

TABLE II

Example Number	Photoconductor	Image formed	Speed	
			Positively charged surface	Negatively charged surface
19	None (control)	No		
20	A	Yes	800	1,100
21	B	Yes	700	320
22	C	Yes	250	320
23	D	Yes	320	450
24	E	Yes	250	320

Similar results to those shown above are obtained when, for example, Dye XIII in the above examples is replaced with equivalent amounts of Dyes I, II, III, V, VI, VIII, X, XI and XIV. These results show that the dyes of this invention effectively spectrally sensitize a wide variety of organic photoconductors. The dyes of this invention are not themselves photoconductive. The photoconductors used in these examples are identified in Table D. These photoconductors have very low photoconductive speed to visible light. The response thereof is substantially the same as that of the photoconductors employed in Table I.

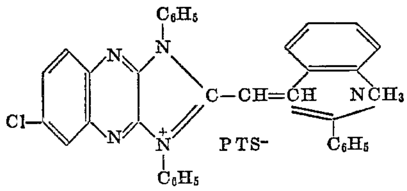
Table D

Identifying Letter:	Photoconductor
A	Triphenylamine.
B	1,3,5-triphenyl-2-pyrazoline.
C	4,4'-bis-diethylamino - 2,2'-dimethyltriphenylmethane.
D	2,3,4,5-tetraphenylpyrrole.
E	4,4'-bis-diethylaminobenzophenone.

Examples 25 and 26 show the sensitization of organic photoconductors with other types of cyanine dyes useful in this invention.

EXAMPLE 25

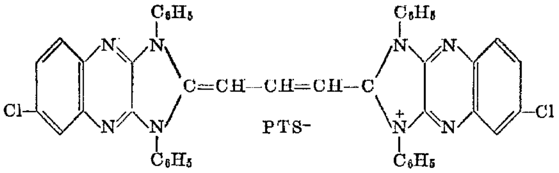
The procedure of Examples 1–18 is repeated except that the coating solution consists of 1.5 g. of the polyester binder described in Examples 1–18; 0.5 g. triphenylamine photoconductor and 0.02 g. of Dye XV, 6-chloro-1'-methyl - 1,2'3 - triphenylimidazo[4,5-b]quinoxalino - 3'-indolocarbocyanine p-toluenesulfonate.



Coating is at 0.004 inch wet thickness on a polyethylene terephthalate support having a cuprous iodide conductive layer and cellulose nitrate barrier layer of the type described in Trevoy U.S. Pat. 3,245,833. The coating is tested as described in Examples 1–18. The speed using a positive charge is 1200, and the speed using a negative charge is 800. The coating has an absorption maximum at 530 nm.

EXAMPLE 26

The procedure of Example 25 is repeated except that Dye XV is replaced with 0.02 g. of Dye XVI, 6,6'-dichloro - 1,1',3,3' - tetraphenylimidazo[4,5-b]quinoxalinocarbocyanine p-toluenesulfonate



The coating has an absorption maximum at 620 nm, a speed of 1200 using a positive charge and a speed of 900 using a negative charge.

This invention is highly unexpected because dyes previously suggested for spectral sensitizers impart weak spectral sensitization to organic photoconductors. Typical dyes proposed by the prior art as spectral sensitizers, which produce weak spectral sensitization in these systems, are shown in Table E.

TABLE E

Dye identification:	Name
A	Pinacyanol.
B	Kryptocyanine.
C	Anhydro-3-ethyl-9-methyl - 3'-(3-sulfobutyl) thiacarbocyanine hydroxide.
D	3,3'-diethyl - 9 - methylthiacarbocyanine bromide.
E	3-carboxymethyl-5 - [(3-methyl-2-thiazolidinylidene)-1-methylethylidene]rhodanine.
F	Anhydro-5,5'-dichloro-3,9-diethyl-3' - (sulfobutyl)thiacarbocyanine hydroxide.
G	1'-ethyl-3-methylthia-2'-cyanine chloride.
H	1,1'-diethyl-2,2'-cyanine chloride.

As noted above, the dyes of this invention are inoperable spectral sensitizers for negative photographic silver halide emulsions, as they strongly desensitize negative silver halide emulsions. In addition, the polarographic characteristics of the present dyes are such that the cathodic half-wave potential is more positive than —1.0 volt and the sum of the anodic and the cathodic polarographic half-wave potentials thereof give a sum more positive than —0.10 volt. However, dyes proposed in the prior art as spectral sensitizers for organic photoconductors, such as those in Table E, fail to possess all those characteristics. This is shown in the data given below.

Polarographic determinations are made with representative dyes in Table C, and with prior art dyes in Table E. These determinations are made using the same procedure given above, with methanol being the solvent in all evaluations, except for dye X which requires an 8 to 2 parts by weight methanol-acetone solution because of the limited solubility of that dye in methanol. The dyes are tested in the absence of oxidizable ions, such as iodide. Thus, for example, dyes listed in the above tables as iodide salts are converted to other salts, such as p-toluenesulfonate or chloride salts for the voltammetric testing. In addition, dyes in Tables C and E are tested by the exact procedure described above, and in a silver bromoiodide emulsion prepared as described above, to determine the extent of desensitization caused by the dye. The polarographic measurements and silver halide emulsion desensitization values obtained are shown in Table III.

Although the invention has been described in considerable detail with reference to certain preferred embodiments thereof, it will be understood that variations and modifications can be effected without departing from the spirit and scope of the invention as described hereinabove and as defined in the appended claims.

TABLE III

Dye	Ec	Ea	Ea plus Ec	Desensitization, log E at 365 mμ
I	>−1.0	>+0.8	>−.10	2.10
II	−0.79	>+0.8	<0.0	1.66
III	−0.63	+0.67	+0.04	1.94
IV	−0.64	>+1.0	>+0.36	1.96
V	−0.88	>+1.0	>+0.12	1.71
VI	−0.58	+1.00	+0.42	1.90
VIII	−0.80	+0.95	+0.15	1.39
IX	−0.58	+0.58	0	1.54
X	−0.33	+0.89	+0.56	2.15
XI	−0.79	>+1.0	>+0.21	1.42
XII	−0.60	>+1.0	>+0.40	1.44
XIII	−0.20	>+1.0	>+0.80	1.86
XIV	−0.89	+0.82	−0.07	1.39
A	−1.11	0.57	−0.54	0.08
B	−0.99	0.19	−0.80	0.94
C	−1.29	0.73	−0.56	0.14
D	−1.16	0.76	−0.40	0.14
E	−1.47	0.49	−0.98	0.10
F	−1.09	0.86	−0.23	0.12
G	−1.08	>1.0	>−0.08	0.02
H	−1.08	0.99	−0.09	0.02

NOTE.—In the above table, ">" means "more positive than" the value given.

We claim:

1. A composition of matter comprising an organic photoconductor spectrally sensitized with a substantially non-photoconductive dye selected from the group consisting of the cyanine, merocyanine and azacyanine dyes, which dye:

(1) has a cathodic polarographic half-wave potential more positive than −1.0 volt;

(2) has an anodic polarographic half-wave potential and a cathodic polarographic half-wave potential which, when added together, give a sum more positive than −0.10 volt; and,

(3) desentitizes a test negative gelatin silver bromoiodide emulsion, consisting of 99.35 mole percent bromide and .65 mole percent iodide, more than 0.4 log E to light having a wavelength of 365 nm. when incorporated in said test emulsion at a concentration of 0.2 millimole of dye per mole of silver.

2. A composition of matter as defined in claim **1** wherein said dye is selected from the group consisting of (1) dyes containing a substituent selected from the group consisting of a nitro group and a trifluoromethyl group; (2) dyes containing a nucleus selected from the group consisting of a 1,2,4,5-cyclohexanetetrone nucleus; an indolizine nucleus; an imidazo[4,5-b]quinoxaline nucleus; and, a 2-aromatically substituted indole nucleus; and, (3) an azacyanine dye.

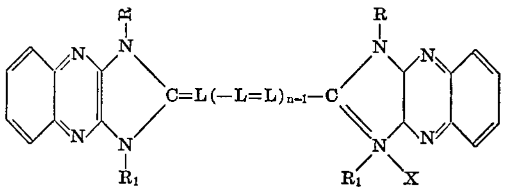
3. A composition of matter as defined in claim **1** wherein said dye is a cyanine dye salt comprising two nuclei joined together by methine linkage, one of said nuclei being an imidazo[4,5-b]quinoxaline nucleus, said nucleus being joined by the 2-carbon atom thereof to said methine linkage, and a second nucleus to complete said cyanine dye.

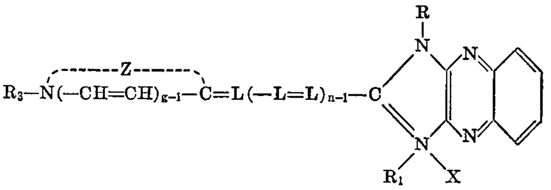
4. A composition of matter as defined in claim **5** wherein said second nucleus of said cyanine dye contains a heterocyclic nitrogen atom, and said methine linkage forms a polyene chain containing an equal number of alternating single and double bonds, one terminal carbon atom of said chain being the 2-carbon atom of an imidazo[4,5-b]quinoxaline nucleus, the other terminal carbon atom of said chain being in said second nucleus and attached to a heterocyclic nitrogen atom in said second nucleus.

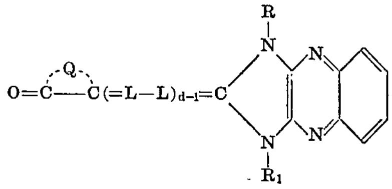
5. A composition of matter as defined in claim **6** wherein said second nucleus of said cyanine dye is a desensitizing nucleus.

6. A composition of matter as defined in claim **1** wherein said dye is a merocyanine dye 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 carbon atoms of said chain being the 2-carbon atom of an imidazo[4,5-b]quinoxaline nucleus, and 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.

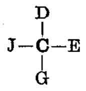
7. A composition of matter as defined in claim **1** wherein said dye has one of the following formulas:







wherein R, R_1, and R_3 are independently selected from the group consisting of alkyl, alkenyl and aryl; each L represents a methine linkage; *g* represents a positive integer of from 1 to 2; *d* represents a positive integer of from 1 to 2; *n* represents a positive integer of from 1 to 2; Z represents the non-metallic atoms required to complete a heterocyclic nucleus containing from 5 to 6 atoms in the heterocyclic ring; Q represents the non-metallic atoms required to complete a 5 to 6 membered heterocyclic ring containing a hetero atom selected from nitrogen, sulfur, selenium and oxygen; and, X represents an acid anion; and, said organic photoconductor has the following formula:



$$J-\overset{\overset{\displaystyle D}{|}}{\underset{\underset{\displaystyle G}{|}}{C}}-E$$

wherein each of D, E and G is an aryl group and J is selected from the group consisting of a hydrogen atom, an alkyl group and an aryl group, at least one of D, E and G containing an amino substituent.

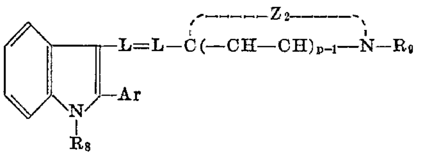
8. A composition of matter as defined in claim **1** wherein said dye comprises two nuclei joined by methine linkage, at least one of said nuclei being a 2-aromatically substituted indole nucleus attached by the 3-carbon atom thereof to said methine linkage.

9. A composition of matter as defined in claim **1** wherein said dye is a trimethine cyanine dye comprising two 2-aromatically substituted indole nuclei each joined by the 3-carbon atom thereof of the respective terminal carbon atoms of the trimethine chain of the dye.

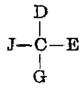
10. A composition of matter as defined in claim **1** wherein said dye is an unsymmetrical dye comprising first and second nuclei joined by methine linkage, said first nucleus being a 2-aromatically substituted indole nucleus joined, by the 3-carbon atom thereof, to said methine linkage, and said second nucleus being a heterocyclic nucleus to complete said dye.

11. A composition of matter as defined in claim **12** wherein the methine linkage of said dye is a dimethine linkage and said second nucleus of said dye is a desensitizing nucleus.

12. A composition of matter as defined in claim **1** wherein said dye has the following formula:



wherein *p* represents a positive integer of from 1 to 2; R_8 represents an alkyl group; R_9 represents a substituent selected from the group consisting of alkyl, alkenyl and aryl; each L represents a methine linkage; Ar represents an aromatic substituent and Z_2 represents the non-metallic atoms required to complete a heterocyclic nucleus containing from 5 to 6 atoms in the heterocyclic ring; and, said organic photoconductor has the following formula:



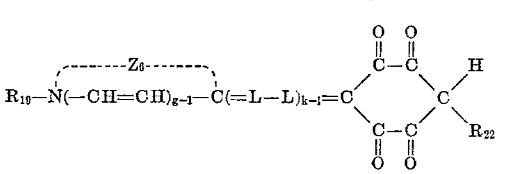
$$\begin{array}{c} D \\ | \\ J-C-E \\ | \\ G \end{array}$$

wherein each of D, E and G is an aryl group and J is selected from the group consisting of a hydrogen atom, an alkyl group and an aryl group, at least one of D, E and G containing an amino substituent.

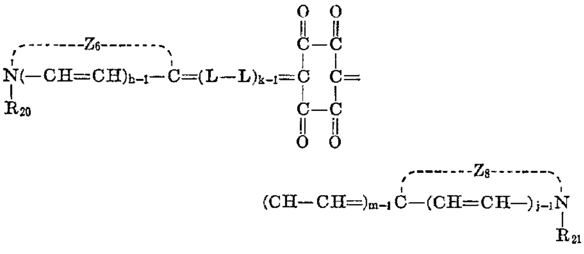
13. A composition of matter as defined in claim **1** wherein said dye contains a nitro group.

14. A composition of matter as defined in claim **1** wherein said dye contains a 1,2,4,5-cyclohexanetetrone nucleus.

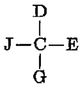
15. A composition of matter as defined in claim **14** wherein said dye has one of the following formulas:



and



wherein R_{19}, R_{20}, R_{21} and R_{22} each represents alkyl, alkenyl or aryl; g, h and j each represents a positive integer of from 1 to 2; *k* and *m* each represents a positive integer of from 1 to 3; each L represents a methine group; and, Z_6, Z_7 and Z_8 each represents the non-metallic atoms required to complete a heterocyclic nucleus containing from 5 to 6 atoms in the heterocyclic ring; and, said organic photoconductor has the following formula:

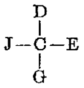


$$\begin{array}{c} D \\ | \\ J-C-E \\ | \\ G \end{array}$$

wherein each of D, E and G is an aryl group and J is selected from the group consisting of a hydrogen atom, an integer of from 1 to 2; *k* and *m* each represents a positive containing an amino substituent.

16. A composition of matter as defined in claim **1** wherein said organic photoconductor is an organic amine photoconductor which contains at least a group selected from a secondary amino group and a tertiary amino group.

17. A composition of matter as defined in claim **2** wherein said organic photoconductor has the following general formula:



$$\begin{array}{c} D \\ | \\ J-C-E \\ | \\ G \end{array}$$

wherein each of D, E and G is an aryl group and J is selected from the group consisting of a hydrogen atom, an alkyl group and an aryl group, at least one of D, E and G containing an amino substituent.

18. A composition of matter comprising from 1 to 75 parts by weight of an organic photoconductor selected from the group consisting of: triphenylamine; 1,3,5-triphenyl-2-pyrazoline; 4,4'-bis-diethylamino-2,2'-dimethyltriphenylmethane; 2,3,4,5-tetraphenylpyrrole; 4,4'-bis-diethylaminobenzophenone; said organic photoconductor being spectrally sensitized with from .01 to 10 parts by weight of a dye selected from the group consisting of

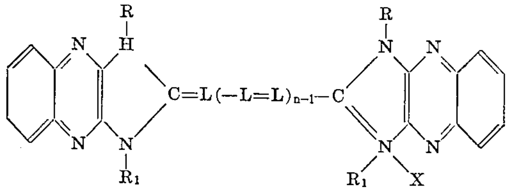
3,3'-di-p-nitrophenylthiacarbocyanine salt;
3,3'-dimethyl-9-trifluoromethylthiacarbocyanine salt;
1,1',3,3'-tetraethylimidazo[4,5-b]quinoxalinodicarbocyanine salt;
3,3'-diethyl-8,9-diazathiacarbocyanine salt;
1,3-diethyl-1',3',3'-trimethylimidazo[4,5-b]quinoxalinoindocarbocyanine salt;
3,3'-diethyl-6,6'-dinitrothiacarbocyanine salt;
3,6-bis[(3-ethyl-2-benzothiazolinylidene)ethylidene]-1,2,4,5-cyclohexanetetrone;
3,6-bis[(3-ethyl-2-benzoxazolinylidene)ethylidene]-1,2,4,5-cyclohexanetetrone;
5-[5-(2-p-carbocyphenyl-3-methyl-1-indolizinyl)-2,4-pentadienylidene]-1,3-diethyl-2-thiobarbituric acid;
2,2',3,3'tetraphenyl-1,1'-indolizinocarbocyanine salt;
1,1'3,3'-tetraethylimidazo[4,5-b]quinoxalinocarbocyanine salt;
1',3-diethyl-6-nitrothia-2'-cyanine salt;
1,1'-dimethyl-2,2'-diphenyl-3,3'-indolocarbocyanine salt;
1,1',3-triethylimidazo[4,5-b]quinoxalino-2'-carbocyanine salt;
6-chloro-1'-methyl-1,2',3-triphenylimidazo[4,5-b]-quinoxalino-3'-indolocarbocyanine salt and
6,6'-dicchloro-1,1',3,3'-tetraphenylimidazo[4,5-b]-quinoxalinocarbocyanine salt.

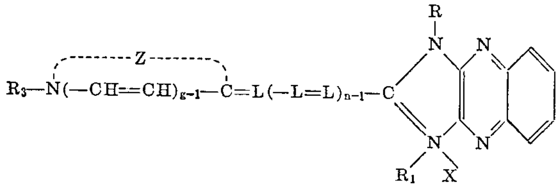
19. An electrophotographic element comprising a conductive support having coated thereon a layer comprising an organic photoconductor in an insulating binder, said organic photoconductor being spectrally sensitized with a substantially non-photoconductive dye selected from the group consisting of the cyanine, merocyanine and azacyanine dyes, which dye:

(1) has a cathodic polarographic half-wave potential more positive than −1.0 volt;
(2) has an anodic polarographic half-wave potential and a cathodic polarographic half-wave potential which, when added together, give a sum more positive than −0.10 volt; and,
(3) desensitizes a test negative gelatin silver bromoiodide emulsion, consisting of 99.35 mole percent bromide and .65 mole percent iodide, more than 0.4 log E to light having a wavelength of 365 nm, when incorporated in said test emulsion at a concentration of 0.2 millimole of dye per mole of silver.

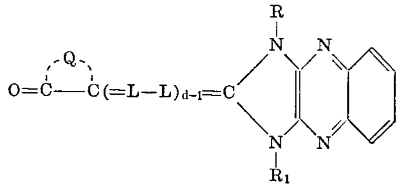
20. An electrophotographic element as defined in claim **19** wherein said dye is selected from the group consisting of (1) dyes containing a substituent selected from the group consisting of a nitro group and a trifluoromethyl group; (2) dyes containing a nucleus selected from the group consisting of a 1,2,4,5-cyclohexanetetrone nucleus; an indolizine nucleus; an indolizine nucleus; an imidazo [4,5-b]quinoxaline nucleus; and, a 2-aromatically substituted indole nucleus; and, (3) an azacyanine dye.

21. An electrophotographic element as defined in claim **19** wherein said dye has one of the following formulas:

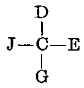




and



wherein R, R_1 and R_3 are independently selected from the group consisting of alkyl, alkenyl and aryl; each L represents a methine linkage; *g* represents a positive integer of from 1 to 2; *d* represents a positive integer of from 1 to 2; *n* represents a positive integer of from 1 to 2; Z represents the non-metallic atoms required to complete a heterocyclic nucleus containing from 5 to 6 atoms in the heterocyclic ring; Q represents the non-metallic atoms required to complete a 5 to 6 membered heterocyclic ring containing a hetero atom selected from nitrogen, sulfur, selenium and oxygen; and, X represents an acid anion; and, said organic photoconductor has the following formula:

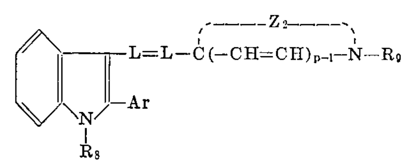


$$J-\underset{G}{\overset{D}{C}}-E$$

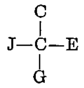
wherein each of D, E and G is an aryl group and J is selected from the group consisting of a hydrogen atom, an alkyl group and an aryl group, at least one of D, E and G containing an amino substituent.

22. An electrophotographic element as defined in claim **19** wherein said dye comprises two nuclei joined by methine linkage, at least one of said nuclein being a 2-aromatically substituted indole nucleus attached by the 3-carbon atom thereof to said methine linkage.

23. An electrophotographic element as defined in claim **19** wherein said dye has the following formula:



wherein *p* represents a positive integer of from 1 to 2; R_8 represents an alkyl group; R_9 represents alkyl, alkenyl or aryl; L represents a methine group; Ar represents an aromatic substituent and Z_2 represents the non-metallic atoms required to complete a heterocyclic nucleus containing from 5 to 6 atoms in the heterocyclic ring; and, said organic photoconductor has the following formula:



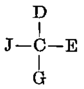
$$J-\underset{G}{\overset{C}{C}}-E$$

wherein each of D, E and G is an aryl group and J is selected from the group consisting of a hydrogen atom, an alkyl group and an aryl group, at least one of D, E and G containing an amino substituent.

24. An electrophotographic element as defined in claim **19** wherein said dye contains a nitro group.

25. An electrophotographic element as defined in claim **20** wherein said organic photoconductor is an organic amine photoconductor which contains at least a group selected from a secondary amino group and a tertiary amino group.

26. An electrophotographic element as defined in claim **25** wherein said organic photoconductor has the following general formula:



$$J-\underset{G}{\overset{D}{C}}-E$$

wherein each of D, E and G is an aryl group and J is selected from the group consisting of a hydrogen atom, an alkyl group and an aryl group, at least one of D, E and G containing an amino substituent.

27. An electrophotographic element comprising a conductive support having coated thereon a layer comprising:

(1) from 25 to 99 parts by weight of a polyester of terephthalic acid and a glycol mixture consisting of a 9:1 weight ratio of 2,2-bis-[4-(2-hydroxyethoxy) phenyl]propane and ethylene glycol, as insulating binder;

(2) from 1 to 75 parts by weight of an organic photoconductor selected from the group consisting of: triphenylamine; 1,3,5-triphenyl-2-pyrazoline; 4,4′-bis-diethylamino-2,2′-dimethyltriphenylmethane; 2,3,4,5-tetraphenylpyrrole; 4,4′ - bis - diethylaminobenzophenone; and

(3) from .01 to 10 parts by weight of a dye selected from the group consisting of

3,3′-di-p-nitrophenylthiacarbocyanine salt;
3,3′-dimethyl-9-trifluoromethylthiacarbocyanine salt;
1,1′,3,3′-tetraethylimidazo[4,5-b]quinoxalinodicarbocyanine salt;
3,3′-diethyl-8,9-diazathiacarbocyanine salt;
1,3-diethyl-1′,3′,3′-trimethylimidazo[4,5-b]quinoxalinoindocarbocyanine salt;
3,3′-diethyl-6,6′-dinitrothiacarbocyanine salt;
3,6-bis[(3-ethyl-2-benzothiazolinylidene)ethylidene]-1,2,4,5-cyclohexanetetrone;
3,6-bis[(3-ethyl-2-benzoxazolinylidene)ethylidene]-1,2,4,5-cyclohexanetetrone;
5-[5-(2-p-carboxyphenyl-3-methyl-1-indolizinyl)-2,4-pentadienylidene]-1,3-diethyl-2-thiobarbituric acid;
2,2′,3,3′-tetraphenyl-1,1′-indolizinocarbocyanine salt;
1,1′,3,3′-tetraethylimidazo[4,5-b]quinoxalinocarbocyanine salt;
1′,3-diethyl-6-nitrothia-2′-cyanine salt;
1,1′-dimethyl-2,2′-diphenyl-3,3′-indolocarbocyanine salt;
1,1′,3-triethylimidazo-[4,5-b]quinoxalino-2′-carbocyanine salt;
6-chloro-1′-methyl-1,2′,3-triphenylimidazo-[4,5-b]quinoxalino-3′-indolocarbocyanine salt;
6,6′-dichloro-1,1′,3,3′-tetraphenylimidazo[4,5-b]quinoxalinocarbocyanine salt.

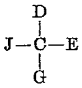
28. A composition of matter as defined in claim **1** wherein said organic photoconductor and said dye are incorporated in an insulating binder.

29. A composition of matter as defined in claim **18** wherein said organic photoconductor and said dye are dispersed in from 25 to 99 parts by weight of a polyester of terephthalic acid and a glycol mixture consisting of a 9:1 weight ratio of 2,2-bis[4-(2-hydroxyethoxy)phenyl]propane and ethylene glycol as insulating binder.

30. A composition of matter as defined in claim **1** wherein said organic photoconductor is selected from the group consisting of the diarylamine and the triarylamine photoconductors.

31. A composition of matter as defined in claim **1** wherein said dye in an azacyanine dye.

32. A composition of matter as defined in claim **1** wherein said dye is an azacyanine dye and said organic photoconductor has the following formula:



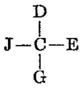
$$\begin{array}{ccccc} & & D & & \\ & & | & & \\ J & - & C & - & E \\ & & | & & \\ & & G & & \end{array}$$

wherein each of D, E and G is an aryl group and J is selected from the group consisting of a hydrogen atom, an alkyl group and an aryl group, at least one of D, E and G containing an amino substituent.

33. A composition of matter as defined in claim **1** wherein said dye is an azacyanine dye and said organic photoconductor is selected from the group consisting of the diarylamine and the triarylamine photoconductors.

34. An electrophotographic element as defined in claim **19** wherein said dye is an azacyanine dye.

35. An electrophotographic element as defined in claim **19** wherein said dye is an azacyanine dye and said organic photoconductor has the following formula:



$$\begin{array}{ccccc} & & D & & \\ & & | & & \\ J & - & C & - & E \\ & & | & & \\ & & G & & \end{array}$$

wherein each of D, E and G is an aryl group and J is selected from the group consisting of a hydrogen atom, an alkyl group and an aryl group, at least one of D, E and G containing an amino substituent.

36. An electrophotographic element as defined in claim **19** wherein said dye is an azacyanine dye and said organic photoconductor is selected from the group consisting of the diarylamine and the triarylamine photoconductors.

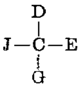
37. A composition of matter comprising an organic photoconductor spectrally sensitized with a substantially non-photoconductive simple cyanine or carbocyanine dye, which dye:

(1) has a cathodic polarographic half-wave potential more positive than −1.0 volt;

(2) has an anodic polarographic half-wave potential and a cathodic polarographic half-wave potential which, when added together, give a sum more positive than −0.10 volt; and

(3) desensitizes a test negative gelatin silver bromoiodide emulsion, consisting of 99.35 mole percent bromide and .65 mole percent iodide, more than 0.4 log E to light having a wavelength of 365 nm. when incorporated in said test emulsion at a concentration of 0.2 millimole of dye per mole of silver.

38. A composition of matter comprising an organic photoconductor having the following formula:



$$\begin{array}{ccccc} & & D & & \\ & & | & & \\ J & - & C & - & E \\ & & | & & \\ & & G & & \end{array}$$

wherein each of D, E and G is an aryl group and J is selected from the group consisting of a hydrogen atom, an alkyl group and an aryl group, at least one of D, E and G containing an amino substituent, which organic photoconductor is spectrally sensitized with a substantially non-photoconductive simply cyanine or carbocyanine dye, which dye:

(1) has a cathodic polarographic half-wave potential more positive than −1.0 volt;

(2) has an anodic polarographic half-wave potential and a cathodic polarographic half-wave potential which, when added together, give a sum more positive than −0.10 volt; and

(3) densensitizes a test negative gelatin silver bromoiodide emulsion, consisting of 99.35 mole percent bromide and .65 mole percent iodide, more than 0.4 log E to light having a wavelength of 365 nm. when incorporated in said test emulsion at a concentration of 0.2 millimole of dye per mole of silver.

References Cited

UNITED STATES PATENTS

3,112,197	11/1963	Neugebauer et al.	96—1.6X
3,288,610	11/1966	Götze et al.	96—1.7X
3,438,774	4/1969	Depoorter et al.	96—1.7
3,455,684	7/1969	Depoorter et al.	96—1.7
3,468,661	9/1969	Libeer et al.	96—1.7
3,476,558	11/1969	Depoorter et al.	96—1.7

GEORGE F. LESMES, Primary Examiner

J. R. MILLER, Assistant Examiner

U.S. Cl. X.R.

96—1.5; 260—37, 40, 41, 240E, 240G, 240R, 240.4, 240.5, 240.6, 240.7, 240.8, 240.65, 304

PO-1050
(5/69)

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,597,196 **Dated** August 3, 1971

Inventor(s) Jean E. Jones and Charles J. Fox

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

In the Specification:

Column 1, line 3, after "CYANINE" should be inserted ---,---.

Column 2, line 46, "cypanine" should read ---cyanine---.

Column 3, line 15, "desicated" should read ---desiccated--

Column 4, line 1, "reefrence" should read ---reference---.

Column 4, line 10, "Kenny" should read ---Kelly---.

Column 4, line 12, "voltammeary" should read ---voltammetr

Column 4, line 12, "ts" should read ---as---.

Column 6, line 20, after "required" "," should be deleted.

Column 6, line 23, "2-thienyl(" should read ---2-thienyl)-

Column 6, line 35, "naphthoothiazole" should read ---napht thiazole---.

Column 6, line 42, "4,5-dimethoxazole" should read ---4,5-dimethyloxazole---.

Column 6, lines 66-67, "3,3,5-trimethyl lindolenine" shoul read ---3,3,5-trimethylindolenine---.

Column 7, lines 51-52, "pseudohydantoi)" should read ---pseudohydantoin)---.

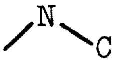
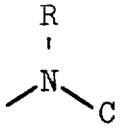
PO-1050
(5/69)

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,597,196 **Dated** August 3, 1971

Inventor(s) Jean E. Jones and Charles J. Fox

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 8, line 6, that part of formula reading "  " should read ---  ---.

Column 8, line 47, "6-6" should read --- 6-7 ---.

Column 9, line 10, "ethylidene]1,3" should read ---ethylidene]-1,3 ---.

Column 10, line 11, "densitizing" should read ---desensitizing---.

Column 10, line 46, "anion" should read ---anion)---.

Column 10, line 57, "ethyl" should read ---methyl---.

Column 11, line 48, that part of formula reading "Z_2" should read ---Z_4---.

Column 11, line 64, "features" should read ---feature---.

Column 13, lines 42-43, "protoconductors" should read ---photoconductors---.

Column 14, line 65, "J-G-E" should read --- J-C-E ---.

Column 18, line 73, "trinitrofluoroenone" should read ---trinitrofluorenone---.

Column 19, line 2, "To." should read ---No.---.

Column 19, in Dye No. I, "nitrophenylthiocarbocyanine" should read ---nitrophenylthiacarbocyanine---.

PO-1050
(5/69)

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,597,196 **Dated** August 3, 1971

Inventor(s) Jean E. Jones and Charles J. Fox

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 19, in Dye No. III, "/4,5-a7" should read ---/4,5-b7---.

Column 19, in the structured formula of Dye No. III, that part of formula reading:

" C-=CH " should read --- C-(CH ---

Column 19, in Dye No. V, "/4,5-a7" should read ---/4,5-b7---.

Column 19, in the structured formula of Dye No. VI, that part of the formula reading:

" $C_2H_5OSO\text{—}_3^{\ominus}$ " should read --- $C_2H_5OSO_3^{\ominus}$ ---.

Column 21, line 1, "To." should read ---No.---.

Column 22, line 75, after "be" should be inserted ---prepared as--

Column 23, line 32, "X" should read ---IX---.

Column 24, lines 37-38, "(sulfobutyl)" should read ---(3-sulfobuty

Column 25, line 5, "< 0.0 " should read --- >0.0 ---.

In the Claims

Column 25, line 56, "5" should read ---3---.

Column 25, line 66, "6" should read ---4---.

Column 26, line 9, that part of formula reading:

" $\begin{matrix}\cancel{R}\\ |\\ N\end{matrix}$ " should read --- $\begin{matrix}R\\ |\\ N\end{matrix}$ ---.

PO-1050
(5/69)

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,597,196 Dated August 3, 1971

Inventor(s) Jean E. Jones and Charles J. Fox

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 26, line 24, between the formula at line 20 and the formula at line 27 should be inserted ---and---.

Column 26, line 72, "12" should read ---10---.

Column 27, line 44, "Z_6" should read ---Z_7---.

Column 27, line 69, "integer of from 1 to 2; k and m each represents a positive" should read ---alkyl group and an aryl group, at least one of D, E and G---.

Column 28, line 73, "an indolizine nucleus;" (second occurrence) should be deleted.

Column 29, lines 5-7, that part of formula reading:

"  " should read ---  ---.

Column 29, line 5, that part of formula reading:

"  $\begin{array}{c} R \\ | \\ H \end{array}$ " should read ---  $\begin{array}{c} R \\ | \\ N \end{array}$ ---.

Column 29, line 53, "nuclein" should read ---nuclei---.

Column 29, line 72, that part of formula reading:

"  $\begin{array}{c} C \\ | \\ C \end{array}$ " should read ---  $\begin{array}{c} D \\ | \\ C \end{array}$ ---.

PO-1050
(5/69)

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,597,196 **Dated** August 3, 1971

Inventor(s) Jean E. Jones and Charles J. Fox

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 32, line 42, the references cited should include:

"UNITED STATES PATENTS

2,930,694	3/1960	Coenen et al	96-105
3,140,951	7/1964	Heseltine et al	96-101
3,180,730	4/1965	Klupfel et al	96-1.5
3,359,113	12/1967	Depoorter et al	96-1

FOREIGN PATENTS

266,448	8/1964	Australia	96-1.5
660,253	2/1965	Belgium	96-101

OTHER REFERENCES

Chemical Abstracts, Vol. 52, page 19677h"

Signed and sealed this 19th day of March 1974.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents