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ORGANIC PHOTOCONDUCTORS SENSITIZED WITH PYRYLIUM CYANINE DYES

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U.S. Cl. 96—1.6 20 Claims

ABSTRACT OF THE DISCLOSURE

Pyrylium dyes are provided which feature a 2-arylindole nucleus, a carbazole nucleus, or an imidazo[4,5-b]-quinoxaline nucleus. Organic photoconductors are sensitized with the novel dyes of this invention.

This invention relates to novel dyes and to materials and elements useful in the electrophotographic processes.

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, for example, such as listed in Table C hereinafter. 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 dyes.

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 photoconductors 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 photoconductors 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, an 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 certain methine dyes containing certain pyrylium, thiapyrylium, xanthylium and thiaxanthylium nuclei 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, desiccated	90.0
Hydroquinone	8.0
Sodium carbonate, monohydrated	52.5
Potassium bromide	5.0

Water to make 1.0 liter.

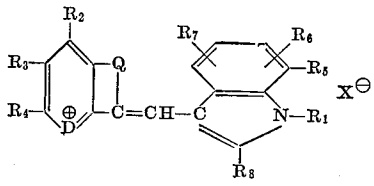
As indicated above, the methine dyes employed in this invention desensitize conventional negative silver halide emulsions. Such emulsions are inherently sensitive to blue radiation. The present dyes reduce that sensitivity. In addition, these dyes fail to provide practical spectral sensitization for such emulsions. Therefore, it was quite unexpected to find that they spectrally sensitized organic photoconductors.

The methine 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 photoconductors used is poor or inefficient, the dyes seem to function as speed increasing compounds as well as spectral sensitizers.

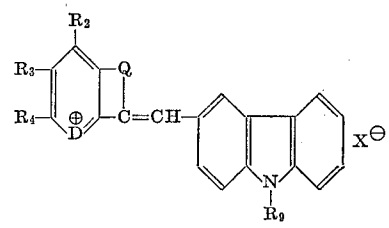
The methine dyes that are useful in practicing the invention include those comprising first and second heterocyclic nuclei joined together by a methine linkage containing from 1 to 3 carbon atoms in the chain, e.g., monomethine to trimethine; the first of said nuclei being a pyrylium or a thiapyrylium nucleus, and a second electron-accepting nucleus selected from (a) a 2-arylindole nucleus joined at the 3-carbon atom thereof to said methine linkage, (b) a carbazole nucleus joined at the 3-carbon atom thereof to said methine linkage, and (c) an imidazo[4,5-b]quinoxaline nucleus joined at the 2-carbon atom thereof to said methine linkage, to complete said dye. The terms "pyrylium" and "thiapyrylium" are used herein broadly to include oxonium and thionium salts which have an aromatic system and contain six atoms in a heterocyclic ring (which ring may have one or more rings or nuclei fused thereto). The pyrylium or thiapyrylium nucleus is preferably joined at a carbon atom thereof, which is ortho para to the hetero oxygen or sulfur atom, to the methine linkage. Typical useful pyrylium and thiapyrylium nuclei include pyrylium; benzopyrylium; naphthopyrylium; thiapyrylium; benzothiapyrylium; naphthothiapyrylium; a 6,7-dihydro - 5H - cyclopenta[b]pyrylium nucleus; a 6,7-dihydro-5H-cyclopenta[b]thiapyrylium nucleus; a 5,6,7,8-tetrahydrocyclohexa[b]pyrylium nucleus; a 5,6,7,8-tetrahydrocyclohexa[b]thiapyrylium nucleus; an 8,9,10-11-tetrahydroxanthylium nucleus, e.g., 8,9,10-11-tetrahydrobenzo[a]xanthylium, etc.; and an 8,9,10-11-tetrahydrothiaxanthylium nucleus, e.g., 8,9,10,11-tetrahydrodrobenzo[a]thiaxanthylium.

The preferred polymethine dyes that are useful herein include those represented by the following general formulas:

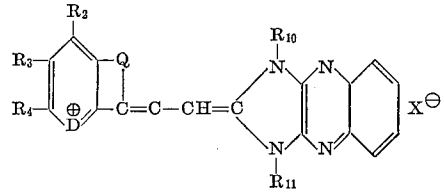
I.



II.

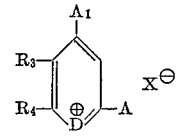


III.



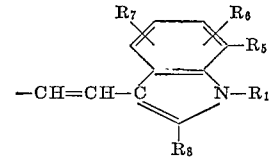
and

IV.

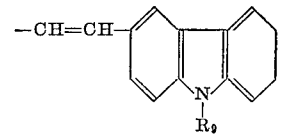


wherein one and only one of A and A_1 represents a group selected from those having the formulas:

(a)

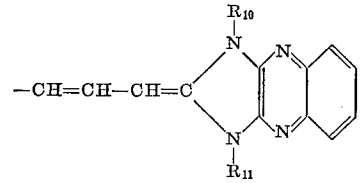


(b)



and

(c)

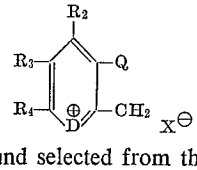


and the other of said A and A_1 represents a hydrogen atom, an alkyl group (preferably a lower alkyl containing from 1 to 4 carbon atoms), e.g., methyl, ethyl, propyl, isopropyl, butyl, hexyl, decyl, etc., or an aryl group, e.g., phenyl, tolyl, naphthyl, chlorophenyl, ethoxyphenyl, nitrophenyl, etc., R_1 represents an alkyl group including substituted alkyl, (preferably a lower alkyl containing from 1 to 4 carbon atoms), e.g., methyl, ethyl, propyl, isopropyl, butyl, hexyl, cyclohexyl, decyl, dodecyl, etc., and substituted alkyl groups, (preferably a substituted lower alkyl containing from 1 to 4 carbon atoms), such as a hydroxyalkyl group, e.g., β-hydroxyethyl, ω-hydroxybutyl, etc., an alkoxyalkyl group, e.g., β-methoxyethyl, ω-butoxybutyl, etc., a carboxyalkyl group e.g., β-carboxyethyl, ω-carboxybutyl, etc., a sulfoalkyl group, e.g., β-sulfoethyl, ω-sulfobutyl, etc., a sulfatoalkyl group, e.g., β-sulfatoethyl, ω-sulfatobutyl, etc., an acyloxyalkyl group, e.g., β-acetoxyethyl, γ-acetoxypropyl, ω-butyryloxybutyl, etc., an alkoxycarbonylalkyl group, e.g., β-methoxycarbonylethyl, ω-ethoxycarbonylbutyl, etc., R_2, R_3, and R_4 each individually represents a hydrogen atom, an alkyl group (preferably a lower alkyl containing from 1 to 4 carbon atoms), e.g., methyl, ethyl, propyl, isopropyl, butyl, hexyl, decyl, etc., or an aryl group, e.g., phenyl, tolyl, naphthyl, chlorophenyl, ethoxyphenyl, nitrophenyl,

etc. and, R_3 and R_4, when taken together represent a fused benzo or naphtho group; R_5, R_6 and R_7 each individually represent a hydrogen atom or R_5 and R_6, taken together, or R_6 and R_7, taken together, represent the atoms required to complete a fused benzo group; R_5 and R_1, taken together, represent an alkylene bridge group containing from 2 to 3 carbon atoms such as ethylene or trimethylene; R_8 represents an aryl group, e.g., phenyl, tolyl, chlorophenyl, methoxyphenyl, 3,4-dichlorophenyl, naphthyl, etc., R_9 represents an alkyl group, preferably a lower alkyl group of from 1 to 4 carbon atoms, e.g., methyl, isopropyl or n-butyl; R_{10} and R_{11} each represents an alkyl group, including substituted alkyl, (preferably a lower alkyl containing from 1 to 4 carbon atoms), e.g., methyl, ethyl, propyl, isopropyl, butyl, hexyl, cyclohexyl, decyl, etc., a hydroxyalkyl group, e.g., β-hydroxyethyl, γ-hydroxypropyl, etc., an alkenyl group, e.g., allyl, 1-propenyl, 2-propenyl, 1-butenyl, 2-butenyl, 3-butenyl, etc., an aralkyl group, e.g., benzyl, β-phenethyl, etc., or an aryl group, e.g., phenyl, tolyl, naphthyl chlorophenyl, 3,4-dichlorophenyl, methoxyphenyl, etc., D represents an atom of oxygen or sulfur; X represents an acid anion, e.g., chloride, bromide, iodide, sulfamate, perchlorate, p-toluenesulfonate, methyl sulfate, etc.; and Q represents an alkylene group containing from 2 to 3 carbon atoms, e.g., an ethylene or trimethylene bridge group. The dyes represented by Formula IV(a) above containing the electron-accepting 2-arylindole, and more particularly and electron-accepting 2-phenylindole nucleus, provide particularly efficacious spectral sensitizing dyes for the photoconductor compositions and elements of this invention. Dyes containing such nuclei are the preferred dye species herein.

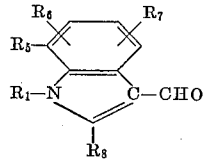
As used herein and in the appended claims, "electron-accepting" nucleus refers to those nuclei which, when converted to a symmetrical carbocyanine dye and added to a gelatin silver chlorobromide emulsion containing 40 mole percent chloride and 60 mole percent bromide, at a concentration of from 0.01 to 0.2 gram dye per mole of silver, cause by electron trapping at least about an 80 percent loss in the blue speed of the emulsion when sensitometrically exposed and developed three minutes in Kodak developer D–19 at 20° C., the composition of which is given above. Preferably, the electron-accepting nuclei are those which, when converted to a symmetrical carbocyanine dye and tested as just 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.

The methine dyes of Formula I and II are prepared conveniently by heating a mixture of (1) a heterocyclic quaternary salt compound of the formula:



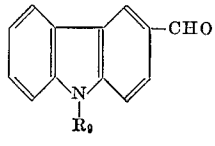
and (2) a compound selected from those represented by the formulas:

VI.



to give the dyes of Formula I above, and

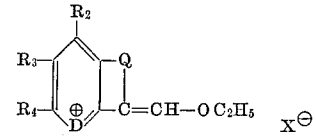
VII.



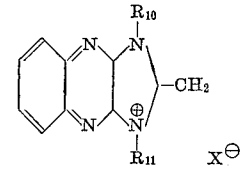
to give the dyes of Formula II above, wherein R_1 through R_{11}, D, X and Q are as previously defined, in approximately equimolar proportions, in an inert solvent medium such as acetic acid. The crude dye is then separated from the reaction mixture, washed, and recrystallized from an appropriate solvent such as acetonitrile, mixtures of methanol and acetic acid, ethanol, etc.

The dyes of Formula III above are advantageously prepared, for example, by heating a mixture of (1) a compound of the formula:

VIII.

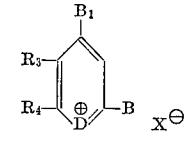


and (2) a compound of the formula:



wherein R_2, R_3, R_4, R_{13}, R_{14}, R_{15}, D, X and Q are as previously defined, in approximately equimolar, in an inert solvent such as acetic anhydride. The crude dye is then separated, washed, and recrystallized from an appropriate solvent such as acetonitrile, mixtures of methanol and acetic acid, etc.

To prepare the dyes of Formula IV(*a*) and IV(*b*) above, a mixture comprising (1) a compound of the formula: X.



and (2) a compound of Formula VI above (for dyes of IV*a*) or a compound of Formula VII above (for dyes of IV*b*) or a 2-formylmethyleneimidazo[4,5-b]quinoxaline intermediate (for dyes of IV(*c*), wherein *n* in the above Formula X; R_3, R_4, D and X are as previously defined, and one and only one of B and B_1 represents a methyl group and the other of B and B_1 represents a hydrogen atom, or an alkyl group, or an aryl group, e.g., methyl, butyl, decyl, phenyl, tolyl, naphthyl, chlorophenyl, ethoxyphenyl, nitrophenyl, etc., is reacted under reflux, in approximately equimolar proportions, the pure dye being obtained in the general manner previously described.

The dyes of the invention defined above can be used alone, or a combination of one or more of the dyes can be used to impart the desired spectral sensitivity. All of them are spectral sensitizers for organic photoconductors. Suitable 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 but generally less than 10 when tested as described in Examples 1 to 7 below) to radiation of 400 to 700 nm.

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'-diethyl-m-toluidine),

those described in Fox U.S. Pat. 3,240,597 issued Mar. 15, 1966, and the like, and (2) triarylamines including (a) non-polymeric triarylamines, such as

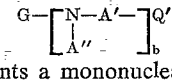
triphenylamine,
N,N,N',N'-tetraphenyl-m-phenylenediamine;
4-acetyltriphenylamine;
4-hexanoyltriphenylamine;
4-lauroyltriphenylamine;
4-hexyltriphenylamine;
4-dodecyltriphenylamine;
4,4'-bis(diphenylamino)-benzil;
4,4'-bis(diphenylamino)-benzophenone;

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.

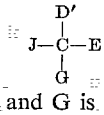
Other very useful photoconductive substances capable of being spectrally sensitized in accordance with this invention are disclosed in Fox U.S. Pat. 3,265,496 issued Aug. 9, 1966, and include those represented by the following general formula:



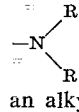
wherein A' represents a mononuclear or polynuclear divalent aromatic radical, either fused or linear, (e.g., phenylene, naphthylene, biphenylene, binaphthylene, etc.), or a substituted divalent aromatic radical of these types wherein said substituent can comprise a member such as an acyl group having 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. Certain nitrogen heterocyclic compounds are also useful photoconductors in the invention such as, for example, 1,3,5-triphenyl-2-pyrazoline, 2,3,4,5-tetraphenylpyrrole, etc.

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 in a copending application of Seus et al. Ser. No. 624,233, "Photoconductive Elements Containing Organic Photoconductors" filed Mar. 20, 1967, now abandoned. 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 materials.

Preferred polyaryl alkane photoconductors can be represented by the formula:



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. The aryl groups can contain substituents such 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 R 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 preferably 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',4''-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 Table B comprises a partial listing of U.S. patents describing such organic photoconductors and compositions which can be used in place of those more particularly described herein.

TABLE B

	Issued	Patent Numbers
Inventor:		
Noe et al	February 25, 1964	3,122,435
Sus et al	March 31, 1964	3,127,266
Schlesinger	April 21, 1964	3,130,046
Cassiers	April 28, 1964	3,131,060
Schlesinger	June 30, 1964	3,139,338
Do	do	3,139,339
Cassiers	July 14, 1964	3,140,946
Davis et al	July 21, 1964	3,141,770
Ghys	September 15, 1964	3,148,982
Cassiers	November 3, 1964	3,155,503
Do	November 24, 1964	3,158,475
Tomanek	December 15, 1964	3,161,505
Schlesinger	December 29, 1964	3,163,530
Do	do	3,163,531
Do	do	3,163,532
Hoegl	February 9, 1965	3,169,060
Stumpf	March 23, 1965	3,174,854
Klupfel et al	April 27, 1965	3,180,729
Do	do	3,180,730
Neugebauer	June 15, 1965	3,189,447
Do	September 14, 1965	3,206,306
Davis et al	July 21, 1964	3,141,770
Hoegl et al	June 5, 1962	3,037,861
Sus et al	June 26, 1962	3,041,165
Schlesinger	November 27, 1962	3,066,023
Bethe	January 8, 1963	3,072,479
Klupfel et al	July 9, 1963	3,047,095
Neugebauer et al	November 26, 1963	3,112,197
Cassiers et al	December 3, 1963	3,113,022
Schlesinger	December 17, 1963	3,114,633
Kosche et al	August 9, 1966	3,265,497
Noe et al	September 20, 1966	3,274,000

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 can 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), styrenebutadiene 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.

The photoconductive compositions of the invention can be coated on any of the electrically conductive supports conventionally used 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. Other useful conducting layers include thin layers of nickel coated by high vacuum deposition and cuprous iodide layers as described in U.S. Pat. 3,245,833. Transparent, translucent or opaque support material can be used. Exposure by reflex requires that the support transmit light while no such requirement is necessary for exposures by projection. Similarly transparent supports are desired 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. Best results are obtained with about .01 to 10 parts by weight dye and about 1 to 75 parts by weight of the organic photoconductor based on the photoconductive composition. 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 protoconductive 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.

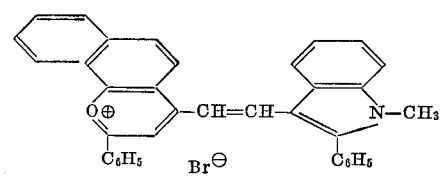
To produce a reproduction of an image utilizing the electrophotographic elements of our invention, the photoconductive layer is preferably dark adapted, and then is charged either negatively or positively by means of, for example, a corona discharge device maintained at a potential of from 600–700 volts. 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.

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

EXAMPLE 1

4-[2-(1-methyl-2-phenyl-3-indolyl)vinyl]-2-phenyl-naphtho-[1,2-b]pyrylium bromide



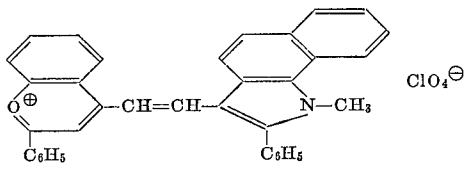
A mixture of 0.70 g. (1 mol.) of 4-methyl-2-phenyl-naphtho[1,2-b]pyrylium bromide, 0.50 g. of 1-methyl-2-phenylindole-3-aldehyde and acetic anhydride (15 ml.) is heated under reflux for 10 minutes. The mixture is allowed to cool, then filtered and dye product first washed with ethyl acetate and then with ethyl alcohol. The purified dye is obtained from this product by two recrystallizations from ethyl alcohol, the yield being 0.28 g. (25%), M.P. 281–282° C.

The above prepared dye containing the electron-accepting 2-phenylindole nucleus is tested for its usefulness as a spectral sensitizer for organic photoconductors by the following procedure.

A solution is 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) and 0.0065 g. of the spectral sensitizing dye of above Example 1. The 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 the 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 a 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. Pats. 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.) Another sample of the coating is tested to determine its electrical speed and maximum sensitivity peak. This is accomplished by giving the element a positive or negative charge 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_o, 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 the 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 results are shown in Table I hereinafter. The dye of above Example 1 shows speeds of 2806 and 502 for the positively and negatively charged surfaces, respectively, with maximum sensitivity peaks at 560 and 625 nm. Accordingly, the dye of this example is an outstanding spectral sensitizer for organic photoconductor compositions and elements.

EXAMPLE 2

4-[2-(1-methyl-2-phenyl-3-benz[g]indolyl)vinyl]-2-phenyl-1-benzopyrylium perchlorate

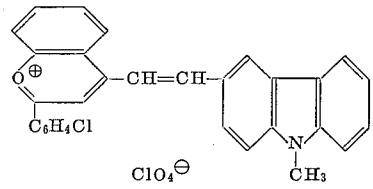


A mixture of 0.65 g. (1 mol.) of 4-methyl-2-phenyl-1-benzopyrylium perchlorate, 0.70 g. (1 mol.) of 1-methyl-2-phenyl-benz[g]indole-3-aldehyde and acetic anhydride (15 ml.) is heated under reflux for 10 minutes. The mixture is allowed to cool, then filtered and the dye product washed with ethyl alcohol. The purified dye is obtained from this product by recrystallization from acetonitrile, the yield being 0.36 g. (31%), M.P. >300° C.

The dyes of this example containing the electron-accepting 2-phenyl-benz[g]indole nucleus is tested as spectral sensitizers for organic photoconductors by the exact procedure described in above Example 1. The results are shown in Table I hereinafter. Referring thereto, it will be noted that the speeds are 650 for both the positively and negatively charged surfaces, with a maximum sensitivity peak at 620 nm. Thus, the dye of this example is an excellent spectral sensitizer for the organic photoconductor compositions and elements of this invention.

EXAMPLE 3

2-(4-chlorophenyl)-4-[2-(9-methyl-3-carbazolyl)vinyl]-1-benzopyrylium perchlorate

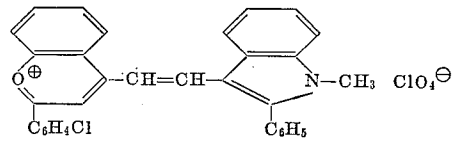


A mixture of 0.90 g. (1 mol.) of 2-(4-chlorophenyl)-4-methyl-1-benzopyrylium perchlorate, 0.60 g. (1 mol.) of 9-methyl-3-carbazole aldehyde and acetic anhydride (20 ml.) is heated under reflux for 10 minutes. The mixture is allowed to cool, then filtered and the dye product washed with ethyl alcohol. The purified dye is recrystallized from a mixture of m-cresol and ethyl alcohol, the yield being 0.80 g. (57%), M.P. >300° C.

The above dye containing the electron-accepting carbazole nucleus is tested by the exact procedure described in above Example 1. The results are recorded in Table I hereinafter. Referring to the table, it will be seen that the speeds are 160 for both the positively and negatively charged surfaces, with a maximum sensitivity peak at 550 nm. Accordingly, the dye of this example is indicated as being a very useful spectral sensitizer for organic photoconductor compositions and elements.

EXAMPLE 4

2-(4-chlorophenyl)-4-[2-(1-methyl-2-phenyl-3-indolyl)vinyl]-1-benzopyrylium perchlorate

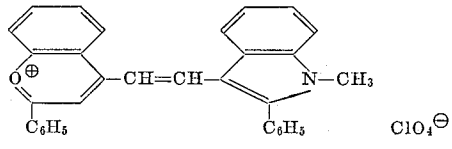


This dye is prepared in the same manner as above Example 3, except that 1-methyl-2-phenylindole-3-aldehyde is used in place of the 9-methyl-3-carbazole aldehyde. The yield of pure dye is 0.62 g. (43%), M.P. >300° C.

The above prepared dye containing the electron-accepting 2-phenylindole nucleus is an outstanding spectral sensitizer for organic photoconductor compositions and element as indicated by the test procedure of above Example 1. The results are set forth in Table 1 hereinafter. Referring to the table, the speeds are 1592 and 1035 for the positively charged and the negatively charged surfaces, respectively, with maximum sensitivity peaks at 585 and 630 nm.

EXAMPLE 5

4-[2-(1-methyl-2-phenyl-3-indolyl)vinyl]-1-benzopyrylium perchlorate

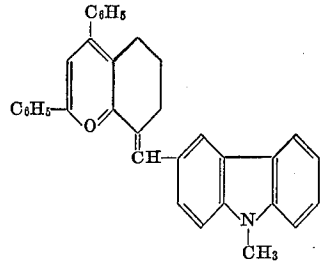


This dye is prepared in the same manner as above Example 3, except that 1-methyl-2-phenylindole is used in place of the 9-methyl-3-carbazole. The yield of pure dye recrystallized from acetonitrile is 0.92 g. (68%), M.P. 276–277° C.

The above prepared dye containing the electron-accepting 2-phenylindole nucleus is tested by the exact procedure described in above Example 1. The results are recorded in Table I hereinafter. Referring thereto, it will be seen that the speeds are 2500 and 900 for the positively charged and negatively charged surfaces, respectively, with a maximum sensitivity peak at 580 nm. Accordingly, the above dye qualifies as an outstanding spectral sensitizer for the organic photoconductors of this invention.

EXAMPLE 6

5,6,7,8-tetrahydro-8-[(9 - methyl - 3 - carbazolyl)methylene]-2,4-diphenylcyclohexa[b]pyrylium perchlorate

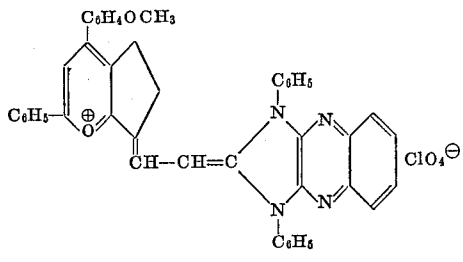


A mixture of 1.94 g. (1 mol.) of tetrahydro-2,4-diphenylcyclohexa[b]pyrylium perchlorate, 1.20 g. (1 mol.) of 1-methyl-9-formylcarbazole and acetic anhydride (15 ml.) is heated under reflux for 10 minutes. The mixture is allowed to cool, ether is added, then the mixture is filtered and the dye product is washed with ether. The purified dye is obtained by two recrystallizations from a 10:1 mixture of methanol and acetic acid, the yield being 0.56 g. (20%), M.P. 198–199° C.

The above dye containing the electron-accepting carbazole nucleus is tested by the exact procedure described in above Example 1. The results are listed in Table I hereinafter. It will be seen from the table that the speeds obtained are 800 and 500 for the positively charged surface and the negatively charged surface, respectively, with a maximum sensitivity peak at 595 nm. These results indicate that this dye is an excellent spectral sensitizer for organic photoconductor compositions and elements.

EXAMPLE 7

3',12 - ethylene - 4' - (4-methoxyphenyl)-1,3,6'-triphenylimidazo[4,5 - b]quinoxalino-2'-pyrylocarbocyanine perchlorate



A mixture of 1.11 g. (1 mol.) of 7-ethoxymethylene-6,7 - dihydro - 4 - (4-methoxyphenyl)-2-phenyl-5H-cyclopenta[b]pyrylium perchlorate, 1.27 g. (1 mol.) of 2-methyl-1,3-diphenylimidazo[4,5-b]quinoxalinium p-toluenesulfonate and acetic anhydride (10 ml.) is heated under reflux for 5 minutes. The mixture is allowed to cool, then filtered and the dye product washed first with ethyl acetate and then with ethyl alcohol. The pure dye is obtained by recrystallization from acetonitrile, the yield being 0.75 g. (40%) M.P. >300° C. This dye likewise is an excellent spectral sensitizer for organic photoconductors.

The above examples show the great increase in speed of organic photoconductors when the dyes employed in this invention are added thereto. This increase in speed is clearly due to the spectral sensitivity imparted to the photoconductor by the dyes described herein. The examples also show that the maximum sensitivity peaks ("Abs. max.") occur in most cases at radiations in the region of the spectrum of from about 490 to 660 nm. A number of the dyes also have more than one maximum sensitivity peak as indicated in Table I hereinafter.

Other highly useful dyes that contain electron-accepting nuclei and function as spectral sensitizers for the organic photoconductors of this invention can be readily prepared, in general, as described in the preceding Examples 1 to 7 by an appropriate selection of intermediates defined hereinabove including for example, dyes such as 5,6,7,8-tetrahydro-8-[(1 - methyl - 2 - phenyl - 3 - indolyl) methylene]-2,4-diphenylcyclohexa[b]pyrylium salt (e.g., the bromide, perchlorate, p-toluenesulfonate, fluoroborate, etc. salt); 8-[(9-methyl-3-carbazolyl)methylene]-8,9,10,11-tetrahydrobenzo[a]xanthylium salt (e.g., the bromide, perchlorate, p-toluenesulfonate, fluoroborate, etc. salt); 8-[(1-methyl - 2 - phenyl-3-indolyl)methylene]-8,9,10,11-tetrahydrobenzo[a]xanthylium salt (e.g., the bromide, perchlorate, p-toluenesulfonate, fluoroborate, etc. salt); 1,3-diethyl - 3',12 - trimethylene - 4',6' - diphenylimidazo-[4,5-b]quinoxalino-2'-pyrylocarbocyanine salt (e.g., the bromide, perchlorate, p-toluenesulfonate, fluoroborate, etc. salt); 3',12-ethylene-1,3-diphenyl-4',6'-di-p-tolylimidazo[4,5-b]quinoxalino-2'-pyrylocarbocyanine salt (e.g., the bromide, perchlorate, p-toluenesulfonate, fluoroborate, etc. salt); perchlorate, p-toluenesulfonate, fluoroborate, etc. salt and the like.

It will be apparent that still other dyes of the invention such as the corresponding thiapyrylium and the thiaxanthylium dyes can also be prepared, in general, by the processes of the above Examples 1 to 7 by appropriate selection of intermediates embraced by Formulas V to X above, and that such dyes will also function as effective spectral sensitizers for organic photoconductors of the invention. Typical dyes include, for example,

4 - [2 - (1 - methyl - 2 - phenyl - 3 - indolyl)vinyl]-2-phenyl naphtho[1,2-b]thiapyrylium bromide;

4 - [2 - (1 - methyl - 2 - phenyl - 3 - indolyl)vinyl]-1-benzothiapyrylium perchlorate;

5,6,7,8 - tetrahydro - 8 - [(9 - methyl-3-carbazolyl) methylene] - 2,4 - diphenylcyclohexa[b]thiapyrylium perchlorate;

3',12 - ethylene - 4' - (4 - methoxyphenyl) 1,3,6'-triphenylimidazo[4,5 - b]quinoxalino-2'-thiapyrylocarbocyanine perchlorate;

8 - [(9 - methyl - 3 - carbazolyl)methylene]8,9,10,11-tetrahydrobenzo[a]thiaxanthylium perchlorate;

2 - [2 - (1,3 - diallylimidazo[4,5-b]quinoxalino)vinyl]-4,5,6 - trimethylpyrylium p-toluenesulfonate;

2 - [2 - (1,3 - diethylimidazo[4,5-b]quinoxalino)vinyl]-pyrylium methane sulfonate;

2 - [2 - (1 - ethyl - 2 - (4 - methoxy)phenyl - 3 - benz-[g]indolyl)vinyl] - 4 - (2 - naphthyl) - 1 - benzopyrylium perchlorate;

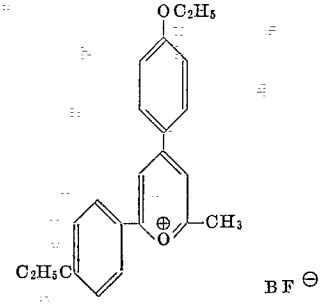
2 - [2 - (9 - methyl-7-nitro-3-carbazolyl)vinyl]pyrylium perchlorate;

and the like dyes.

The following Example A through G illustrate the preparation of some of the intermediates employed in the preparation of the dye compounds of the invention.

EXAMPLE A

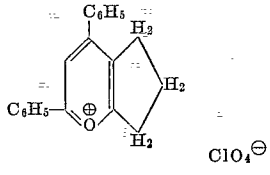
4,6 - di - (4-ethoxyphenyl)-2-methylpyrylium fluoroborate



To a mixture of 4'-ethoxyacetophenone (82.1 g.) and acetic anhydride (150 ml.) boron trifluoride ethyl etherate (150 ml.) is added and the mixture heated at 50° C. for 24 hours, after which it is allowed to cool, diluted with ether and chilled. The product is collected on the filter. The yield is 42 g. (39%). The brownish orange crystals melt at 226–228° C. with decomposition.

EXAMPLE B

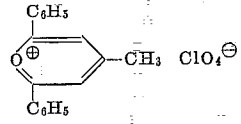
6,7 - dihydro - 2,4 - diphenyl - 5H - cyclopenta[b] pyrylium perchlorate



To a solution of chalcone (69 g.) in ether (275 ml.) perchloric acid (70%, 50 mls.) is added slowly and the mixture chilled. To the chilled mixture, acetic anhydride (220 ml.) is added dropwise during two hours; the mixture is allowed to reach room temperature and cyclopentanone (30 g.) is added and the mixture stirred for two hours. The product is collected on the filter and washed with acetic acid and then with ether. The yield is 39 g. (31%); the brownish orange crystals melt at 240–241° C., with decomposition.

EXAMPLE C

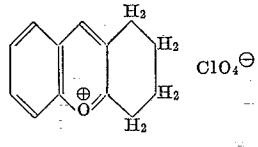
4-methyl-2,6-diphenylpyrylium perchlorate



To a solution of 1-phenyl-2-butene-1-one (29.2 g.) in ether (150 ml.) perchloric acid (70%, 29 mls.) is added and the mixture chilled. Acetic anhydride (142 ml.) is added dropwise during 90 minutes and the mixture allowed to reach room temperature. Acetophenone (25 g.) is added and the mixture is stirred for two hours. The product is collected on the filter, and washed with acetic acid and then with ether. The yield is 10 g. (15%). The bright yellow crystals melt at 247–248° C., with decomposition.

EXAMPLE D

1,2,3,4-tetrahydroxanthylium perchlorate



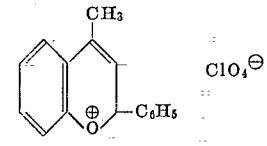
To a cooled mixture of perchloric acid (70%, 30 ml.) and acetic acid (300 ml.), a mixture of salicylaldehyde (24.4 g.) and cyclohexanone (20 g.) is slowly added. The

product is collected on the filter and washed with ether. The yield is 18 g. (31%). The brown crystals melt at 168–169° C., with decomposition.

8,9,10,11 - tetrahydro-benzo[a]xanthylium perchlorate is similarly prepared from 2-hydroxy-1-naphthaldehyde. The yield is 21%; the pale greenish crystals melt at 221–222° C., with decomposition.

EXAMPLE E

4 - methyl - 2 - phenyl-1-benzopyrylium perchlorate

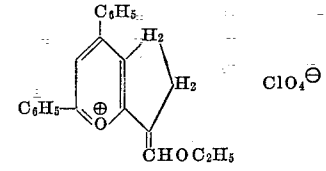


To a stirred suspension of ferric chloride (108 g.) in acetic acid (100 ml.) a mixture of acetophenone (60 g.) and 2'-hydroxyacetophenone (68 g.) is added; hydrochloric acid (100 ml.) is then added and the mixture heated under reflux for 3 hours. The product is collected on the filter and washed with ether. The yield is 54 g. (28%); the pale green crystals melt at 169–170° C., with decomposition.

To a suspension of the product in water (750 ml.) perchloric acid (70%, 2 ml.) and sodium perchlorate (30 g.) is added and the mixture stirred for 2 hours at 50° C. The mixture is allowed to cool and the product collected on the filter and washed several times with water and then with methanol. The yield is 32 g. (20%). After recrystallization from acetic acid, the green crystals melt at 213–214° C., with decomposition.

EXAMPLE F

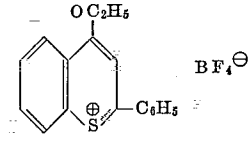
7 - ethoxymethylene-6,7 - dihydro - 2,4 - diphenyl-5H-cyclopenta[b]pyrylium perchlorate



A mixture of 6,7 - dihydro - 2,4-diphenyl-5H-cyclopenta[b]pyrylium perchlorate (19 g.), ethylorthoacetate (10 ml.) and acetic anhydride (100 ml.) is heated under reflux for 10 minutes. The mixture is allowed to cool and the product collected on the filter and washed with acetic acid and then with ether. The yield is 11.8 g. (55%). The dark brown crystals melt at 173–174° C., with decomposition.

EXAMPLE G

6-ethoxy-2-phenyl-1-benzothiapyrylium fluoroborate



To 1-thioflavone (8 g.) in methylene chloride (150 ml.) is added triethyl oxonium fluoroborate (6 g.) and the mixture is stirred and left overnight in an icebox. Then 50 ml. of methylene chloride is added to the mixture and the product is filtered out and washed with ether. The yield of above compound is 6.5 g. (55%) of yellow crystals, M.P. 126–128° C.

The intermediate 1-thioflavone for above Example G is prepared by heating a mixture of benzene thiol (10.5 g.), ethylbenzoyl acetate (25.0 g.) and polyphosphoric acid (350 g.), with occasional stirring, on a steam bath for a period of about one hour. The mixture is heated for another 3 hours at 90–100° C. and then poured over 500 g. of ice, stirred, the product filtered out and washed.

The yield of 1-thioflavone is 22 g. (92%), M.P. 55–57° C.

The preparations of a number of intermediates such as 2-substituted indoles; imidazo[4,5-b]quinoxalines; and carbazoles are described in copending applications such as Mee et al., Ser. No. 609,792, filed Jan. 17, 1967, now abandoned, Brooker et al. Ser. No. 609,791, filed Jan. 17, 1967 now Pat. No. 3,431,111, Mee et al. Ser. No. 609,740, filed Jan. 17, 1967 now U.S. Pat. No. 3,492,123, and Mee et al. Ser. No. 639,030 filed May 17, 1967.

The effectiveness of the dyes of the invention as spectral sensitizers for organic photoconductor compositions and elements of the invention was determined by the exact testing procedure described in above Example 1. The results are listed in the following Table I for a number of the dye combinations of the preceding examples.

TABLE I

Example No.	Image formed	Shoulder speeds: Positively charged surface	Shoulder speeds: Negatively charged surface	Sensitivity (abs. max.) nm.
Control (No Dye)	Yes	8	7	
1	Yes	2,806	502	580; 625
2	Yes	650	650	620
3	Yes	160	160	550
4	Yes	1,592	1,035	585; 630
5	Yes	2,500	900	580
6	Yes	800	500	595
Z	Yes	2	2	660; 490

Referring to the above Table I, it will be seen that the control containing the same organic photoconductor but no dye shows speeds of only 8 and 7 for the positively and negatively charged surfaces, respectively, whereas the corresponding values for the dyes of this invention represented by Examples 1 to 6 are clearly of a different order of magnitude. For example, the highest speed is shown by Example 1 of 2806 and 502 for the positively and negatively charged surfaces, respectively, with maximum sensitivity peaks at 580 and 625 nm., thus indicating a speed increase over that of the control by a factor of about 350 for the positively charged and about 62 for the negatively charged. Also of great significance is the extension of the absolute sensitivity to the region of 625 nm. Even with the least speed shown for the compositions and elements of the invention as illustrated by Example 3 the improvement in speed is impressive in comparison with that of the control by factors of about 20 and 22 for the positively charged and negatively charged surfaces, respectively. Results similar to those of Examples 1–6 are obtained when the dye used is the dye of Example 7 or any of the dyes mentioned in the second paragraph following Example 7. Example Z is included in the above table to show that related pyrylium type dyes outside the scope of this invention, i.e., devoid of electron-accepting nuclei such as those set forth for the dyes of this invention, do not function effectively as sensitizers for organic photoconductors. The dye in this example is 2,2′ - diphenyl - 4,4′ - (1 - benzopyrylo) - carbocyanine perchlorate. It was tested by the exact procedure described in above Example 1. It will be noted from the table that though the spectral sensitivity is extended to maximum peaks of 660 and 490, the speed is only Z, a value substantially below that of even the control example.

Similar results to those shown in above Table I are obtained, when, for example, the organic photoconductor 4,4′ - bis(diethylamino) - 2,2′ - dimethyltriphenylmethane is replaced in the above examples with 0.15 g. of triphenylamine (using the p-toluenesulfonate salt of each dye) or 1,3,5 - triphenyl - 2 - pyrazolin, or 2,3,4,5-tetraphenylpyrrole, or 4,4′ - bis - diethylaminobenzophenone or when other dyes of the invention embraced by Formula I above are used. 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 in themselves photoconductive. Also, it should be noted that the above mentioned photoconductors when used alone have very low photoconductive speed to visible light. However, as shown by the tests, the combination of the dyes of the invention with the photoconductors of the invention provide compositions and elements of outstanding speed and excellent quality of image.

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 C below.

TABLE C

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′-(3-sulfobutyl)thiacarbocyanine hydroxide.
G	1′-ethyl-3-methylthia-2′-cyanine chloride.
H	1,1′-diethyl-2,2′-cyanine chloride.

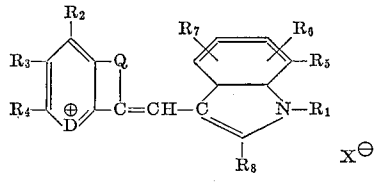
In contrast, as indicated previously, the dyes of this invention are inoperable as spectral sensitizers for conventional negative type photographic silver halide emulsions because they strongly desensitize such emulsions.

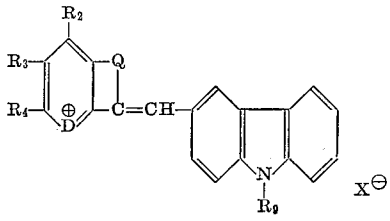
Although the invention has been described in considerable detail with particular reference to certain preferred embodiments thereof, it will be understood that variations and modifications can be effected within the spirit and scope of the invention as described hereinabove, and as defined in the appended claims.

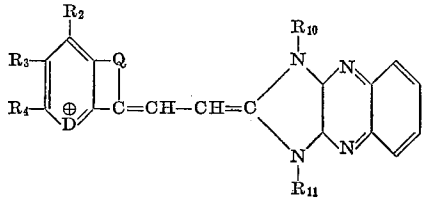
We claim:

1. A composition of matter comprising an organic photoconductor spectrally sensitized with a methine dye selected from those comprising first and second heterocyclic nuclei joined together by a methine linkage selected from the group consisting of a monomethine linkage and a dimethine linkage; the first of said nuclei being selected from the group consisting of a pyrylium nucleus and a thiapyrylium nucleus joined at a carbon atom thereof to said methine linkage; and, said second nucleus being selected from the group consisting of: a 2-arylindole nucleus joined at the 3-carbon atom thereof to said methine linkage; a carbazole nucleus joined at the 4-carbon atom thereof to said methine linkage; and, an imidazo[4,5-b]quinoxaline nucleus joined at the 2-carbon atom thereof to said methine linkage.

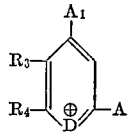
2. A composition of matter comprising an organic photoconductor spectrally sensitized with a methine dye selected from those having one of the following formulas:





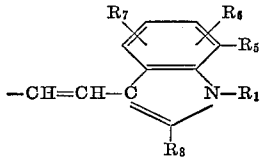


and

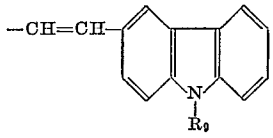


wherein one and only one of A and A_1 represents a group selected from those having the formulas:

(a)

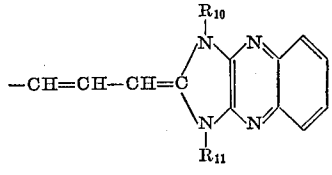


(b)



and

(c)



and the other of said A and A_1 represents a member selected from the group consisting of a hydrogen atom, an alkyl group and an aryl group; R_9 represents an alkyl group; R_2, R_3 and R_4 each represents a member selected from the group consisting of a hydrogen atom, an alkyl group and an aryl group, and R_3 and R_4 when taken together, represent a member selected from the group consisting of a benzo group and a naphtho group; R_5, R_6 and R_7 each represents a member selected from the group consisting of a hydrogen atom, an alkyl group, a nitro group and a halogen atom and, R_5 and R_6 when taken together, and R_6 and R_7 when taken together, represents a benzo group; and R_5, when taken together with R_1, represents an alkylene group, R_1 being alkyl when not taken together with R_5; R_8 represents an aryl group; R_{10} and R_{11} each represents a member selected from the group consisting of an alkyl group, an alkenyl group and an aryl group; D represents a member selected from the group consisting of an oxygen atom and a sulfur atom; X represents an acid anion; and Q represents a member selected from the group consisting of an ethylene group and a trimethylene group.

3. A composition as defined in claim 2 wherein said organic photoconductor has the following formula:



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 substitutent selected from the group consisting of a secondary amino group and a tertiary amino group.

4. A composition as defined in claim 2 wherein said organic photoconductor is selected from the group consisting of:

triphenylamine;
1,3,5-triphenyl-2-pyrazoline;
4,4'-bis(diethylamino)-2,2'-dimethyltriphenylamine;
2,3,4,5-tetraphenylpyrrole; and
4,4'-bis-diethylaminobenzophenone.

5. 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;

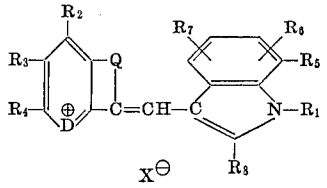
said organic photoconductor being spectrally sensitized with from .01 to 10 parts by weight of a dye selected from the group consisting of

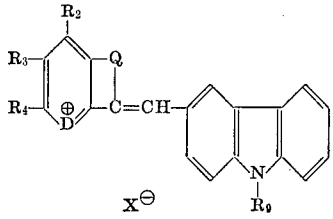
4-[2-(1-methyl-2-phenyl-3-indolyl)vinyl]-2-phenyl-naphtho[1,2-b]pyrylium salt;
4-[2-(1-methyl-2-phenyl-3-benz[g]indolyl)vinyl]-2-phenyl-1-benzopyrylium salt;
2-(4-chlorophenyl)-4-[2-(9-methyl-3-carbazolyl)vinyl]-1-benzopyrylium salt;
2-(4-chlorophenyl)-4-[2-(1-methyl-2-phenyl-3-indolyl)-vinyl]-1-benzopyrylium salt;
4-[2-(1-methyl-2-phenyl-3-indolyl)-vinyl]-1-benzo-pyrylium salt; and
5,6,7,8-tetrahydro-8-[(9-methyl-3-carbazolyl)methyl-ene]-2,4-diphenylcyclohexa[b]pyrylium salt.

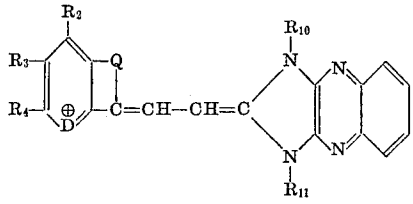
6. An electrophotographic element comprising a conductive support having thereon a layer comprising an organic photoconductor in an insulating binder, said organic photoconductor being spectrally sensitized with a methine dye selected from those comprising first and second heterocyclic nuclei joined together by a methine linkage selected from the group consisting of a monomethine linkage and a dimethine linkage; the first of said nuclei being selected from the group consisting of a pyrylium nucleus and a thiapyrylium nucleus joined at a carbon atom thereof to said methine linkage; and, said second nucleus being selected from the group consisting of: a 2-arylindole nucleus joined at the 3-carbon atom thereof to said methine linkage; a carbazole nucleus joined at the 4-carbon atom thereof to said methine linkage; and, an imidazo-[4,5-b]quinoxaline nucleus joined at the 2-carbon atom thereof to said methine linkage.

7. An electrophotographic element comprising a conductive support having thereon a layer comprising an organic photoconductor spectrally sensitized with a

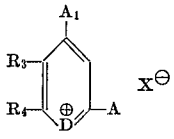
methine dye selected from those having one of the following formulas:





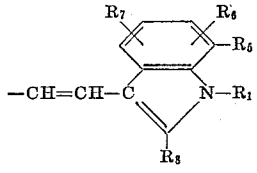


and

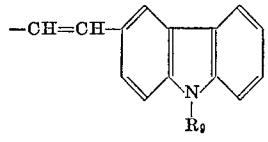


wherein one and only one of A and A_1 represents a group selected from those having the formulas:

(a)

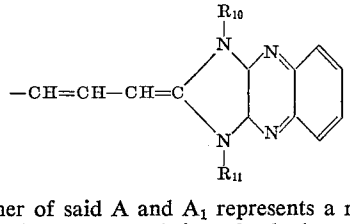


(b)



and

(c)



and the other of said A and A_1 represents a member selected from the group consisting of a hydrogen atom, an alkyl group and an aryl group; R_9 represents an alkyl group; R_2, R_3 and R_4 each represents a member selected from the group consisting of a hydrogen atom, an alkyl group and an aryl group and R_3 and R_4 when taken together, represent a member selected from the group consisting of a benzo group and a naphtho group; R_5, R_6 and R_7 each represents a member selected from the group consisting of a hydrogen atom, an alkyl group, a nitro group and a halogen atom and R_5 and R_6 when taken together and R_6 and R_7 when taken together, represents a benzo group; and R_5, when taken together with R_1, represents an alkylene group, R_1 being alkyl when not taken together with R_5; R_8 represents an aryl group; R_{10} and R_{11} each represents a member selected from the group consisting of an alkyl group, an alkenyl group and an aryl group; D represents a member selected from the group consisting of an oxygen atom and a sulfur atom; X represents an acid anion; and Q represents a member selected from the group consisting of an ethylene group and a trimethylene group.

8. An electrophotographic element as defined in claim 7 wherein said D represents said oxygen atom.

9. An electrophotographic element as defined in claim 7 wherein each of said R_2 and R_4 of said dye represents said aryl group.

10. An electrophotographic element as defined in claim 7 wherein said R_3 and R_4 of said dye together represent said fused benzo ring.

11. An electrophotographic element as defined in claim 7 wherein said R_3 and R_4 of said dye together represent said fused naphtho ring.

12. An electrophotographic element as defined in claim 7 wherein said A of said dye represents said aryl group, and said A_1 of said dye represents said (a) group.

13. An electrophotographic element as defined in claim 7 wherein said A of said dye represents said aryl group, and said A_1 of said dye represents said (b) group.

14. An electrophotographic element as defined in claim 7 wherein said organic photoconductor has the following formula:



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 selected from the group consisting of a secondary amino group and a tertiary amino group.

15. An electrophotographic element as defined in claim 7 wherein said organic photoconductor is selected from the group consisting of: triphenylamine; 1,3,5-triphenyl-2-pyrazoline; 4,4' - bis - (diethylamino)-2,2'-dimethyltriphenylamine; 2,3,4,5-tetraphenylpyrrole; and 4,4'-bis-diethylaminobenzophenone.

16. An electrophotographic element as defined in claim 7 wherein said organic photoconductor comprises from 1 to 75 parts by weight of said composition, said photoconductor being spectrally sensitized with from .01 to 10 parts by weight of said composition of said cyanine dye.

17. An electrophotographic element as defined in claim 7 wherein said organic photoconductor and said dye are incorporated in an insulating binder.

18. An electrophotographic element as defined in claim 7 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.

19. An electrophotographic element comprising a conductive support having thereon a layer 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

4-[2-(1-methyl-2-phenyl-3-indolyl)vinyl]-2-phenyl-naphtho[1,2-b]pyrylium salt;
4-[2-(1-methyl-2-phenyl-3-benz-[g]indolyl)vinyl]-2-phenyl-1-benzopyrylium salt;

2-(4-chlorophenyl)-4-[2-(9-methyl-3-carbazolyl) vinyl]-1-benzopyrylium salt;
2-(4-chlorophenyl)-4-[2-(1-methyl-2-phenyl-3-indolyl) vinyl]-1-benzopyrylium salt;
4-[2-(1-methyl-2-phenyl-3-indolyl)vinyl]-1-benzopyrylium salt and
5,6,7,8-tetrahydro-8-[(9-methyl-3-carbazolyl)methylene]-2,4-diphenylcyclohexa[b]pyrylium salt.

20. An electrophotographic element as defined in claim **19** wherein said organic photoconductor and said dye are dispersed in an insulating binder.

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GEORGE F. LESMES, Primary Examiner

J. C. COOPER III, Assistant Examiner

U.S. Cl. X.R.

96—1.7, 102, 106; 260—240