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3,745,160

NOVEL BORINIUM CYANINE DYES

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No Drawing. Original application Sept. 23, 1968, Ser. No. 761,860, now Patent No. 3,567,439, dated Mar. 2, 1971. Divided and this application Oct. 30, 1970, Ser. No. 85,710

Int. Cl. C09b 23/00, 23/14

U.S. Cl. 260—240 D

5 Claims

ABSTRACT OF THE DISCLOSURE

Novel methine dyes are provided which feature a 1,3,2-dioxaborinium salt moiety, a 1,3,2 - oxazaborinium salt moiety or a 1,3,2-diazaborinium salt moiety. Organic photoconductors are spectrally sensitized with the novel dyes of this invention. Novel intermediates and methods for the preparation of such intermediates are also provided.

This application is a division of our copending application Ser. No. 761,860 filed Sept. 23, 1968 now U.S. Pat. 3,567,493 issued Mar. 2, 1971

This invention relates to novel dyes and their use in electrophotography.

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 image-wise 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 D 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.

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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.

5 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.

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

Another object is to provide a novel class of spectral sensitizing dyes and means for preparing these dyes.

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

15 In accordance with one embodiment of this invention, novel cyanine dyes are provided which contain a moiety selected from the group consisting of a 1,3,2-dioxaborinium salt moiety, a 1,3,2-oxazaborinium salt moiety and a 1,3,2-diazaborinium salt moiety.

20 In accordance with another embodiment of this invention, novel compositions of matter are provided comprising organic photoconductors spectrally sensitized with the cyanine dyes of this invention. These compositions can be incorporated in a suitable binder and coated on a conductive support for use in electrophotography.

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

30 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 herein.

35 In another embodiment of this invention, novel compounds are provided selected from the group consisting of a 1,3,2-dioxaborinium salt; a 1,3,2-oxazaborinium salt and a 1,3,2-diazaborinium salt.

40 The spectral sensitizing dyes which are employed in this invention, when incorporated in a test negative gelatin silver bromide 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 the appended claims, the "test" negative silver bromide emulsions are prepared as follows:

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

(A)

55 Potassium bromide -----g-- 165
Potassium iodide -----g-- 5
60 Gelatin -----g-- 65
Water -----cc-- 1700

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

(B)

65 Silver nitrate -----g-- 200
Water -----cc-- 2000

70 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 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 cyanine 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.

In accordance with this invention, a new class of methine dyes are provided which contain a 1,3,2-dioxaz-, a 1,3,2-oxaza- or a 1,3,2-diazaborinium salt moiety.

Particularly useful methine dyes provided by this invention are styryl dyes which comprise two nuclei joined together by a methine linkage, e.g., a vinyl or butadienyl linkage; the first of said nuclei being a 1,3,2-dioxaz-, a 1,3,2-oxaza- or a 1,3,2-diazaborinium salt nucleus, joined at the 4-carbon atom thereof to said linkage; and said second nucleus being a phenyl nucleus joined at a carbon atom thereof to said linkage, to complete said dye.

Other useful methine dyes provided by this invention are simple cyanine and carbocyanine dyes which comprise two nuclei joined together by a methine linkage, e.g., monomethine, trimethine or pentamethine linkage; the first of said nuclei being a 1,3,2-dioxaz-, a 1,3,2-oxaza- or a 1,3,2-diazaborinium salt nucleus, joined at the 4-carbon atom thereof to said linkage; and said second nucleus being a nitrogen containing heterocyclic nucleus of the type used in cyanine dyes having from 5 to 6 atoms in the heterocyclic ring and joined at a carbon atom to said linkage to complete said dye.

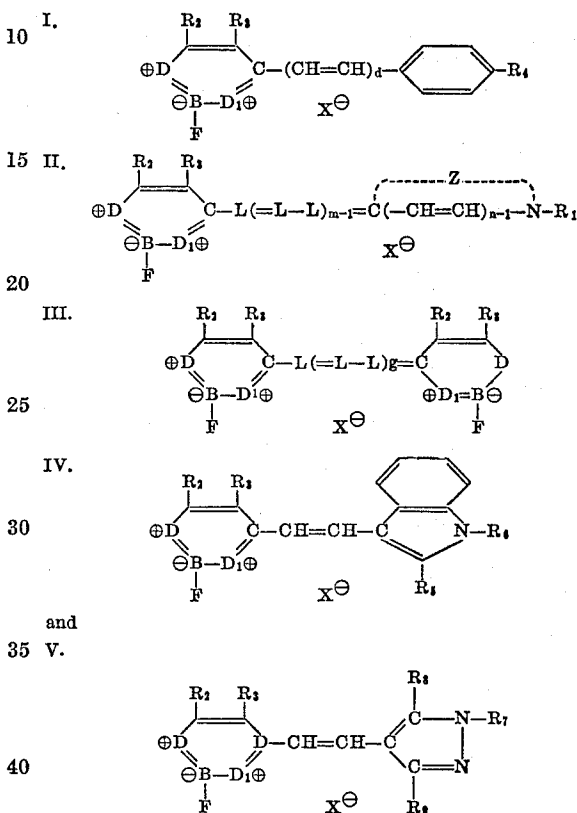
Further methine dyes provided by this invention are symmetrical cyanine dyes which comprise two nuclei joined together at the 4-carbon atoms thereof by a methine linkage, e.g., a monomethine, trimethine or pentamethine linkage; said nuclei being selected from the group consisting of a 1,3,2-dioxaborinium salt nucleus, a 1,3,2-oxazaborinium salt nucleus and a 1,3,2-diazaborinium salt nucleus.

Still other useful cyanine dyes provided by this invention are the 1-alkyl-2-arylindole type dyes which comprise two nuclei joined together by a methine linkage, e.g., a vinyl linkage; the first of said nuclei being a 1,3,2-dioxaz-, a 1,3,2-oxaza- or a 1,3,2-diazaborinium salt nucleus joined at the 4-carbon atom thereof to said linkage; and said second nucleus being a 1-alkyl-2-arylindole nucleus joined at the 3-carbon atom thereof to said linkage, to complete said dye.

Other useful cyanine dyes provided by this invention are the pyrazole type dyes which comprise two nuclei

joined together by methine linkage, e.g., a vinyl linkage; the first of said nuclei being a 1,3,2-dioxaz-, a 1,3,2-oxaza- or a 1,3,2-diazaborinium salt nucleus, joined at the 4-carbon atom thereof to said linkage; and said second nucleus being a pyrazole nucleus joined at the 4-carbon atom thereof to said linkage, to complete said dye.

Typical useful dyes of this invention include those represented by one or more of the following formulas:



wherein *d*, *g*, *m* and *n* each represents a positive integer of from 1 to 2; *L* represents a methine linkage, e.g., $-\text{CH}=\text{CH}-$, $-\text{C}(\text{CH}_3)=$, $-\text{C}(\text{C}_6\text{H}_5)=$, etc.; *R*₁ represents an alkyl group, including substituted alkyl (preferably a lower alkyl containing from 1 to 4 carbon atoms), e.g., methyl, ethyl, propyl, isopropyl, butyl, hexyl, cyclohexyl, decyl, dodecyl, etc.; 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 -methoxycarbonyl, ω -ethoxycarbonyl, benzyl, phenethyl, etc.; *R*₂ represents an aryl group (such as phenyl or naphthyl), a 2-thienyl group or, taken together with *R*₃, the atoms required to complete a benzo or naphtho group including substituted nuclei thereof such as chlorobenzo, methylbenzo, nitrobenzo, chloronaphtho, etc.; *R*₃, taken alone, represents a hydrogen atom; *R*₄ represents a dialkylamino group (preferably those wherein each alkyl is a lower alkyl containing from 1 to 4 carbon atoms), e.g., dimethylamino, dibutylamino, etc.; an alkoxy group (preferably a lower alkoxy containing from 1 to 4 carbon atoms), e.g., methoxy, butoxy, etc.; a styryl group, or a nitro group, etc.; *R*₅ represents an aryl group, e.g., phenyl, tolyl, chlorophenyl, methoxyphenyl, nitrophenyl, naphthyl, etc.; *R*₆ represents an alkyl group (preferably a lower alkyl containing from 1 to 4 carbon atoms), e.g., methyl, propyl, isopropyl, butyl, decyl, etc.; *R*₇ represents an aryl group, e.g., phenyl, tolyl, methoxyphenyl, chlorophenyl, nitrophenyl, naphthyl,

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etc.; R_8 and R_9 each represents an alkyl group (preferably a lower alkyl containing from 1 to 4 carbon atoms), e.g., methyl, ethyl, isopropyl, butyl, decyl, etc.; X represents an acid anion, e.g., chloride, bromide, iodide, fluoride, thiocyanate, sulfamate, perchlorate, p-toluenesulfonate, methyl sulfate, etc.; D and D_1 each represents an oxygen atom or an imino group, such as an imino group of the formula $-N(R)-$, wherein R represents hydrogen or aryl, e.g., imino, e.g., methylimino, butylimino, etc., or an arylimino, e.g., phenylimino, tolylimino, naphthylimino, etc., D_1 being an imino group when D represents an imino group; and Z represents the non-metallic atoms required to complete a heterocyclic nucleus containing from 5 to 6 atoms in the heterocyclic ring, which nucleus may contain a second hetero atom such as oxygen, sulfur, selenium or nitrogen, such as used in cyanine dyes, and including the following nuclei: a thiazole nucleus, e.g., thiazole, 4-methylthiazole, 4-phenylthiazole, 5-methylthiazole, 5-phenylthiazole, 4,5-dimethylthiazole, 4,5-diphenylthiazole, 4-(2-thienyl)thiazole, benzothiazole, 4-chlorobenzothiazole, 4-chloro-5-nitrobenzothiazole, 5-chlorobenzothiazole, 6-chlorobenzothiazole, 7-chlorobenzothiazole, 4-methylbenzothiazole, 5-methylbenzothiazole, 6-methylbenzothiazole, 4- or 5-nitrobenzothiazole, 6-nitrobenzothiazole, 5-bromobenzothiazole, 6-bromobenzothiazole, 5-chloro-6-nitrobenzothiazole, 4-phenylbenzothiazole, 4-methoxybenzothiazole, 5-methoxybenzothiazole, 6-methoxybenzothiazole, 5-iodobenzothiazole, 6-iodobenzothiazole, 4-ethoxybenzothiazole, 5-ethoxybenzothiazole, tetrahydrobenzothiazole, 5,6-dimethoxybenzothiazole, 5,6-dioxyethylenebenzothiazole, 5-hydroxybenzothiazole, 6-hydroxybenzothiazole, naphtho[2,1-d]thiazole, naphtho[1,2-d]thiazole, naphtho[2,3-d]thiazole, 5-methoxynaphtho[2,3-d]thiazole, 5-ethoxynaphtho[1,2-d]thiazole, 8-methoxynaphtho[2,1-d]thiazole, 7-methoxynaphtho[2,1-d]thiazole, 5-methoxythianaphtheno[7,6-d]thiazole, nitro substituted naphthothiazoles, etc.; an oxazole nucleus, e.g., 4-methyloxazole, 4-nitrooxazole, 5-methyloxazole, 4-phenyloxazole, 4,5-diphenyloxazole, 4-ethyloxazole, 4,5-dimethyloxazole, 5-phenyloxazole, benzoxazole, 5-methylbenzoxazole, 5-phenylbenzoxazole, 5- or 6-nitrobenzoxazole, 5-chloro-6-nitrobenzoxazole, 6-methylbenzoxazole, 5,6-dimethylbenzoxazole, 4,6-dimethylbenzoxazole, 5-methoxybenzoxazole, 5-ethoxybenzoxazole, 5-chlorobenzoxazole, 6-methoxybenzoxazole, 5-hydroxybenzoxazole, 6-hydroxybenzoxazole, naphtho[2,1-d]oxazole, naphtho[1,2-d]oxazole, nitro substituted naphthoxazoles, etc.; a selenazole nucleus, e.g., 4-methylselenazole, 4-nitroselenazole, 4-phenylselenazole, benzoselenazole, 5-chlorobenzoselenazole, 5-methoxybenzoselenazole, 5-hydroxybenzoselenazole, 5- or 6-nitrobenzoselenazole, 5-chloro-6-nitrobenzoselenazole, tetrahydrobenzoselenazole, naphtho[2,1-d]selenazole, naphtho[1,2-d]selenazole, nitro substituted naphthoselenazoles, etc.; a thiazoline nucleus, e.g., thiazoline, 4-methylthiazoline, 4-nitrothiazoline, etc.; a pyridine nucleus, e.g., 2-pyridine, 5-methyl-2-pyridine, 4-pyridine, 3-methyl-4-pyridine, nitro substituted pyridines, etc.; a quinoline nucleus, e.g., 2-quinoline, 3-methyl-2-quinoline, 5-ethyl-2-quinoline, 6-chloro-2-quinoline, 6-nitro-2-quinoline, 8-chloro-2-quinoline, 6-methoxy-2-quinoline, 8-ethoxy-2-quinoline, 8-hydroxy-2-quinoline, 4-quinoline, 6-methoxy-4-quinoline, 6-nitro-4-quinoline, 7-methyl-4-quinoline, 8-chloro-4-quinoline, 1-isoquinoline, 6-nitro-1-isoquinoline, 3,4-dihydro-1-isoquinoline, 3-isoquinoline, etc.; a 3,3-dialkylindolenine nucleus, preferably having a nitro or cyano substituent, e.g., 3,3-dimethyl-5- or 6-nitroindolenine, 3,3-dimethyl-5- or 6-cyanoindolenine, etc.; and, an imidazole nucleus, e.g., imidazole, 1-alkylimidazole, 1-alkyl-4-phenylimidazole, 1-alkyl-4,5-dimethylimidazole, benzimidazole, 1-alkylbenzimidazole, 1-aryl-5,6-dichlorobenzimidazole, 1-alkyl-1H-naph[1,2-d]imidazole, 1-aryl-3H-naphth[1,2-d]imidazole, 1-alkyl-5-methoxy-1H-naphth[2,1-d]imidazole, etc.; an imidazo-

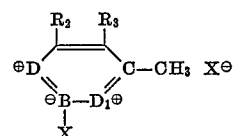
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[4,5-b]quinoxaline nucleus, e.g., a 1,3-dialkylimidazo[4,5-b]quinoxaline such as 1,3-diethylimidazo[4,5-b]quinoxaline, 6-chloro-1,3-diethylimidazo[4,5-b]quinoxaline, etc., a 1,3-dialkylimidazo[4,5-b]quinoxaline such as 1,3-diallylimidazo[4,5-b]quinoxaline, 6-chloro-1,3-diallylimidazo[4,5-b]quinoxaline, etc., a 1,3-diarylimidazo[4,5-b]quinoxaline such as 1,3-diphenylimidazo[4,5-b]quinoxaline, 6-chloro-1,3-diphenylimidazo[4,5-b]quinoxaline, etc.; a 3,3-dialkyl-3H-pyrrolo[2,3-b]pyridine nucleus, e.g., 3,3-dimethyl-3H-pyrrolo[2,3-b]pyridine, 3,3-diethyl-3H-pyrrolo[2,3-b]pyridine etc.; a thiazolo[4,5-b]quinoline nucleus; and the like. The nuclei wherein Z in above Formula II represents the atoms necessary to complete an electron-accepting nucleus such as a nitro substituted thiazole, oxazole, selenazole, thiazoline, pyridine, quinoline, 3,3-dialkylindolenine or imidazole nucleus; or an imidazo[4,5-b]quinoxaline, 3,3-dialkyl-3H-pyrrolo[2,3-b]pyridine or thiazolo[4,5-b]quinoline nucleus; and the like; provide useful spectral sensitizing dyes for the photoconductor compositions and elements of this invention. The styryl type dyes of the invention defined by Formula I above are especially efficacious sensitizers and are the preferred dyes of this invention.

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.

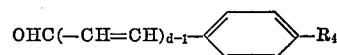
The cyanine dyes of Formula I above are conveniently prepared, for example, by heating a mixture of (1) a heterocyclic compound of the formula:

VI.



and (2) an aldehyde of the formula:

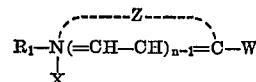
VII.



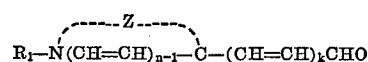
wherein d , R_2 , R_3 , R_4 , D, D_1 and X are as previously defined and d represents a positive integer of from 1 to 2, in approximately equimolar proportions, in a solvent medium such as acetic anhydride. The solid which separated on cooling the reaction mixture is collected and purified by one or more recrystallizations from an appropriate solvent such as acetonitrile.

The cyanine dyes of Formula II above are readily prepared, for example, by heating a mixture comprising (1) a compound of Formula VI above with (2) a heterocyclic compound having one of the formulas:

VIII.



VIIIa



wherein n , R_1 , X and Z are as previously defined; k represents 0 or 1; and, W represents the group $-SR_{10}$ wherein R_{10} is an alkyl or aryl group, e.g., methyl, phenyl, etc.

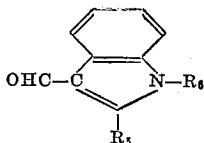
for the preparation of the simple cyanine dyes of the invention, or W represents the group



for example. Advantageously, the reaction is carried out in approximately equimolar proportions of the compounds comprising (1) a compound of Formula VI above and (2) a compound such as a dialkoxymethylacetate, e.g., diethoxymethylacetate, or a trialkoxypropene, e.g., trimethoxypropene, etc., is reacted by heating to boiling in the presence of a weakly basic condensing agent, e.g., 2,6-lutidine, in a solvent medium such as acetic anhydride in the proportions of about 2 moles of (1) and at least 1 mole of (2) the crude dyes obtained are purified by one or more recrystallizations from appropriate solvents such as acetonitrile.

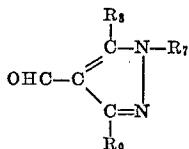
For the preparation of the symmetrical cyanine dyes of this invention defined by Formula III above, a mixture comprising (1) a compound of Formula VI above and (2) a compound such as a dialkoxymethylacetate, e.g., diethoxymethylacetate, or a trialkoxypropene, e.g., trimethoxypropene, etc., is reacted by heating to boiling in the presence of a weakly basic condensing agent, e.g., 2,6-lutidine, in a solvent medium such as acetic anhydride in the proportions of about 2 moles of (1) and at least 1 mole of (2) the crude dyes obtained are purified by one or more recrystallizations from appropriate solvents such as acetonitrile.

The cyanine dyes defined by Formulas IV and V above are conveniently prepared by heating a mixture comprising (1) a compound of Formula VI above and (2) a compound selected from (a) a compound of the formula:



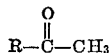
or (b) a compound of the formula:

X.



wherein R_1 and R_5 to R_9 are as previously defined, following the general procedure described above for the preparation of the cyanine dyes represented by Formula I above.

The intermediates represented by Formula VI above can be readily prepared by reacting (1) a compound represented by the formula:



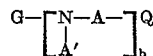
wherein R is a suitably substituted aryl e.g., 2-amino-phenyl, 2-hydroxyphenyl, 2-hydroxy- α -naphthyl, etc. or an acyl substituted methyl e.g., acetylmethyl, CH_3COCH_2 , 2-thienoylmethyl, etc. or a precursor which can be converted to the latter in the presence of (2) and acetic anhydride, for example 6(2-thienyl)-4-methyl-1,3,2-dioxaborinium fluoride from 2-thienyl-methyl ketone, with (2) boron-trifluoride ethyl ether complex to give the corresponding 1,3,2-dioxaborinium or the 1,3,2-oxazaborinium salts. By treatment with an arylamine, e.g., aniline, the above salts are converted to the 3-arylimido substituted 1,3,2-oxazaborinium and 3-arylimino substituted 1,3,2-diazaborinium salts, respectively.

Dyes such as illustrated 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. 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 insen-

sitive, 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 6 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) nonpolymeric triarylamines, such as triphenylamine, N,N,N' -tetraphenyl-m-phenylenediamine, 4-acetyltriphenylamine, 4-hexanoyltriphenylamine; 4-lauroyltriphenylamine; 4-hexyltriphenylamine, 4-dodecyltriphenylamine, 4,4'-bis(diphenylamino)-benzil, 4,4'-bis(didiphenylamino)-benzophenone, and the like, and (b) polymeric triarylamines such as poly- $[N,4'-(N,N',N'$ -triphenylbenzidine)]; polydipyltriphenylamine, 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., phenyl, naphthyl, biphenyl, binaphthyl, 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.

Polyacrylalkane photoconductors are particularly useful in producing the present invention. Such photoconduc-

tors 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. These photoconductors include leuco bases of diaryl or triaryl methane dye salts, 1,1,1-triaryllkanes 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. 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 parapositions, ortho-substituted phenyl being preferred. The aryl groups can also be jointed together or cyclized to form a fluorene moiety, for example. The amino substituent can be represented by the formula



wherein each R₁₁ 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, pyrrol, 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 polyaryllkane photoconductors include the compounds listed below:

TABLE A

Compound Number	
(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''-dimethyldiphenylmethane.
(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

Inventor	Issued	Patent Number
Noe et al.....	Feb. 25, 1964.....	3,122,435
Sus et al.....	Mar. 31, 1964.....	3,127,266
Schlesinger.....	Apr. 21, 1964.....	3,130,046
Cassiers.....	Apr. 28, 1964.....	3,131,060
Schlesinger.....	June 30, 1964.....	3,139,338
Schlesinger.....	June 30, 1964.....	3,139,339
Cassiers.....	July 14, 1964.....	3,140,946
Davis et al.....	July 21, 1964.....	3,141,770
Ghys.....	Sept. 16, 1964.....	3,148,982
Cassiers.....	Nov. 3, 1964.....	3,156,503
Cassiers.....	Nov. 24, 1964.....	3,158,475
Tomanek.....	Dec. 15, 1964.....	3,161,505
Schlesinger.....	Dec. 29, 1964.....	3,163,630
Schlesinger.....	Dec. 29, 1964.....	3,163,631
Schlesinger.....	Dec. 29, 1964.....	3,163,632
Hoegl.....	Feb. 9, 1965.....	3,169,060
Stumpf.....	Mar. 23, 1965.....	3,174,854
Klupfel et al.....	Apr. 27, 1965.....	3,180,729
Klupfel et al.....	Apr. 27, 1965.....	3,180,730
Neugebauer.....	June 15, 1965.....	3,189,447
Neugebauer.....	Sept. 14, 1965.....	3,206,306
Davis et al.....	July 21, 1964.....	3,141,770
Hoegl et al.....	June 6, 1962.....	3,037,881
Sus et al.....	June 26, 1962.....	3,041,165
Schlesinger.....	Nov. 27, 1962.....	3,066,023
Bethe.....	Jan. 8, 1963.....	3,072,479
Klupfel et al.....	July 9, 1963.....	3,047,095
Neugebauer et al.....	Nov. 26, 1963.....	3,112,197
Cassiers et al.....	Dec. 3, 1963.....	3,113,022
Schlesinger.....	Dec. 17, 1963.....	3,114,633
Kosche et al.....	Aug. 9, 1966.....	3,265,497
Noe et al.....	Sept. 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), 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.

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 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.

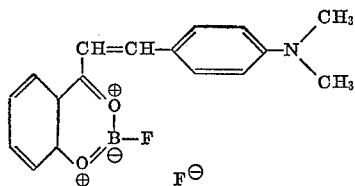
To produce a reproduction of an image utilizing the electrophotographic elements of our invention, the photoconductive layer is preferably dark adapted, and then is charged either negatively or positively by means of, for example, a corona discharge device maintained at a potential of from 6000-7000 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 1-100 μ 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

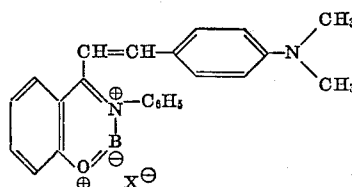
4-(4-dimethylaminostyryl)-2-fluoro-benzo[e]-1,3,2-dioxaborinium fluoride



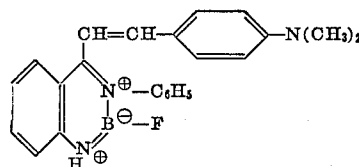
A mixture of 2-fluoro-4-methyl-1,3,2-benzo[e]dioxaborinium fluoride (1.84 g.), p-dimethylaminobenzaldehyde (1.51 g.) and acetic anhydride (20 mls.) is heated under reflux for ten minutes and allowed to cool; the dye is collected on a filter and washed with ethylacetate. The yield is 2.42 g. (77%). After recrystallization from acetonitrile, the green crystals melt at 256-257° C., with decomposition.

By substituting an equivalent amount of other intermediate aldehydes embraced by Formulas VII, IX and X in place of the p-dimethylaminobenzaldehyde in the procedure of above Example 1, the corresponding cyanine

dyes of the invention are readily obtained. Typical dyes prepared in this manner include 4-(4-dimethylaminostyryl) - 2 - fluoro - 3 - phenyl - benzo[e][1,3,2]oxazaborinium salt (e.g., the chloride, bromide, iodide, fluoride, perchlorate, p-toluenesulfonate, etc. salts).



or 4 - (4 - dimethylaminostyryl) - 2 - fluoro - 3 - phenyl - benzo[e][1,3,2]diazaborinium salt (e.g., the chloride, bromine, iodide, fluoride, perchlorate, p-toluenesulfonate, etc. salts).



and the like dyes.

Still other dyes that are readily prepared in accordance with the general procedure of above Example 1 include the following typical dye examples, the yields and melting points being listed in Table 1.

- (A) 2 - fluoro - 4 - (4 - methoxystyryl) - benzo[e]-1,3,2-dioxaborinium fluoride
- (B) 2 - fluoro - 4 - (4 - nitrostyryl) - benzo[e] - 1,3,2-dioxaborinium fluoride
- (C) 2 - fluoro - 4 - [2 - (1 - methyl-2-phenyl-3-indolyl)-vinyl] - benzo[e]-1,3,2-dioxaborinium fluoride
- (D) 4 - [2 - (3,5-dimethyl-1-phenyl-4-pyrazolyl)-vinyl] - 2-fluoro-benzo[e]-1,3,2-dioxaborinium fluoride
- (E) 4 - [4 - dimethylaminophenyl] - 1,3 - butadienyl] - 2-fluoro-benzo[e]-1,3,2-dioxaborinium fluoride
- (F) 4 - fluoro - 4 - (4 - styryl-styryl) - benzo[e]-1,3,2-dioxaborinium fluoride
- (G) 4 - (4 - dimethylaminostyryl) - 2 - fluoro-naphtho[1,2-d]-1,3,2-dioxaborinium fluoride
- (H) 4 - [4 - (4 - dimethylaminophenyl)-1,3-butadienyl] - 2-fluoro-naphtho[1,2-d]-1,3,2-dioxaborinium fluoride

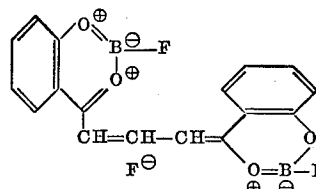
TABLE 1

Compound	Percent yield	Melting point, ° C.
A-----	47	243-235
B-----	32	290-291
C-----	68	236-237
D-----	59	268-269
E-----	32	242-243
F-----	29	272-273
G-----	60	276-277
H-----	82	246-257

EXAMPLE 2

2,2'-difluoro-4,4'-(benzo[e]-1,3,2-dioxaborino)-carbo-cyanine fluoride

(A)



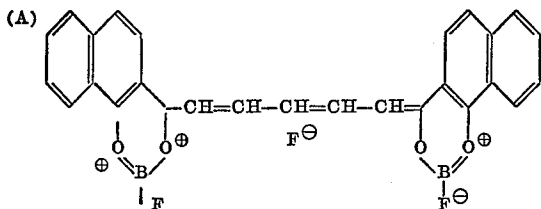
A mixture of 2-fluoro-4-methyl-benzo[e]-1,3,2-dioxaborinium fluoride (3.68 g.) and acetic anhydride (20 mls.) is heated until solution is complete. Diethoxymethylacetate (1.61 g.) is added and the mixture heated to boiling. 2,6-lutidine (2 mls.) is added and the mixture heated under reflux for 3 minutes. The mixture is allowed to cool

and is then poured over ether (400 mls.). The dye is collected on a filter and washed with ether. The yield is 0.74 g. (20%). After recrystallization from acetonitrile, the dark crystals melt at 183–184° C., with decomposition.

(B) 2,2'-difluoro-4,4'-naphtho[1,2-d]-1,3,2-dioxaborinocarbocyanine fluoride is prepared similarly. The yield is 14%. The dark crystals melt at 203°–204° C., with decomposition.

EXAMPLE 3

2,2'-difluoro-4,4'-naphtho[1,2-d]-1,3,2-dioxaborinodiborocyanine fluoride

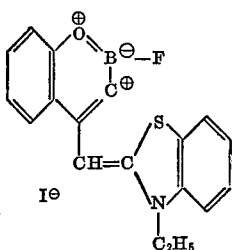


A mixture of 2-fluoro-4-methylnaphtho[1,2-d]-1,3,2-dioxaborinium fluoride (2.34 g.), trimethoxypropene (0.66 g.) and acetic anhydride (20 mls.) is heated to boiling and 2,6-lutidine (2 mls.) added. The mixture is heated under reflux for 3 minutes; it is allowed to cool and poured over ether (400 mls.). The dye is collected on a filter and washed with ether. The yield is 1.10 g. (45%). After recrystallization from acetonitrile, the dark crystals did not melt below 300° C.

(B) 2,2'-difluoro-4,4'-(benzo[e]-1,3,2-dioxaborino)-diborocyanine fluoride is prepared similarly. The yield after recrystallization from acetonitrile is 4%. The dark crystals melt at 151–152° C., with decomposition.

EXAMPLE 4

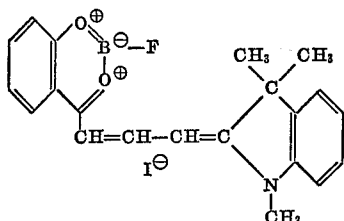
3'-ethyl-2-fluoro-4-(benzo[e]-1,3,2-dioxaborino)-2'-thiacyanine iodide



A mixture of 2-fluoro-4-methyl-benzo[e]-1,3,2-dioxaborinium fluoride (1.84 g.), 2-phenylthio-3-ethylbenzothiazolium iodide (3.99 g.) and acetic anhydride (15 mls.) is heated until solution is complete; 2,6-lutidine (1 ml.) is added. The mixture is heated under reflux for 3 minutes and allowed to cool and then poured over ether. The yield is 1.27 g. (26%). After recrystallization from acetonitrile, the reddish crystals melt at 253–254° C.

EXAMPLE 25

2-fluoro-1',3',3'-trimethyl-4-(benzo[e]-1,3,2-dioxaborino)-2'-indocarbocyanine iodide



A mixture of 2-fluoro-4-methyl-benzo[e]-1,3,2-dioxaborinium fluoride (0.82 g.), 2-β-acetanilidovinyl-1,2,3-trimethyl-3H-indolium iodide (2.23 g.) and acetic anhydride

(15 mls.) is heated until solution is complete; pyridine (2 mls.) is added and the mixture is heated under reflux for 3 minutes. The mixture is allowed to cool and then poured over ether (400 mls.). The ether is decanted and the dye washed with ether. After recrystallization from acetonitrile the yield of dye is 0.16 g. (3%). The dark crystals melt at 222–223° C. with decomposition.

In place of the 2-β-acetanilidovinyl-1,3,3-trimethyl-3H-indolium iodide in the above example, there is substituted an equivalent amount of any other of the intermediates coming under Formula VIII above to give the corresponding carbocyanine dyes. Typical dyes prepared in this manner include such as the following.

(A) 3'-ethyl-2-fluoro-4-naphtho[1,2-d]-1,3,2-dioxaborino-2'-oxacarbocyanine iodide

(B) 3'-ethyl-2-fluoro-4-naphtho[1,2-d]-1,3,2-dioxaborino-2'-thiacarbocyanine iodide

(C) 1'-ethyl-2-fluoro-4-naphtho[1,2-d]-1,3,2-dioxaborino-2'-carbocyanine iodide

TABLE 2

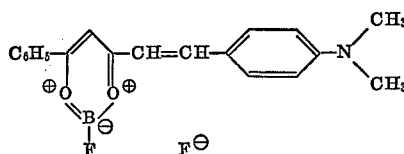
Compound	Percent yield	Melting point, ° C.
A-----	35	>300
B-----	13	210–212
C-----	15	224–226

¹ After recrystallization.

It will be apparent from the foregoing that the procedure of above Example 5 can also be advantageously used to prepare still other cyanine dyes of the invention embraced by Formula II above, for example, 3'-methyl-2-fluoro-4-(benzo[e]-1,3,2-dioxaborino) - 2' - selenacarbocyanine salt (e.g., the chloride, bromide, iodide, fluoride, perchlorate, p-toluenesulfonate, etc. salts) by replacing the 2 - β - acetanilidovinyl - 1,3,3-trimethyl-3H-indolium iodide with an equivalent amount of 2-β-acetanilidovinyl-1-methylbenzoselenazolium salt.

EXAMPLE 6

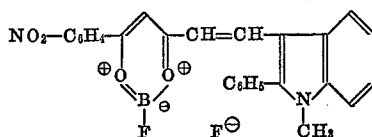
4-(4-dimethylaminostyryl)-2-fluoro-6-phenyl-1,3,2-dioxaborinium fluoride



A mixture of 2-fluoro-4-methyl-6-phenyl-1,3,2-dioxaborinium fluoride (1.05 g.), p-dimethylaminobenzaldehyde (0.80 g.) and acetic anhydride (10 ml.) is heated under reflux five minutes and allowed to cool; the dye is collected on a filter and washed with ether. The yield is 1.20 g. (70%). After recrystallization from acetonitrile, the crystals melt at 231–232° C.

EXAMPLE 7

2-fluoro-4-[2-(1-methyl-2-phenyl-3-indolyl)vinyl]-6-(4-nitrophenyl)-1,3,2-dioxaborinium fluoride

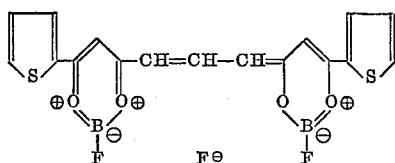


A mixture of 2-fluoro-4-methyl-6-(4-nitrophenyl)-1,3,2-dioxaborinium fluoride (1.04 g.), 1-methyl-2-phenyl-3-indolcarboxaldehyde (0.80 g.) and acetic anhydride (10 ml.) is heated under reflux for five minutes and allowed to cool; the dye is collected on a filter and washed with ether. The yield of dye is 1.10 g. (57%). After recrystallization from acetonitrile, the crystals melt at 266–268° C.

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EXAMPLE 8

2,2'-difluoro-6,6'-di-(2-thienyl)-4,4'-(1,3,2-dioxaborino)-carbocyanine fluoride

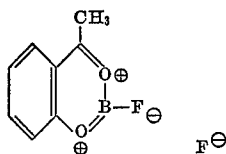


A mixture of 2-fluoro-4-methyl-6-(2-thienyl)-1,3,2-dioxaborinium fluoride (2.16 g.), diethoxymethylacetate (0.81 g.) and butyrolactone (10 ml.) is heated to boiling and 2,6-lutidine (1 ml.) added. The mixture is heated under reflux for three minutes; it is allowed to cool, filtered and washed with ether. The yield of dye is 0.82 g. (31%). After recrystallization from acetonitrile the crystals melt at 197–199° C.

To prepare the novel 1,3,2-dioxa(or oxaza or diaza) borinium salt intermediates of the invention defined by Formula VI above, a number of variations in method are required. These are illustrated by the following examples.

EXAMPLE 9

2-fluoro-4-methyl-benzo[e]-1,3,2-dioxaborinium fluoride



2-hydroxyacetophenone (6.8 g.) is slowly added to chilled, stirred boron trifluoride ethyl ether complex (20 mls.). The product, which precipitates immediately, is collected on the filter and washed with ether. The yield is 5.6 g. (62%). The yellow crystals melt at 146–147° C., with decomposition.

By replacing the 2-hydroxyacetophenone in the above example with other appropriate hydroxy substituted aryl-methylketones, a 1,3-diketone, the following other intermediates are prepared.

(A) 2 - fluoro - 4 - methyl - 6 - phenyl-1,3,2-dioxaborinium fluoride

(B) 2 - fluoro - benzo[e]-1,3,2-dioxaborinium fluoride

(C) 2-fluoro-naphtho[1,2-d]-1,3,2-dioxaborinium fluoride

(D) 2 - fluoro - 7,8 - dihydroxy - 4 - methylbenzo[e]-1,3,2-dioxaborinium fluoride

(E) 2 - fluoro - 4 - methyl-naphtho[1,2-d]-1,3,2-dioxaborinium fluoride

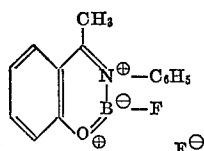
TABLE 3

Compound	Percent yield	Melting point, ° C.
A-----	72	156-157
B-----	60	-----
C-----	82	-----
D-----	93	> 140
E-----	96	240-241

¹ Decomposition.

EXAMPLE 10

2-fluoro-4-methyl-3-phenyl-benzo[e]-1,3,2-oxazaborinium fluoride



To a suspension of 2-fluoro-4-methyl-benzo[e]-1,3,2-dioxaborinium fluoride (18.4 g.) in benzene (150 mls.)

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aniline (18.6 g.) is added and the mixture is heated under reflux with a water take-off for two hours. The mixture is allowed to cool when the product separates as a white solid. It is collected on the filter and washed with ether. The yield is 22.5 g. (81%). After recrystallization from acetonitrile, the white crystals melt at 175–176° C., with decomposition.

In place of the 2-fluoro-4-methyl-1,3,2-benzodioxaborinium fluoride in the above example, there is substituted other appropriate borinium salts to give the following typical compounds.

(A) 2 - fluoro - 4 - methyl - 3,6-diphenyl-1,3,2-benzoxazaborinium fluoride

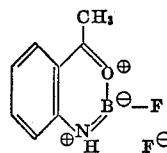
(B) 2 - fluoro - 4 - methyl - 3 - phenyl-naphtho[1,2-d]-1,3,2-oxazaborinium fluoride

TABLE 4

Compound	Percent yield	Melting point, ° C.
A-----	72	198-199
B-----	78	268-269

EXAMPLE 11

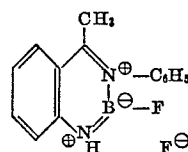
2-fluoro-4-methyl-benzo[d]-1,3,2-oxazaborinium fluoride



2-aminoacetophenone (4.5 g.) is slowly added to chilled, stirred boron trifluoride ethyl ether complex (25 mls.). The mixture is stirred at room temperature for 15 minutes. The yellow product is collected on a filter and washed with ether. The yield is 5.9 g. (97%). The pale yellow crystals melt at 161–165° C., with decomposition.

EXAMPLE 12

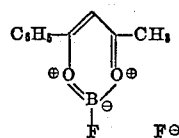
2-fluoro-4-methyl-1-phenyl-benzo[e]-1,3,2-diazaborinium fluoride



To a suspension of 2-fluoro-3-hydro-4-methyl-benzo[d]-1,3,2-oxazaborinium fluoride (3.7 g.) in benzene (100 mls.) aniline (4.0 g.) is added and the mixture is heated under reflux for two hours with a water take-off. The mixture is allowed to cool and the product collected on the filter and washed with ligroin. The yield is 3.1 g. (61%). The pale yellow crystals melt at a temperature over 300° C. with decomposition.

EXAMPLE 13

2-fluoro-4-methyl-6-phenyl-1,3,2-dioxaborinium fluoride

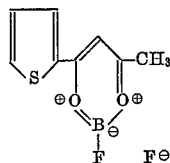


To a solution of benzoylacetone (32.4 g.) in ether (150 ml.), there is added boron trifluoride ethyl ether complex (150 ml.). The mixture is stirred for one hour. The precipitated compound is then filtered off and washed with ether. The yield is 30 g. (72%), M.P. 156–157° C.

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EXAMPLE 14

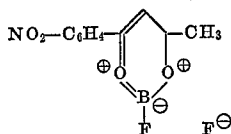
2-fluoro-4-methyl-6-(2-thienyl)-1,3,2-dioxaborinium fluoride



A mixture of 2-thienylmethylketone (42 g.), borontrifluoride ethyl ether complex (110 ml.) and acetic anhydride (107 g.) is stirred for 15 minutes and then warmed at 55° C. for 30 minutes. The mixture is suspended in water and stirred two hours at room temperature, filtered and the collected product washed. The yield is 17 g. (24%). The grayish powder melts at 170–172° C.

EXAMPLE 15

2-fluoro-4-methyl-6-(4-nitrophenyl)-1,3,2-dioxaborinium fluoride



The procedure of above Example 14 is repeated, except that the 2-thienylmethylketone is replaced with p-nitroacetophenone (55 g.). The yield of compound is 20 g. (24%), M.P. 188–189° C.

The dyes of the invention prepared in accordance with the preceding examples markedly increase the speed of organic photoconductors when added thereto. This increase in speed is due to the spectral sensitivity imparted to the photoconductor by the dyes described herein. The evaluations set forth in Table 5 below show greatly increased speeds with maximum sensitivity peaks ("Abs. max.") extending to radiations in the region of the spectrum of from about 500 to 600 nm. The method of evaluation is as follows:

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) and 0.0065 g. of the spectral sensitizing dye indicated by identifying number from above Table A. 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 image-wise 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) pages 469–484, can be used with similar results.) An image is formed on each sample, as indicated in Table 5. Another sample of each coating is tested to determine its electrical speed and

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maximum sensitivity peak. This is accomplished by giving each element a positive or negative charge (as indicated in Table 5) 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 1 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 5 below.

TABLE 5

Dye of Ex. No.	Image formed	Shoulder speeds		Sensitivity (absolute maximum) nm.
		Positively charged surface	Negatively charged surface	
Control (no dye)	Yes	8	7	
1	Yes	280	200	565
2A	Yes	25	5	545

Referring to the above Table 5, it will be seen that the control example containing the same 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 dye of Example 1 are 280 and 200 for the positively and negatively charged surfaces, respectively, with maximum sensitivity peak at 565 nm., thus indicating a speed increase over that of the control by a factor of about 35 for the positively charged and about 25 for the negatively charged surfaces. Also of great significance is the extension of the absolute sensitivity up to about the orange region of the spectrum. Even with the least speed shown for the compositions and elements of the invention as illustrated by Example 2A improvement in speed is impressive in comparison with that of the control by a factor of about 3 for the positive charged surface with maximum sensitivity at 545 nm.

Similar results to those shown in above Table 5 are obtained, when, for example, the organic photoconductor 4,4'-bis(diethylamino) - 2,2' - dimethyltriphenylmethane is replaced with 0.15 g. of triphenylamine, or 1,3,5-triphenyl-2-pyrazoline, 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 following:

TABLE C

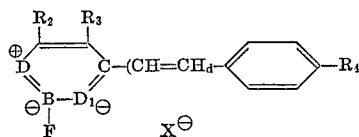
Dye Identification	Name
A.....	Pinacyanol.
B.....	Kryptocyanine.
C.....	Anhydro-3-ethyl-9-methyl-3'-(3-sulfo-4-butyl)-thiacarbocyanine hydroxide.
D.....	3,3'-diethyl-9-methylthiacarbocyanine bromide.
E.....	3-carboxymethyl-5-[3-methyl-2-thiazolidinylidene]-1-methylethylidene]rhodanine.
F.....	Anhydro-5,5'-dichloro-3,9-diethyl-3'-(3-sulfo-4-butyl)-thiacarbocyanine 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 styryl dye represented by the following formula:



wherein d represents a positive integer of from 1 to 2; R_2 represents a member selected from the class consisting of an aryl of 6-10 carbon atoms group, a 2-thienyl group and, taken together with R_3 , the atoms required to complete a benzo or naphtho group; R_3 taken alone represents a hydrogen atom; R_4 represents a member selected from the group consisting of a dialkylamino group, an alkoxy group, a styryl group, and a nitro group; X represents an acid anion; and D and D_1 each represents a member selected from the group consisting of an oxygen atom and an imino group, D_1 being an imido group when D is an imino group.

2. 4-(4-dimethylaminostyryl)-2-fluoro-benzo[e]-1,3,2-dioxaborinium fluoride.

3. A methine dye selected from the group consisting of 2-fluoro-4-(4-methoxystyryl)-benzo[e]-1,3,2-dioxaborinium fluoride;

2-fluoro-4-(4-nitrostyryl)-benzo[e]-1,3,2-dioxaborinium fluoride;

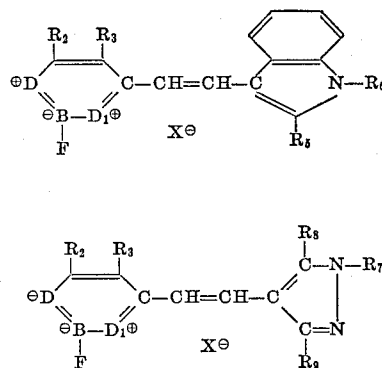
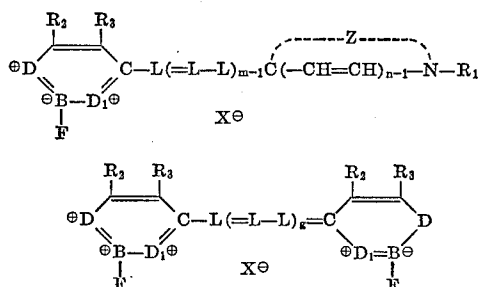
2-fluoro-4-[2-(1-methyl-2-phenyl-3-indolyl)-vinyl]-benzo[e]-1,3,2-dioxaborinium fluoride;

4-[2-(3,5-dimethyl-1-phenyl-4-pyrazolyl)-vinyl]-2-fluorobenzo[e]-1,3,2-dioxaborinium fluoride;

4-fluoro-4-(4-styryl-styryl)-benzo[e]-1,3,2-dioxaborinium fluoride and

4-(4-dimethylaminostyryl)-2-fluoro-naphtho[1,2-d]-1,3,2-dioxaborinium fluoride.

4. A methine dye represented by one of the following formulas:



wherein d , g , m and n each represents a positive integer of from 1 to 2; L represents a methine linkage; R_1 and R_6 each represents an alkyl group of 1-4 carbon atoms; R_2 represents a member selected from the class consisting of an aryl group of 6-10 carbon atoms, a 2-thienyl group and, taken together with R_3 , the atoms required to complete a benzo or naphtho group; R_3 when taken alone represents a hydrogen atom; R_5 represents an aryl group of 6-10 carbon atoms; R_7 represents an aryl group of 6-10 carbon atoms; R_8 and R_9 each represents an alkyl group of 1-4 carbon atoms; X represents an acid anion; D and D_1 each represents a member selected from the group consisting of an oxygen atom and an imino group, D_1 being an imino group when D is an imino group; and Z represents the non-metallic atoms necessary to complete a nitrogen containing heterocyclic nucleus selected from the group consisting of a thiazole nucleus, an oxazole nucleus, a selenazole nucleus, a thiazoline nucleus, a pyridine nucleus, a quinoline nucleus, a 3,3-dialkylindolenine nucleus, an imidazole nucleus, an imidazo[4,5-b]quinoxaline nucleus, a 3,3-dialkyl-3H-pyrrolo[2,3-b]pyridine nucleus and a thiazolo[4,5-b]quinoline nucleus.

5. A methine dye selected from the group consisting of 2,2'-difluoro-4,4'-(benzo[e]-1,3,2-dioxaborino)-carbocyanine fluoride;

2,2'-difluoro-4,4'-naphtho[1,2-d]1,3,2-dioxaborinodiborocyanine fluoride;

3'-ethyl-2-fluoro-4-(benzo[e]-1,3,2-dioxaborino)-2'-thiacyanine iodide;

2-fluoro-1',3',3'-trimethyl-4-(benzo[e]-1,3,2-dioxaborino)-2'-indocarbocyanine iodide;

2-fluoro-4-[2-(1-methyl-2-phenyl-3-indolyl)vinyl]-6-(4-nitrophenyl)-1,3,2-dioxaborinium fluoride;

2,2'-difluoro-6,6'-di-(2-thienyl)-4,4'-(1,3,2-dioxaborino)-carbocyanine fluoride and

2-fluoro-4-methylbenzo[e]-1,3,2-dioxaborinium fluoride.

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U.S. Cl. X.R.

96-1.6, 1.7, 129, 131, 132, 134; 260-240 E, 240 R, 240.5, 240.65, 240.9, 551 B