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3,796,573

SENSITIZERS FOR N-TYPE ORGANIC PHOTOCONDUCTORS

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9 Claims

ABSTRACT OF THE DISCLOSURE

Photoconductive compositions are prepared from n-type photoconductors, electron donating sensitizing dyes and polymeric binders. The electron donating sensitizing dyes (1) have a cathodic polarographic half-wave potential more negative than -1.0 volt; (2) have an anodic polarographic half-wave potential and a cathodic half-wave polarographic potential which added together, give a sum more negative than 0.00 volt; and (3) do not desensitize negative silver bromide emulsions, containing 99.35 mole percent bromide, more than $0.4 \log E$ at radiation of 365 nm. when incorporated therein at a concentration of 0.2 millimole of dye per mole of silver halide. The photoconductive compositions exhibit excellent spectral response and high speed characteristics.

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

The process of electrophotography, as disclosed by Carlson in U.S. Pat. 2,297,691, employs an electrophotographic element comprising a support material bearing a coating of an insulating material, the electrical resistance of which varies with the amount of incident actinic radiation it receives during an imagewise exposure. The element, commonly termed a photoconductive element, is first given a uniform surface charge after a suitable period of dark adaptation. The element is then exposed to a pattern of actinic radiation which has the effect of differentially reducing the potential of the surface charge in accordance with the relative energy contained in various parts of the radiation pattern. The differential surface charge or electrostatic latent image remaining on the electrophotographic element is then made visible by contacting the surface with a suitable electroscopic marking material. Such marking material or toner, whether contained in an insulating liquid or on a dry carrier, can be deposited on the exposed surface in accordance with the charge pattern. The deposited marking material can then be permanently fixed to the surface of the sensitive element by known means such as heat, pressure, solvent vapor and the like or it can be transferred to a second element to which it can be similarly fixed. Likewise, the electrostatic latent image can be transferred to a second element and developed there.

Various photoconductive insulating materials have been employed in the manufacture of electrophotographic elements. For example, vapors of selenium or vapors of selenium alloys deposited on a suitable support and particles of photoconductive zinc oxide held in a resinous film-forming binder have found wide application in present-day copying applications.

Since the introduction of electrophotography, a great many organic compounds have been found to possess some degree of photoconductivity. Many organic compounds such as the n-type photoconductor 2,4,7-trinitro-9-fluorenone have revealed a useful level of photoconductivity and have been incorporated into photoconductive compositions. Translucent organic photoconductor-containing elements can be especially useful in electrophotography. Such electrophotographic elements may be

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exposed through a transparent base, if desired, thereby providing unusual flexibility in equipment design. Such compositions, when coated as a film or layer on a suitable support, also yield an element which is reusable; that is, it can be used to form subsequent images after residual toner from prior images has been removed by transfer and/or cleaning.

Although many organic photoconductor materials are inherently light sensitive, their degree of sensitivity is usually low so that it is often necessary to add materials to increase their speed. Increasing the electrophotographic speed has several advantages in that it reduces exposure time, allows projection printing through various optical systems, etc. By increasing the speed through the use of sensitizing dyes, photoconductors which would otherwise have been unsatisfactory are useful in processes where higher speeds are required. However, a major disadvantage of many prior sensitized organic photoconductor systems has been the highly colored nature of such systems.

Accordingly, it is an object of this invention to provide novel n-type photoconductive compositions which have good spectral response.

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

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

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

A further object of this invention is to provide methods for spectrally sensitizing n-type 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 n-type organic photoconductors spectrally sensitized with the dyes defined more fully below. These compositions can be incorporated in a suitable binder and then coated on a conductive support for use in electrophotography.

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

The spectral sensitizing electron donating dyes which are employed in this invention are the cyanine, rhodacyanine, merocyanine, styryl, and hemioxonol dyes which, 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, do not 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 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 bromiodide emulsions are prepared as follows:

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

(A)

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

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

(B)

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

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 noted above, the dyes employed in this invention do not desensitize conventional negative silver halide emulsions but act to provide practical spectral sensitization for such silver halide emulsions. Such dyes cause severe speed losses in p-type photoconductive systems. Therefore, it was quite unexpected to find that they spectrally sensitized n-type organic photoconductor elements.

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

The dyes of this invention increase the speed of n-type organic photoconductors by extending or increasing the response of the photoconductor to longer wavelengths. In the concentrations used of 1 to 75 parts by weight photoconductor, .01 to 10 parts by weight dye and 60 to 90 parts by weight binder, the dyes herein appear to function as spectral sensitizers when employed with efficient n-type organic photoconductors. When the n-type organic photoconductor used is poor or inefficient, the dyes seem to function as speed increasing compounds as well as spectral sensitizers.

The dyes useful herein are further distinguished by having a cathodic polarographic half-wave potential more negative than -1.0 volt, and an anodic polarographic half-wave potential and a cathodic half-wave polarographic potential which, when added together algebraically, produce a value more negative than 0.00 volt.

As used herein and in the appended claims, polaro-

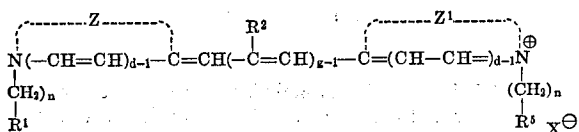
graphic measurements are made in accordance with the following procedure. Cathodic polarographic half-wave values are obtained against an aqueous silver-silver chloride reference electrode for the electrochemical reduction of the test dye using controlled-potential polarographic techniques. A 1×10^{-4} M methanol solution of the test dye is prepared. The solvent is 100% methanol, if the dye is soluble therein. In some instances, it is necessary to use mixtures of methanol and another solvent, e.g., acetone, to prepare the 1×10^{-4} M solution of dye. There is present in the test solution, as supporting electrolyte, 0.1 M lithium chloride. Only the most positive (least negative) half-wave potential value observed is considered, and it is designated herein as E_c . Voltametric electropositive (anodic) half-wave values are determined against an aqueous silver-silver chloride reference electrode for the electrochemical oxidation of the dyes at a pyrolytic graphite electrode, and are obtained by controlled-potential voltametry using solutions identical to those used to determine the cathodic polarographic values. Only the most negative (least positive) half-wave potential observed is utilized, and it is designated herein as E_a . In both measurements, the reference electrode (aqueous silver-silver chloride) is maintained at 20° C. Signs are given according to the recommendation of IUPAC at the Stockholm Convention, 1953. The well-known general principles of polarographic measurements are used. See Kolthoff and Lingane, "Polarography," 2nd ed. Interscience Publishers, New York (1952). The principles of controlled-potential electrochemical instrumentation which allows precise measurements in solvents of low conductivity is described by Kelly, Jones and Fisher, *Anal. Chem.*, 31, 1475 (1959). The theory of potential sweep voltametry such as that employed in obtaining the anodic determinations is described by Delahay, "New Instrumental Methods in Electrochemistry," Interscience Publishers, New York (1954) and Nicholson and Shain, *Anal. Chem.*, 36, 706 (1964). Information concerning the utility and characteristics of the pyrolytic graphite electrode is described by Chuang, Fried and Elving, *Anal. Chem.*, 36 (1964). It should be noted that the spectral sensitizing dyes operable in this invention include those dyes which contain oxidizable ions, such as iodide. For example, many dyes which are iodide salts are useful herein. However, the polarographic measurements referred to above cannot be determined in the presence of oxidizable ions. Therefore, such dyes are converted, just for purposes of making polarographic determinations, to an anion such as chloride or p-toluenesulfonate, which do not interfere in making accurate polarographic measurements. Hence, dyes containing oxidizable ions are included within the scope of the useful dyes defined herein and in the appended claims.

As noted above, this invention is applicable to the spectral sensitization of n-type organic photoconductors with certain dyes. The term "cyanine dye," as used herein, is to be construed broadly as inclusive of simple cyanines, carbocyanines, dicarbocyanines, tricarbo-cyanines, merocyanines, rhodacyanines, styryl, etc. The term includes symmetrical and unsymmetrical cyanine dyes, as well as dyes substituted in the polymethine chain.

The cyanine dyes which can be used according to this invention include dyestuffs having an amidinium-ion system such as cyanine dyes including simple cyanine, carbocyanine, dicarbocyanine, etc., cyanine dyes wherein the prefix defines the length of the conjugated polymethine carbon bridge, as well as holopolar cyanines, hemicyanines, trinuclear cyanines, p-dialkylaminostyryl dyes and the like dye classes. Also included herein as defined by the term polymethine dyes are nonionized, undissociated dyes containing the amidic system such as merocyanine dyes. Dyes of each of these two systems are conveniently designated herein as polymethine dyes since they exhibit a common characteristic, that being the presence of at least one nitrogen-containing heterocyclic nucleus which is

joined to a conjugated polymethine carbon chain or linkage by a carbon atom of the heterocyclic nucleus.

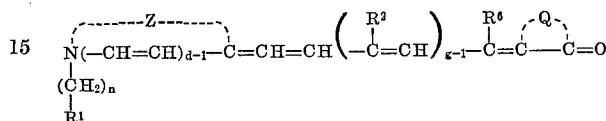
Exemplary polymethine dyes include dyes such as those having the following formula:



wherein each of Z and Z¹ represent the nonmetallic atoms necessary to complete a heterocyclic nucleus of the type used in cyanine dyes, and more particularly a heterocyclic ring of from 5 to 6 atoms including a nitrogen atom and from 4 to 5 additional atoms of which from 3 to 4 atoms are carbon atoms and wherein the remaining additional atom is selected from either carbon, nitrogen, oxygen, sulfur or selenium atoms. The nitrogen atom is desirably substituted as described herein. Exemplary heterocyclic nuclei completed by nonmetallic Z and Z¹ atoms include those nuclei of the indole series such as indolenine; those of the benzindole series like benz(e) indole and those of the naphthindole series such as naph(e) indole; those of the imidazole series such as benzimidazole compounds like 5-chlorobenzimidazole and also including compounds of the naphthimidazole series; those of the thiazole series like thiazole, 4-methylthiazole, 4-phenylthiazole, 5-methylthiazole, 5-phenylthiazole, 4,5-dimethylthiazole, 4,5-diphenylthiazole, 4-(2-thienyl)thiazole, etc.; those of the benzothiazole series such as benzothiazole, 4-chlorobenzothiazole, 5-chlorobenzothiazole, 6-chlorobenzothiazole, 7-chlorobenzothiazole, 4-methylbenzothiazole, 5-methylbenzothiazole, 6-methylbenzothiazole, 5-bromobenzothiazole, 6-bromobenzothiazole, 4-phenylbenzothiazole, 5-phenylbenzothiazole, 4-methoxybenzothiazole, 5-methoxybenzothiazole, 6-methoxybenzothiazole, 5-iodobenzothiazole, 6-iodobenzothiazole, 4-ethoxybenzothiazole, 5-ethoxybenzothiazole, tetrahydrobenzothiazole, 5,6-dimethoxybenzothiazole, 5,6-dioxybenzothiazole, 5-hydroxybenzothiazole, 6-hydroxybenzothiazole, etc.; those of the naphthothiazole series like naphtho[2,1-d]thiazole, 8-methoxynaphtho[2,1-d]thiazole, 7-methoxynaphtho[2,1-d]thiazole, etc.; those of the thionaphtho-7',6',4,5-thiazole series such as 4-methoxythionaphtho-7',6',4,5-thiazole, etc.; those of the oxazole series for example, 4-methyloxazole, 5-methyloxazole, 4-phenyloxazole, 4,5-diphenyloxazole, 4-ethyloxazole, 4,5-dimethyloxazole, 5-phenyloxazole, etc.; those of the benzoxazole series like benzoxazole, 5-chlorobenzoxazole, 5-methylbenzoxazole, 5-ethoxybenzoxazole, 5-chlorobenzoxazole, 6-methoxybenzoxazole, 5-hydroxybenzoxazole, 6-hydroxybenzoxazole, etc.; those of the naphthoxazole series such as naphtho[2,1-d]oxazole, etc.; those of the selenazole series, for example, 4-methylselenazole, 4-phenylselenazole, etc.; those of the benzoselenazole series like benzoselenazole, 5-chlorobenzoselenazole, 5-methoxybenzoselenazole, 5-hydroxybenzoselenazole, tetrahydrobenzoselenazole, etc.; those of the naphthoselenazole series such as naphtho[2,1-d]selenazole; and those of the quinoline series such as quinoline, 4-methylquinoline, 5-ethylquinoline, 6-chloroquinoline, 8-chloroquinoline, 6-methoxyquinoline, 8-hydroxyquinoline, 7-methyl-4-quinoline, isoquinoline, etc. The organic substituent represented by each of R¹ and R⁵ is selected from either (1) a hydrogen atom, (2) a hydroxyl radical, (3) a carboxyl radical, (4) a cyano radical, (5) an acyl radical, (6) an acyloxy radical, (7) an alkoxy radical, (8) a sulfo radical, (9) a 1-hydroxy-1-sulfoalkyl radical, (10) an aryl radical; each of R², R³ and R⁴ represents either a hydrogen atom, an alkyl radical or an aryl radical, and preferably methyl, ethyl or phenyl, X[⊖] represents an anion including a wide variety of such anions as halide anions like bromide, chloride and iodide, as well as additional anions, e.g., sulfates including sul-

fate, hydrosulfate and lower alkylsulfates like methylsulfate, ethylsulfate, aromatic sulfonates such as p-toluenesulfonate and benzenesulfonate, acid anions derived from carboxylic acids like acetate, trifluoroacetate, propionate and a wide variety of other anions including anions such as, for example, perchlorate, cyanate, thiocyanate, sulfamate, benzoate, etc.; d represents a positive integer having a value of from 1 to 2; n represents an integer having a value from 1 to 4; g represents a positive integer having a value of from 1 to 3.

Other polymethine dyes of the described types include merocyanine dyes such as those having the formulas:



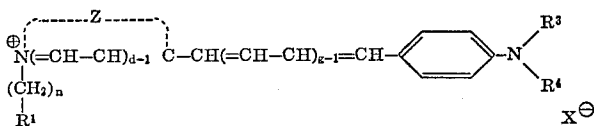
wherein g, n, d, Z, R¹, and R² are as defined above; Q represents the nonmetallic atoms necessary to complete a heterocyclic nucleus containing from 5 to 6 atoms in the heterocyclic ring, 3 to 4 being carbon and two of said atoms being selected from nitrogen, oxygen or sulfur with at least one of said two atoms being nitrogen; R⁶ represents a member selected from either a hydrogen atom, an alkyl radical or an aryl radical.

In the merocyanine dyes described herein, advantageous heterocyclic nuclei completed by the nonmetallic atoms represented herein by Q include those of the thiazolone series, for example 2-thiazolin-4-one; those of the 2,4-thiazolidinedione series such as 2,4-thiazolidinedione, 3-alkyl-2,4-thiazolidinediones (e.g., 3-ethyl-2,4-thiazolidinedione, etc.) 3-phenyl-2,4-thiazolidinedione, 3-α-naphthyl-2,4-thiazolidinedione, etc.; those of the 2-thio-2,4-thiazolidinedione (rhodanine) series, such as 3-alkyl-2-thio-2,4-thiazolidinedione (3-alkylrhodanines), (e.g., 3-ethyl-2-thio-2,4-thiazolidinedione (or 3-ethylrhodanine), 3-phenyl-2-thio-2,4-thiazolidinedione (3-phenylrhodanine), 3-α-naphthyl-2-thio-2,4-thiazolidinedione (3-α-naphthylrhodanine), 3-(1-benzothiazyl)-2-thio-2,4-thiazolidinedione (3-(1-benzothiazyl)rhodanine, etc., those of the 2-thio-2,5-thiazolidione series, such as 3-alkyl (e.g., 3-methyl, 3-ethyl, etc.)-2-thio-2,5-thiazolidinediones, etc., those of the 2-alkylmercapto-2-thiazolin-4-one series, such as 2-ethylmercapto-2-thiazolin-4-one, etc., those of the thiazolidinone series, such as 4-thiazolidinone or its 3-alkyl (e.g., ethyl etc.), 3-phenyl or 3-α-naphthyl derivatives, those of the 2-alkylphenylamino-2-thiazolin-4-one series (e.g., 2-ethylphenylamino-2-thiazolin-4-one, etc.), those of the 2-diphenylamino-2-thiazolin-4-one series, those of the 2-thiazolin-5-one series, such as 2-ethylthio-2-thiazolin-5-one, 2-benzylthio-2-thiazolin-5-one, etc., those of the oxazolone series, for example; those of the 2-thio-2,4-oxazolidinedione series, such as 3-alkyl-2-thio-2,4-oxazolidinediones (e.g., 3-ethyl-2-thio-2,4-oxazolidinedione, etc.), those of the 2-amino-4-oxazolidinone (pseudohydantoin) series, etc., those of the 2-oxazolin-5-one series, such as 2-phenyl-2-oxazolin-5-one, 2-ethyl-2-oxazolin-5-one, etc., those of the 2-isoxazolin-5-one series, such as 3-phenyl-2-isoxazolin-5-one, etc., those of the imidazolone series, for example; those of the hydantoin series, such as hydantoin, or its 3-alkyl (e.g., ethyl, propyl, etc.), 3-phenyl or 3-α-naphthyl derivatives as well as its 1,3-dialkyl (e.g., 1,3-diethyl, etc.), 1-alkyl-3-phenyl (e.g., 1-ethyl-3-phenyl, etc.), 1-alkyl-3-naphthyl (e.g., 1-ethyl-3-α-naphthyl, etc.), 1,3-diphenyl, etc. derivatives, those of the 2-thiohydantoin series, such as 2-α-thiohydantoin, or its 3-alkyl (e.g., 3-ethyl, etc.), 3-phenyl or 3-α-naphthyl derivatives as well as its 1,3-dialkyl (e.g., 1,3-diethyl, etc.), 1-alkyl-3-phenyl (e.g., 1-ethyl-3-phenyl, etc.), 1-alkyl-3-naphthyl (e.g., 1-ethyl-3-α-naphthyl), 1,3-diphenyl, etc. derivatives, those of the 2-alkylmercapto-2-imidazolin-5-one series, such as 2-n-propylmercapto-2-imidazolin-5-one; those of the thionaphthenone series, such as 2-(3H)benzothiophenone or

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3-(2H)benzothiophenone; those of the pyrazolone series, such as 2-pyrazolin-5-one or its 1-alkyl (e.g., methyl, ethyl, etc.), 1-phenyl, 1-naphthyl (e.g., 1- α -naphthyl), 3-alkyl (e.g., methyl, ethyl, etc.), 3-phenyl, 3-naphthyl (3- α -naphthyl) 1-alkyl-3-phenyl (e.g., 1-methyl-3-phenyl, etc.), 3-alkyl-1-phenyl (e.g., 3-methyl-1-phenyl, etc.), 1, 3-dialkyl (e.g., 1,3-diphenyl, etc.), 1,3-diphenyl etc. derivatives; those of the oxindole series such as 3-(2H)indolinone and like five-membered heterocyclic nuclei; those of the 2,4,5-triketohexahydropyrimidine series, for example, barbituric acid (2,4,6-triketohexahydropyrimidine), 2-thiobarbituric acid (2-thio-2,4,6-triketohexahydropyrimidine) as well as their 1-alkyl (e.g., 1-ethyl, etc.), of 1,3-dialkyl(1,3-diethyl, etc.) derivatives.

Other advantageous polymethine dyes of the types described herein include styryl dyes such as those having the formula:

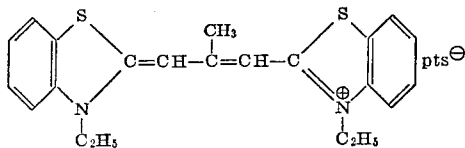


wherein Z, $\text{X}^{\ominus}$, n , R^1 , R^3 and R^4 are as defined above, and g represents an integer of from 1 to 2. Especially advantageous styryl dyes include those wherein n is 2, wherein the heterocyclic nuclei completed by the atoms represented by Z is either an indole nucleus, an imidazole nucleus, an oxazole nucleus, a thiazole nucleus, a selenazole nucleus or a quinoline nucleus such as those described hereinabove.

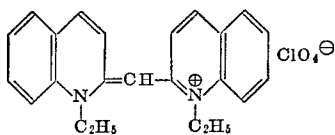
Exemplary electron donating dyes which can be used according to this invention are listed in the following table.

TABLE I

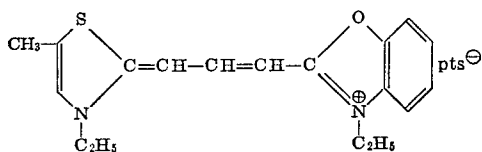
Dye A: 3,3'-diethyl-9-methylthiacarbocyanine paratoluenesulfonate



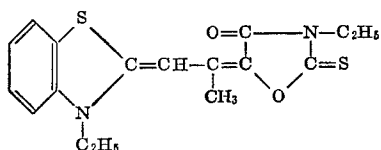
Dye B: 1,1'-diethyl-2,2'-cyanine perchlorate



Dye C: 3,3'-diethyl-4'-methyloxathiazolocarbo-cyanine paratoluenesulfonate

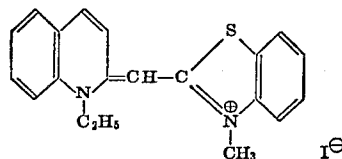


Dye D: 3-ethyl-5-[(3-ethyl-2-benzothiazolinyldene)-1-methylethyldene]-2-thio-2,4-oxazolidinedione

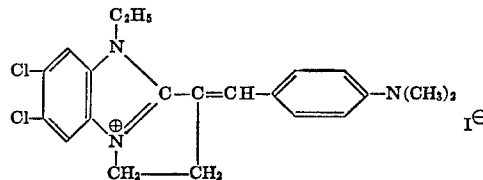


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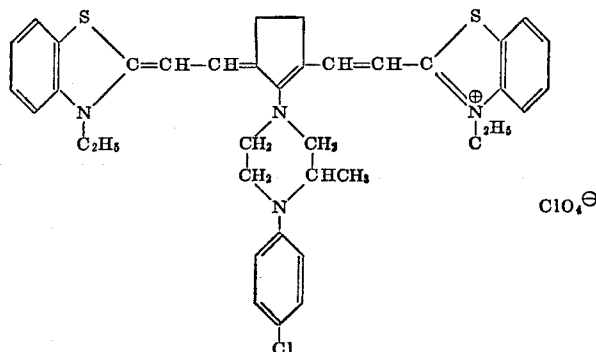
Dye E: 3-methyl-1'-ethylthia-2'-cyanine iodide



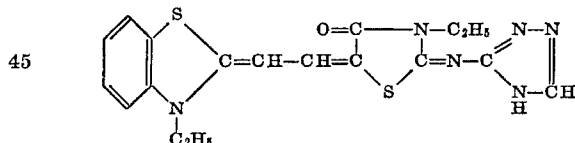
Dye F: 6,7-dichloro-3-p-dimethylaminobenzylidene-4-ethyl-2,3-dihydro-1H-pyrrolo[1,2-a]benzimidazolium iodide



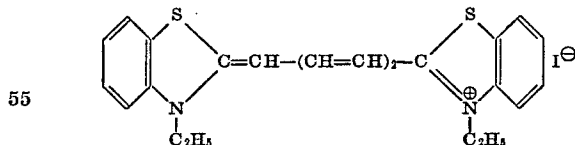
Dye G: 11-[4-(4-chlorophenyl)-3-methyl-1-piperazinyl]-3,3'-diethyl-10,12-ethylenethiatricarbocyanine perchlorate



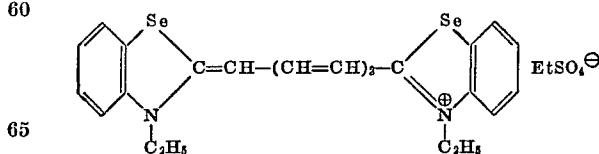
Dye H: 3-ethyl-5-[(3-ethyl-2-benzothiazolinyldene) ethylidene-2-(1,2,4-triazol-3-yl)imino-4-thiazolidinone]



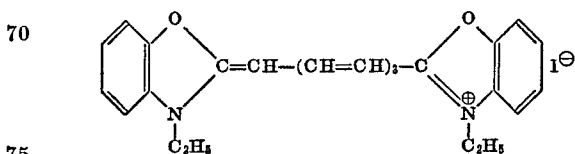
Dye I: 3,3'-diethylthiadicarbo-cyanine iodide



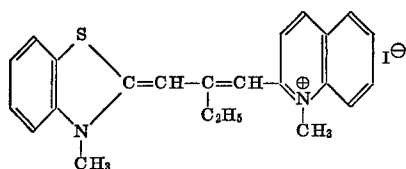
Dye J: 3,3'-diethylselenadicarbo-cyanine ethylsulfate



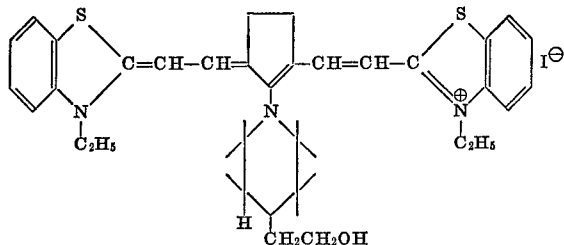
Dye K: 3,3'-diethyloxatricarbocyanine iodide



Dye L: 9-ethyl-1,3'-dimethylthia-2'-carbocyanine iodide



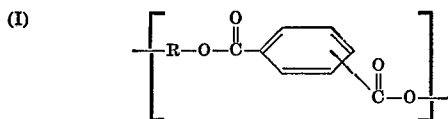
Dye M: 3,3'-diethyl-10,12-ethylene-11-[4-(2-hydroxy-ethyl)piperidino]thiatricarbocyanine iodide



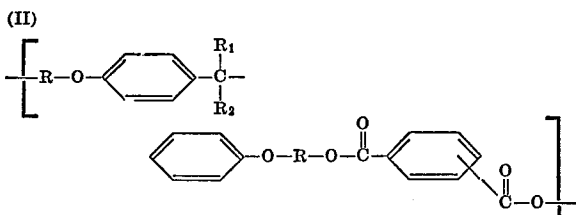
The n-type organic photoconductors which can be sensitized in accordance with this invention include the photoconductors such as described by Hoegl, The Journal of Physical Chemistry, vol. 69, No. 3, March 1965, e.g. 2,4,7-trinitro - 9 - fluorenone, 1,5 - dinitronaphthalene, 2,4,5,7-tetranitro - 9 - fluorenone, phthalic anhydride, p-chloranil, benzil, 9,10 - dibromoanthracene, 9 - acetylanthracene, pyrene - 3 - aldehyde, 1,2 - benzantraquinone, 1,8-dinitronaphthalene, 1,4,5-trinitronaphthalene, 1,5-dichloronaphthalene and 1,4-dibromonaphthalene.

The organic photoconductor and sensitizing dye may be dispersed in a polymeric binder. Particularly useful classes of polymeric binders are the polyester, polycarbonate and polystyrene resins.

Suitable polyester resin binders include those containing the following recurring units:



and



wherein R represents an alkylene radical of from 2 to 4 carbon atoms such as ethylene, propylene, and butylene and each of R₁ and R₂ can represent an alkyl radical having from 1 to 6 carbon atoms or when taken together with the carbon atom to which they are attached, can represent the carbon atoms necessary to complete a cycloalkylene radical having up to 12 carbon atoms and including polycycloalkylene radicals. Particularly useful polyester resins include poly(ethylene alkaryloxyalkylene terephthalate) and poly(ethylene alkaryloxyalkylene isophthalate) resins, with poly(4,4' - isopropylidenebisphenoxyethyl - co - ethylene terephthalate) being especially useful.

The polyester resin is mixed with a suitable n-type photoconductor such as 2,4,7-trinitro-9-fluorenone in the presence of a sensitizing dye and a solvent such as methylene chloride. The materials are thoroughly stirred and the resultant coating dope is coated onto a support and dried. Coating thicknesses of the photoconductive composition on a support can vary widely. In general, a coating in the range of about 2.5μ to about 500μ before drying is useful for the practice of this invention. The preferred range of

coating thickness is found to be in the range from about 10μ to about 300 μ before drying, although useful results can be obtained outside of this range.

Suitable supporting materials for coating the photoconductive layers of the present invention can include any of a wide variety of electrically conducting supports, for example, paper (at a relative humidity above 20 percent), aluminum foil-paper laminates; metal foils such as aluminum foil, zinc foil, etc.; metal plates, such as aluminum, copper, zinc, brass and galvanized plates; vapor deposited metal layers such as silver, nickel, aluminum and the like coated on paper or conventional photographic film bases such as cellulose acetate, polystyrene, poly(ethylene terephthalate), etc. Such conducting materials as nickel can be coated by vacuum deposition on transparent film supports in sufficiently thin layers to allow electrophotographic elements prepared therewith to be exposed from either side of such elements. An especially useful conducting support can be prepared by coating a support material such as poly(ethylene terephthalate) with a conducting layer containing a semiconductor dispersed in a resin. Such conducting layers both with and without insulating barrier layers are described in U.S. Pat. No. 3,245,833. Likewise, a suitable conducting coating can be prepared from the sodium salt of the carboxyester lactone of maleic anhydride and a vinyl acetate polymer. Such kinds of conducting layers and methods for their optimum preparation and use are disclosed in U.S. Pats. 3,007,901 and 3,267,807.

The photoconductive response of various materials is measured on an apparatus as described in Robinson et al. U.S. Pat. No. 3,449,658. To measure the electrophotographic speed, a suitable element bearing a coating of a photoconductive composition is electrostatically charged under a corona source until the surface potential, as measured by an electrometer probe, reaches about 600 volts. The charged element is then exposed to a 3000 K. tungsten light source through a stepped density gray scale. The exposure causes reduction of the surface potential of the elements under each step of the gray scale from its initial potential, V₀, 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 then plotted on a graph of surface potential V vs. log exposure for each step. The actual positive or negative speed of the photoconductive composition used can then be expressed in terms of the reciprocal of the exposure required to reduce the surface potential to any fixed arbitrarily selected value. The actual positive or negative speed can be expressed as the numerical expression of 10⁴ divided by the exposure in meter-candle-seconds required to reduce the 600 volt charged surface potential to a value of 500 volts (100 volts shoulder speed) or to a value of 100 volts (100 volt toe speed). For comparative purposes, the positive or negative shoulder speed of one element normally the control element, is arbitrarily set at 100 and other elements in that series are then measured in comparison for a determination of relative speed.

In preparing the elements of the present invention, the polyester resin is typically added in an amount of from about 60 to about 90% by weight of the composition. The remainder is usually comprised of a suitable n-type photoconductor and sensitizing dye. Of course, other suitable addenda can be added such as coating aids, plasticizers, etc.

Elements formed according to the present invention can be employed in any of the well-known electrophotographic processes which require photoconductive layers. One such process is the xerographic process. In a process of this type, the electrophotographic element is given a blanket electrostatic charge by placing the same under a corona discharge which serves to give a uniform charge to the surface of the photoconductive layer. This charge is retained on the layer by virtue of the substantial insulating property of the layer, i.e., the low conductivity of the layer in the dark. The electrostatic charge formed on

the surface of the photoconducting layer is then selectively dissipated from the surface of the layer by exposure to light through an image-bearing transparency by a conventional exposure operation such as, for example, by contact-printing technique, or by lens projection of an image, etc., to form an electrostatic latent image in the photoconducting layer. By exposure of the surface in this manner, a charged pattern is created by virtue of the fact that light causes the charge to be conducted away in proportion to the intensity of the illumination in a particular area. The charge pattern remaining after exposure is then developed, i.e., rendered visible, by treatment with a medium comprising electrostatically attractable particles having optical density. The developing electrostatically attractable particles can be in the form of a dust or a pigment in a resinous binder, or a liquid developer can be used in which the developing particles are carried in an electrically insulating liquid carrier. Methods of development of this type are widely known and have been described in the patent literature in such patents, for example, as U.S. 2,297,691 and in Australian Pat. 212,315. In processes of electrophotographic reproduction such as in xerography, by selecting a developing particle which has a low melting resin as one of its components, it is possible to treat the developed photoconductive material with heat and cause the power to adhere permanently to the surface of the photoconductive layer. In other cases, a transfer of the image formed on the photoconductive layer can be made to a second support which would then become the final print. Techniques of the type indicated are well known in the art and have been described in a number of U.S. and foreign patents such as U.S. Pats. 2,297,691 and 2,551,582 and in "RCA Review," vol. 15 (1954), pp. 469-484.

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

EXAMPLE 1

Coatings are made by dissolving 0.6 gram of 2,4,7-trinitro-9-fluorenone with 1.4 grams of the binder poly(4,4'-isopropylidenebisphenoxyethyl-o-ethylene terephthalate) and 0.020 gram of sensitizing dye in 16 cc. of methylene chloride solvent. The dopes are coated at a wet thickness of about 100 microns onto a 4 mil poly(ethylene terephthalate) film support carrying a conductive layer of the sodium salt of a polymeric lactone as described in U.S. Pat. No. 3,260,706. The supports are held on plates maintained at a temperature of about 32° C. during coating. The elements are charged, exposed and measured for electrical speed by the technique described previously. The positive and negative 100 volt shoulder and toe relative speeds are shown in Table II along with the extension of the sensitivity of the system.

TABLE II

Dye	Relative positive speed		Relative negative speed		Region of sensitization	
	Shoulder	Toe	Shoulder	Toe	Max. (nm.)	Limits (nm.)
None (control)-----	25	-----	100	3.5	-----	<580
A-----	60	5	500	20	550	<620
B-----	80	5	280	18	530	<600
C-----	80	0	125	12	525	<550
D-----	40	0	325	9	500	<550
E-----	50	3	100	12	480	<520
F-----	40	3	125	8	490	<525
G-----	90	5	225	16	700	-----
H-----	25	0	280	5	500	>600
I-----	60	9	225	18	675	>720
J-----	55	5	160	12	675	>720
K-----	55	6	175	25	700	>750
L-----	90	6	125	20	610	>700
M-----	55	10	225	20	730	>750

EXAMPLE 2

Coatings are made and tested in a manner similar to that described in Example 1 except that Lexan 145, a

Bisphenol A polycarbonate from General Electric is utilized as the binder. The following results are obtained:

TABLE III

Dye	Relative positive speed		Relative negative speed		Region of sensitization	
	Shoulder	Toe	Shoulder	Toe	Max. (nm.)	Limits (nm.)
None (control)-----	40	0	100	0	410	<450
A-----	440	35	2,000	100	550	480-600
B-----	800	40	1,280	80	540	450-575
C-----	480	28	480	90	525	430-550

EXAMPLE 3

Coatings are made and tested in a manner similar to that described in Example 1 except that polystyrene is utilized as the binder. The following results are obtained:

TABLE IV

Dye	Relative positive, shoulder	Relative negative, shoulder
None (control)-----	70	100
A-----	550	450

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

I claim:

1. A composition of matter comprising

(A) an organic photoconductor selected from the group consisting of 2,4,7 - trinitro - 9 - fluorenone, 1,5-dinitronaphthalene, 2,4,5,7-tetranitro - 9 - fluorenone, phthalic anhydride, p-chloranil, benzil, 9,10-dibromanthracene, 9-acetylanthracene, pyrene - 3 - aldehyde, 1,2 - benzanthraquinone, 1,8-dinitronaphthalene, 1,4,5 - trinitronaphthalene, 1,5 - dichloronaphthalene and 1,4-dibromonaphthalene;

(B) a polymeric binder; and,

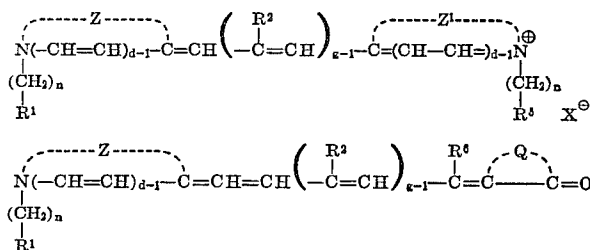
(C) a substantially non-photoconductive electron donating sensitizing dye selected from the group consisting of a cyanine, a merocyanine and a styryl dye, which dye:

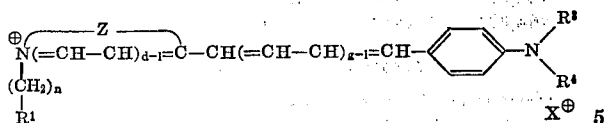
(1) has a cathodic polarographic half-wave potential more negative than -1.0 volt;

(2) has an anodic polarographic half-wave potential and a cathodic polarographic half-wave potential which, when added together, give a sum more negative than 0.00 volt; and

(3) does not desensitize a test negative gelatin silver bromide emulsion, consisting of 99.35 mole percent bromide and .65 mole percent iodide, more than 0.4 log E to light having a wavelength of 365 nm. when incorporated in said test emulsion at a concentration of 0.2 millimole of dye per mole of silver.

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





wherein Z and Z¹ represent the nonmetallic atoms necessary to complete a heterocyclic nucleus of the type used in cyanine dyes; Q represents the nonmetallic atoms necessary to complete a heterocyclic nucleus containing from 5 to 6 carbon atoms, 3 to 4 of said atoms being carbon and 2 of said atoms being selected from nitrogen, oxygen or sulfur with at least one of said two atoms being nitrogen; R¹ and R⁵ each represents a hydrogen atom, a hydroxyl radical, a carboxyl radical, a cyano radical, an acyl radical, an acyloxy radical, an alkoxy radical, a sulfo radical or an aryl radical and each of R², R³, R⁴ and R⁶ represents a hydrogen atom, an alkyl radical of 1-8 carbon atoms or an aryl radical of 6-20 carbon atoms; X[⊖] represents an anion; d represents a positive integer from 1 to 2; n represents an integer from 1 to 4 and g represents a positive integer from 1 to 3.

3. A composition of matter as defined in claim 2 wherein said dye is selected from the group consisting of

- 3,3'-diethyl-9-methyl thiacyanobocyanine paratoluenesulfonate;
- 1,1'-diethyl-2,2'-cyanine perchlorate;
- 3,3'-diethyl-4'-methyloxathiazolocarbo-cyanine paratoluenesulfonate;
- 3-ethyl-5-[(3-ethyl-2-benzothiazolinyli-dene)-1-methylethylidene]-2-thio-2,4-oxazolidinedione;
- 3-methyl-1'-ethylthia-2'-cyanine iodide;
- 6,7-dichloro-3-p-dimethylaminobenzylidene-4-ethyl-2,3-dihydro-1H-pyrrolo[1,2-a]benzimidazolium iodide;
- 11-[4-chlorophenyl]-3-methyl-1-piperaziny]-3,3'-diethyl-10,12-ethylenethiatricarbo-cyanine perchlorate;
- 3-ethyl-5-[(3-ethyl-2-benzothiazolinyli-dene)-ethylidene-2-(1,2,4-triazol-3-yl)imino-4-thiazolidinone];
- 3,3'-diethylthiadibocyanine iodide;
- 3,3'-diethylselenadibocyanine ethylsulfate;
- 3,3'-diethyloxatricarbo-cyanine iodide;
- 9-ethyl-1,3'-dimethylthia-2'-carbocyanine iodide; and
- 3,3'-diethyl-10,12-ethylene-11-[4-(hydroxyethyl) piperidino]thiatricarbo-cyanine iodide.

4. A composition of matter as defined in claim 1 wherein said polymeric binder is selected from the class consisting of polyester, polycarbonate and polystyrene resins.

5. A composition of matter as defined in claim 1 comprising from 1 to 75 parts by weight of the n-type photoconductor, 0.1 to 10 parts by weight of the dye and 60 to 90 parts by weight binder.

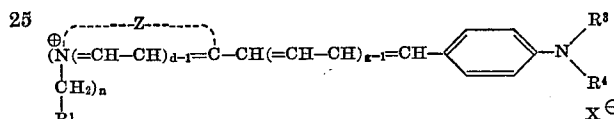
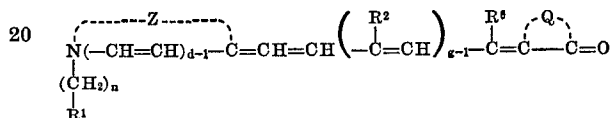
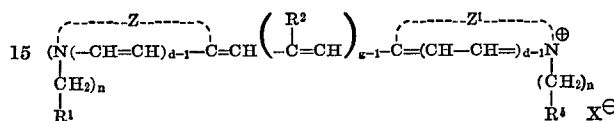
6. An electrophotographic element comprising a conductive support having coated thereon a layer comprising an n-type organic photoconductor selected from the group consisting of 2,4,7 - trinitro - 9 - fluorenone, 1,5-dinitro-naphthalene, 2,4,5,7 - tetranitro - 9 - fluorenone, phthalic anhydride, p-chloranil, benzil, 9,10 - dibromoanthracene, 9 - acetylanthracene, pyrene - 3 - aldehyde, 1,2 - benzanthraquinone, 1,8 - dinitronaphthalene, 1,4,5 - trinitro-naphthalene, 1,5 - dichloronaphthalene and 1,4 - dibromo-naphthalene in a polymeric binder, said organic photoconductor being spectrally sensitized with a substantially nonphotoconductive electron donating dye selected from the group consisting of the cyanine, merocyanine, and styryl dyes, which dye:

- (1) has a cathodic polarographic half-wave potential more negative than -1.0 volt;
- (2) has an anodic polarographic half-wave potential and a cathodic polarographic half-wave potential

which, when added together, give a sum more negative than 0.00 volt; and

- (3) does not sensitize a test negative gelatin silver bromoiodide emulsion, consisting of 99.35 mole percent bromide and .65 mole percent iodide, more than 0.4 log E to light having a wavelength of 365 nm., when incorporated in said test emulsion at a concentration of 0.2 millimole of dye per mole of silver.

7. The element as defined in claim 6 wherein said dye has one of the following formulas:



wherein Z and Z¹ represent the nonmetallic atoms necessary to complete a heterocyclic nucleus of the type used in cyanine dyes; Q represents the nonmetallic atoms necessary to complete a heterocyclic nucleus containing from 5 to 6 carbon atoms, 3 to 4 of said atoms being carbon and 2 of said atoms being selected from nitrogen, oxygen or sulfur with at least one of said two atoms being nitrogen; R¹ and R⁵ each represents a hydrogen atom, a hydroxyl group, a carboxyl group, a cyano group, an acyl group, an acyloxy group, an alkoxy group, a sulfo group or an aryl group and each of R², R³, R⁴ and R⁶ represents a hydrogen atom, an alkyl group of 1-8 carbon atoms or an aryl group of 6-20 carbon atoms; X[⊖] represents an anion; d represents a positive integer from 1 to 2; n represents an integer from 1 to 4 and g represents a positive integer from 1 to 3.

8. The element as defined in claim 7 wherein said dye is selected from the group consisting of

- 3,3'-diethyl-9-methyl thiacyanobocyanine paratoluenesulfonate;
- 1,1'-diethyl-2,2'-cyanine perchlorate;
- 3,3'-diethyl-4'-methyloxathiazolocarbo-cyanine paratoluenesulfonate;
- 3-ethyl-5-[(3-ethyl-2-benzothiazolinyli-dene)-1-methylethylidene]-2-thio-2,4-oxazolidinedione;
- 3-methyl-1'-ethylthia-2'-cyanine iodide;
- 6,7-dichloro-3-p-dimethylaminobenzylidene-4-ethyl-2,3-dihydro-1H-pyrrolo-[1,2-a]benzimidazolium iodide;
- 11-[4-(4-chlorophenyl)-3-methyl-1-piperaziny]-3,3'-diethyl-10,12-ethylenethiatricarbo-cyanine perchlorate;
- 3-ethyl-5-[(3-ethyl-2-benzothiazolinyli-dene)-ethylidene-2-(1,2,4-triazol-3-yl)imino-4-thiazolidinone];
- 3,3'-diethylthiadibocyanine iodide;
- 3,3'-diethylselenadibocyanine ethylsulfate;
- 3,3'-diethyloxatricarbo-cyanine iodide;
- 9-ethyl-1,3'-dimethylthia-2'-carbocyanine iodide; and
- 3,3'-diethyl-10,12-ethylene-11-[4-(2-hydroxyethyl)-piperidino]thiatricarbo-cyanine iodide.

9. The element as defined in claim 6 wherein said polymeric binder is selected from the class consisting of polyester, polycarbonate and polystyrene resins.

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ROLAND E. MARTIN, JR., Primary Examiner

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96—1.5; 260—240 R, 240.4, 240.6, 240.65, 240.9