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3,681,068

ORGANIC PHOTOCONDUCTORS

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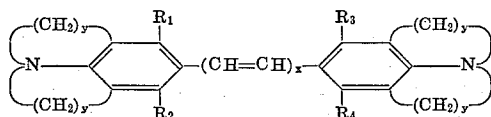
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U.S. Cl. 96—1.5

4 Claims

ABSTRACT OF THE DISCLOSURE

Compounds having the formula:



are useful as photoconductors.

This invention relates to electrophotography and more particularly to a novel class of photoconductive materials and to the compositions and elements produced therefrom.

Electrophotographic imaging processes and techniques are based on the discovery that certain materials which are normally insulating become conductive during exposure to electromagnetic radiation of certain wavelengths after being electrically charged. Such materials, which may be either organic or inorganic, are termed photoconductors. They are conveniently formed into usable image-forming elements by coating a layer of the photoconductive composition, together with an electrically insulating resinous binder, where necessary or desirable, onto a suitable support. Such an element will accept and retain an electrostatic charge in the absence of actinic radiation. In use, the surface of the element is charged in the dark to a uniform potential and exposed to an imagewise pattern of actinic radiation, which selectively reduces the surface potential to produce a charge pattern corresponding to the imagewise radiation pattern. The resultant charge pattern or electrostatic latent image may be developed by contacting it with suitably charged marking particles which adhere in accordance with the charge pattern, or it may be transferred to another insulating surface upon which it is developed. The particles may then be fused or fixed to the surface by known means, such as heat or solvent vapor, or they may be transferred to another surface to which they may similarly be fixed, to produce a permanent reproduction of the original radiation pattern.

Various photoconductive insulating materials have been employed in the manufacture of electrophotographic elements. For example, vapors of selenium and 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 document-copying applications.

Since the introduction of electrophotography, a great many organic compounds have been found to possess some degree of photoconductivity. Many organic compounds have revealed a useful level of photoconduction and have been incorporated into photoconductive compositions. Optically clear organic photoconductor-containing elements having desirable electrophotographic properties can be especially useful in electrophotography. Such electrophotographic elements may be 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

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to form subsequent images after residual toner from prior images has been removed by transfer and/or cleaning.

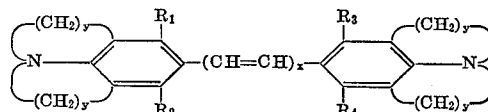
Typical of these organic photoconductors are the triphenylamines and the triarylmethane leuco bases. Optically clear photoconductor-containing elements having desirable electrophotographic properties can be especially useful in electrophotography. Such electrophotographic elements can be exposed through 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. Thus far, the selection of various compounds for incorporation into photoconductive compositions to form electrophotographic layers has proceeded on a compound-by-compound basis. Nothing as yet has been discovered from the large number of different photoconductive substances tested which permits effective prediction, and therefore selection of the particular compounds exhibiting the desired electrophotographic properties.

It is, therefore, an object of this invention to provide a novel class of photoconductive compounds.

It is another object of this invention to provide novel photoconductive compositions which have useful electrophotographic speeds without requiring additional sensitizer.

It is a further object to provide a process utilizing the novel photoconductive compositions described.

These and other objects of this invention are accomplished through the use as a photoconductor of a compound corresponding to the general formula:



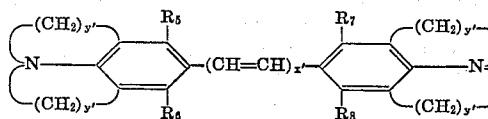
wherein:

R₁, R₂, R₃ and R₄ may each be a hydrogen atom, an alkyl radical, an aryl radical including an aminoaryl radical, an alkoxy radical or a halogen atom;

x is an integer from 0 to 5; and

y is an integer from 2 to 5.

Preferred photoconductors of the invention are those corresponding to the formula:



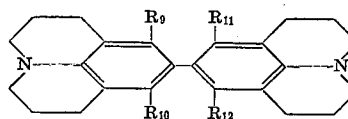
wherein:

R₅, R₆, R₇ and R₈ may each be a hydrogen atom, a lower alkyl radical, a lower alkoxy radical, a phenyl radical including a substituted phenyl radical or a halogen atom;

x' is an integer from 0 to 2; and

y' is an integer of 2 or 3.

Particularly preferred photoconductors of the invention are those corresponding to the formula:



wherein:

R₉, R₁₀, R₁₁ and R₁₂ may each be hydrogen, an alkyl

radical having from 1 to 2 carbon atoms, an alkoxy radical having from 1 to 2 carbon atoms in the alkyl moiety, a phenyl radical or a halogen atom.

The term "alkyl" refers to an aliphatic alkyl radical having from 1 to about 8 carbon atoms, e.g., methyl, ethyl, isopropyl, tert-butyl, hexyl, octyl, etc., including a substituted alkyl group having from 1 to about 8 carbon atoms such as:

(a) Aminoalkyl, e.g., aminobutyl, aminoethyl, aminopropyl, etc.,

(b) Aralkyl, e.g., benzyl, phenethyl, etc.,

(c) Alkylaminoalkyl, e.g., ethylaminopropyl, methylaminoethyl, etc., and also including dialkylaminoalkyl, e.g., diethylaminoethyl, dimethylaminopropyl, propylaminoctyl, etc.,

(d) Arylaminoalkyl, e.g., phenylaminoethyl and also including diarylaminoalkyl, e.g., diphenylaminomethyl, N-phenyl-N-ethylaminopentyl, dinaphthylaminopropyl, etc.

(e) Cyanoalkyl, e.g., cyanopropyl, cyanobutyl, etc.,

(f) Haloalkyl, e.g., chloromethyl, bromopentyl, chlorooctyl, etc.,

(g) Carboxyalkyl, e.g., carboxymethyl, carboxyethyl, etc.

The term "lower alkyl" refers to an aliphatic alkyl radical as defined hereinabove having from 1 to about 4 carbon atoms, e.g., alkyl groups from methyl to about butyl including substituted groups.

The term "aryl" refers to an aromatic radical, e.g., phenyl, anthryl, naphthyl, etc., and including a substituted aryl group such as:

(a) Aminoaryl, e.g., aminophenyl, aminonaphthyl, aminoanthryl, etc.,

(b) Alkylaminoaryl, e.g., ethylaminophenyl, methylaminonaphthyl, etc., and also including dialkylaminoaryl, e.g., diethylaminophenyl, dipropylaminonaphthyl, etc.,

(c) Arylaminoaryl, e.g., phenylaminophenyl, and also including diarylaminoaryl, e.g., diphenylaminophenyl, N-phenyl-N-ethylaminophenyl, dinaphthylaminophenyl, etc.,

(d) Alkaryl, e.g., tolyl, ethylphenyl, propyl-naphthyl, etc.,

(e) Cyanoaryl, e.g., cyanophenyl, cyanonaphthyl, etc.,

(f) Haloaryl, e.g., chlorophenyl, bromonaphthyl, etc.

The term "alkoxy" refers to an alkoxy radical having from 1 to about 8 carbon atoms in the alkyl moiety, e.g., methoxy, ethoxy, butoxy, octoxy, etc.

The term "lower alkoxy" refers to an alkoxy radical having from 1 to about 4 carbon atoms in the alkyl moiety, e.g., methoxy, ethoxy, propoxy, butoxy, etc.

The term "halogen" is used in its usual meaning to represent an atom of chlorine, fluorine, bromine or iodine.

Electrophotographic elements can be prepared with the photoconductive compounds of the invention in the usual manner, i.e., by blending a dispersion or solution of a photoconductive compound together with a binder, when necessary or desirable, and coating or forming a self-supporting layer with the photoconductor-containing materials. Mixtures of the photoconductors described herein can be employed. Likewise, other photoconductors known in the art such as those described in Light, British Pat. 1,153,506 dated May 29, 1969, can be combined with the present photoconductors.

The photoconductive layers of the invention can also incorporate supplemental materials in amounts effective to change the spectral sensitivity or electrophotosensitivity when it is desired to produce the characteristic effect of such materials. Compounds which may be useful to produce these effects can be selected from a wide variety of materials, including such materials as pyrylium dye salts including thiapyrylium dye salts and selenapyrylium dye salts disclosed in Van Allan et al., U.S. Pat. 3,250,615 issued May 10, 1966; hexaphenyl-p-rosaniline; fluorenes, such as 7,12-dioxo-13-dibenzo(a,h)fluorene, 5,10-dioxo-4a,11-diazobenzob(b)fluorene, 3,13-dioxo-7-oxadibenzo(b,g)fluorene, and the like; aggregate-type sensitizers of

the type described in Light, British Pat. 1,153,506 dated May 29, 1969; aromatic nitro compounds of the kinds described in Minsk, U.S. Pat. 2,610,120 issued Sept. 9, 1952; anthrones like those disclosed in Zvanut, U.S. Pat. 2,670,284 issued Feb. 23, 1954; quinones as those in Minsk, U.S. Patent 2,670,286 issued Feb. 23, 1954; benzophenones as those in Minsk, U.S. Patent 2,260,287 issued Feb. 23, 1954; thiazoles as those of Robertson, U.S. Patent 2,732,301 issued Jan. 24, 1956; mineral acids, carboxylic acids, such as maleic acid, dichloroacetic acid, trichloroacetic acid and salicylic acid; sulfonic and phosphoric acids; and various dyes, such as cyanine (including carbocyanine and polycarbocyanine), merocyanine, diarylmethane, thiazine, azine, oxazine, xanthene, phthalein, acridine, azo, anthraquinone dyes and the like and mixtures thereof.

Where a sensitizing compound is employed with the binder and organic photoconductor to form a sensitized electrophotographic element, it is the normal practice to mix a suitable amount of the sensitizing compound with the coating composition so that, after thorough mixing, the sensitizing compound is uniformly distributed in the coated layer. Other methods of incorporating the sensitizer or the effect of the sensitizer may, however, be employed consistent with the practice of this invention. In preparing the photoconductive layers of this invention, no sensitizing compound is required to impart photoconductivity; therefore, no sensitizer need be present in a particular photoconductive layer. However, since relatively minor amounts of sensitizing compound can give rise to substantial improvements in certain situations, the use of a sensitizer may be preferred in those situations. The amount of sensitizer that can be added to a photoconductor-incorporating layer to give effective increases in speed can vary widely. The optimum concentration in any given case will vary with the specific photoconductor and sensitizing compound used. In general, substantial speed gains can be obtained where an appropriate sensitizer is added in a concentration range from about 0.0001 to about 30 percent by weight based on the weight of the film-forming coating composition. Normally, a sensitizer is added to the coating composition in an amount by weight from about 0.005 to about 5.0 percent by weight of the total coating composition.

Preferred binders for use in preparing the present photoconductive layers are film-forming, hydrophobic polymeric binders having fairly high dielectric strength which are good electrically insulating film-forming vehicles. Typical of these materials are:

(I) Natural resins including gelatin, cellulose ester derivatives such as alkyl esters of carboxylated cellulose, hydroxy ethyl cellulose, carboxy methyl cellulose, carboxy methyl hydroxy ethyl cellulose, etc.;

(II) Vinyl resins including:

(a) Polyvinyl esters such as a vinyl acetate resin, a copolymer of vinyl acetate and crotonic acid, a copolymer of vinyl acetate with an ester of vinyl alcohol and a higher aliphatic carboxylic acid such as lauric acid or stearic acid, polyvinyl stearate, a copolymer of vinyl acetate and maleic acid, a poly(vinylhaloarylate) such as poly(vinyl-m-bromobenzoate-co-vinyl acetate), a terpolymer of vinyl butyral with vinyl alcohol and vinyl acetate, etc.;

(b) Vinyl chloride and vinylidene chloride polymers such as a poly(vinylchloride), a copolymer of vinyl chloride and vinyl isobutyl ether, a copolymer of vinylidene chloride and acrylonitrile, a terpolymer of vinyl chloride, vinyl acetate and vinyl alcohol, poly(vinylidene chloride), a terpolymer of vinyl chloride, vinyl acetate and maleic anhydride, a copolymer of vinyl chloride and vinyl acetate, etc.;

(c) Styrene polymers such as polystyrene, a nitrated polystyrene, a copolymer of styrene and monoisobutyl maleate, a copolymer of styrene with methacrylic acid, a

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copolymer of styrene and butadiene, a copolymer of dimethylitaconate and styrene, polymethylstyrene, etc.;

(d) Methacrylic acid ester polymers such as a poly(alkylmethacrylate), etc.;

(e) Polyolefins such as chlorinated polyethylene, chlorinated polypropylene, poly(isobutylene), etc.;

(f) Poly(vinyl acetals) such as poly(vinyl butyral), etc.; and

(g) Poly(vinyl alcohol);

(III) Polycondensates including:

(a) A polyester of 1,3-disulfobenzene and 2,2-bis-(4-hydroxyphenyl)propane;

(b) A polyester of diphenyl-p,p'-disulphonic acid and 2,2-bis(4-hydroxyphenyl)propane;

(c) A polyester of 4,4'-dicarboxyphenyl ether and 2,2-bis(4-hydroxyphenyl)propane;

(d) A polyester of 2,2-bis(4-hydroxyphenyl)propane and fumaric acid;

(e) Polyester of pentaerythritol and phthalic acid;

(f) Resinous terpene polybasic acid;

(g) A polyester of phosphoric acid and hydroquinone;

(h) Polyphosphites;

(i) Polyester of neopentylglycol and isophthalic acid;

(j) Polycarbonates including polythiocarbonates such as the polycarbonate of 2,2-bis(4-hydroxyphenyl)propane;

(k) Polyester of isophthalic acid, 2,2-bis[4-(β -hydroxyethoxy)phenyl]propane and ethylene glycol;

(l) Polyester of terephthalic acid, 2,2-bis[4-(β -hydroxyethoxy)phenyl]propane and ethylene glycol;

(m) Polyester of ethylene glycol, neopentyl, glycol, terephthalic acid and isophthalic acid;

(n) Polyamides;

(o) Ketone resins; and

(p) Phenolformaldehyde resins;

(IV) Silicone resins;

(V) Alkyd resins including styrene-alkyd resins, silicone-alkyd resins, soya-alkyd resins, etc.;

(VI) Paraffin; and

(VII) Mineral waxes.

Solvents useful for preparing coating compositions with the photoconductors of the present invention can include a wide variety of organic solvents for the components of the coating composition. Typical solvents include:

(1) Aromatic hydrocarbons such as benzene, naphthalene, etc., including substituted aromatic hydrocarbons such as toluene, xylene, methylene, etc.;

(2) Ketones such as acetone, 2-butanone, etc.;

(3) Halogenated aliphatic hydrocarbons such as methylene chloride, chloroform, ethylene chloride, etc.;

(4) Ethers including cyclic ethers such as tetrahydrofuran, ethylether;

(5) Mixtures of the above.

In preparing the coating compositions utilizing the photoconducting compounds disclosed herein, useful results are obtained where the photoconductive substance is present in an amount equal to at least about 1 weight percent of the coating composition. The upper limit in the amount of photoconductive material present can be widely varied in accordance with usual practice. It is normally required that the photoconductive material be present in an amount ranging from about 1 weight percent of the coating composition to about 99 weight percent of the coating composition. A preferred weight range for the photoconductive material in the coating composition is from about 10 weight percent to about 60 weight percent.

Coating thicknesses of the photoconductive composition on a support can vary widely. Normally, a wet coating thickness in the range of about 25 microns to about 250 microns is useful in the practice of the invention. A preferred range of coating thickness is from about 50 microns to about 150 microns before drying, although such thicknesses can vary widely depending on the particular application desired for the electrophotographic element.

Suitable supporting materials for the photoconductive layers of the present invention can include any of the

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electrically conducting supports, for example, various conducting papers; aluminum-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 or aluminum on conventional film supports such as cellulose acetate, poly(ethylene terephthalate), polystyrene and the like conducting support.

An especially useful electrically conducting support can be prepared by coating a transparent film support material such as poly(ethylene terephthalate) with a layer containing a semiconductor dispersed in a resin. A suitable conducting coating can be prepared from the sodium salt of a carboxy-ester lactone of a maleic anhydride-vinyl acetate copolymer, cuprous iodide and the like. Such conducting layers and methods for their optimum preparation and use are disclosed in U.S. Pats. 3,007,901 by Minsk issued Nov. 7, 1961, 3,245,833 by Trevoy issued Apr. 12, 1966, and 3,262,807 by Sterman et al. issued July 26, 1966.

The compositions of the present invention can be employed in photoconductive elements useful in any of the well-known electrophotographic process which require photoconductive layers. One such process is the xerographic process. In a process of this type, an electrophotographic element held in the dark is given a blanket positive or negative electrostatic charge as desired by placing it under a corona discharge to give a uniform charge to the surface of the photoconductive layer. This charge is retained by the layer because of the substantial dark 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 photoconductive layer is then selectively dissipated from the surface of the layer by image-wise exposure to light by means of a conventional exposure operation such as, for example, by a contact-printing technique, or by lens projection of an image, or by reflex techniques and the like, to thereby form a latent electrostatic image in the photoconductive layer. Exposing the surface in this manner forms a pattern of electrostatic charge as the light energy striking the photoconductor causes the electrostatic charge in the exposed areas to be conducted away from the surface in proportion to the illuminance on a particular area.

The charge pattern produced by exposure is then developed or transferred to another surface and developed. Either the charged or uncharged areas can be rendered visible, by treatment with a suitable developer composition containing marking particles. The marking particles are electrostatically responsive and can be in the form of a dust, or powder, and generally comprise a toner in the form of a pigment in a resinous binder. A preferred method of applying such a toner to an electrostatic image for solid area development is by the use of a magnetic brush. Methods of forming and using a magnetic brush toner applicator are known in the art, e.g., U.S. Pats. 2,786,439 by Young, 2,786,440 by Giaimo and 2,786,441 by Young, all issued Mar. 26, 1957. Liquid development of the latent electrostatic image can also be used. In liquid development, the toner or marking particles are carried to the image-bearing surface in an electrically insulating liquid carrier. Methods of development of this type are widely known and have been described in the patent literature, for example, Metcalfe et al., U.S. Pat. 2,907,674 issued Oct. 6, 1959. In dry developing processes, the most widely used method of obtaining a permanent record is achieved by selecting a toner particle which has as one of its components a low-melting resin. Heating the developed image then causes the resin to melt or fuse into or on the element resulting in a fixed developed image. In other cases, a transfer of the charge image or unfixed toner image formed on the photoconductive layer can be made to a second support such as paper which would then become the final print after developing and/or fusing. Techniques of the type indicated are well-known in the

art and have been described in the literature, such as in RCA Review, vol. 15 (1954), pp. 469-484.

The compositions of the present invention can be used in electrophotographic elements having many structural variations. For example, the photoconductive composition can be coated in the form of single layers or multiple layers on a suitable opaque or transparent conducting support. Likewise, the layers can be contiguous or spaced having layers of insulating material or other photoconductive material between layers or overcoated or interposed between the photoconductive layer or sensitizing layer and the conducting layer. It is also possible to adjust the position of the support and the conducting layer by placing a photoconductor layer over a support and coating the exposed face of the support or the exposed or overcoated face of the photoconductor with a conducting layer. Configurations differing from those contained in the examples can be useful or even preferred for the same or different application for the electrophotographic element.

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

EXAMPLE 1

A composition in the form of a dope consisting of the following materials is coated at a wet thickness of 150 microns on a poly(ethylene terephthalate) film support bearing a conductive layer comprising vapor-deposited nickel:

Photoconductor—9,9'-bifulolidyl	G.
Binder—poly(4,4'-isopropylidene - bisphenyleneoxy-ethylene-coethylene terephthalate	0.25
Dichloromethane	1.00
	9.60

The support is held on a coating block maintained at a temperature of about 32° C. during coating and until the solvent is removed. In a darkened room, the surface of the photoconductive layer so prepared is charged to a potential of about +600 volts under a corona charger. The layer is then covered with a transparent sheet bearing a pattern of opaque and light-transmitting areas and exposed to the radiation from an incandescent lamp with an illumination intensity of about 75 meter-candles for 12 seconds. The resulting electrostatic charge pattern is developed by cascading over the surface of the layer negatively charged, black thermoplastic toner particles on glass bead carriers. A good image is obtained.

EXAMPLE 2

The element of Example 1 is charged under a corona charger until the surface potential, as measured by an electrometer probe, reaches about 600 volts. It is then exposed from behind a stepped density gray scale to a 3000° K. source. The exposure causes reduction of the surface potential of the element under each step of the gray scale from its initial value, V_0 , to some lower potential, V , whose exact value depends on the actual amount of exposure received by the area. The results of the measurements are plotted on a graph of surface potential, V , vs. log exposure for each step. The speed of the element, as indicated herein, is the numerical expression of 10^4 multiplied by the reciprocal of the exposure in meter-candle-seconds required to reduce the 600-volt charged surface potential to 100 volts (the resultant value is known as the toe speed) or to reduce the potential to 100 volts below the initial potential, V_0 (shoulder speed). The speeds thus obtained are shown in Table 1 below for both positive and negative charging.

TABLE 1

Charging polarity	Speed	
	Shoulder	Toe
Positive.....	320	32
Negative.....	320	32

As a control, an equimolar weight of triphenylamine is

substituted in the above formulation in place of the 9,9'-bifulolidyl. The speeds thus obtained, under the same conditions, are a shoulder speed of 35 and a toe speed of 0, for both positive and negative modes of charging. Only when a spectral-sensitizing dye, such as 2,6-bis(4-ethylphenyl)-4-(4-n-amyloxyphenyl)thiapyrylium perchlorate, is added, does the speed of the triphenylamine composition increase under these exposure conditions. When an amount of 0.004 gram of this sensitizer is included in the composition, the shoulder and toe speeds increase to 640 and 40, respectively, for positive charging, and 640 and 30, respectively, for negative charging.

EXAMPLE 3

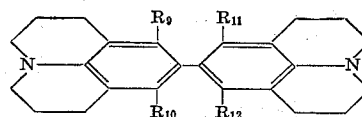
The photoconductor of Example 2 is prepared by the general procedure described by Smith and Yu, J. Org. Chem., 17, 1281-90, as follows: A stirred solution of 52 g. (0.3 mole) of julolidine in 300 ml. of water, 300 ml. of concentrated hydrochloric acid and 100 ml. of glacial acetic acid is kept at 2° C. to which is added (during 5 minutes) a solution of 20.8 g. (0.3 mole) of sodium nitrite in 60 ml. of water. Stirring is continued for 4½ hours, during which time the temperature reaches 28° C. The resulting dark red mixture is cooled below 15° C. and treated with 900 ml. of concentrated ammonium hydroxide. The solid which precipitates is filtered, washed with water and dried in a vacuum oven at 60° C. The dark brown solid is boiled for about 45 minutes in 1 liter of ethanol mixed with 50 ml. of water and filtered while still hot. The insoluble light tan solid is recrystallized from 1 liter of ethanol mixed with 260 ml. of benzene. There is obtained 9.9 g. of brown needles having a melting point in the range 207-211° C. The theoretical values calculated for $C_{24}H_{28}N_2$ and the values actually found are as follows:

Calculated (percent): C, 83.7; H, 8.1; N, 8.1. Found (percent): C, 83.8; H, 8.0; N, 8.2.

Although the invention has been described in considerable detail with particular reference to certain preferred embodiments thereof, variations and modifications can be effected within the spirit and scope of the invention.

I claim:

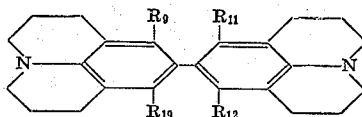
1. A photoconductive composition comprising an organic, electrically insulating, film-forming polymeric binder having therein a photoconductive compound having the formula:



R_9 , R_{10} , R_{11} and R_{12} are each selected from the group consisting of a hydrogen atom, an alkyl radical having from 1 to about 2 carbon atoms, an alkoxy radical having from 1 to about 2 carbon atoms, a phenyl radical and a halogen atom.

2. A composition as described in claim 1 additionally comprising from about 0.005 to about 5% by weight of a sensitizer therefor based on the dry weight of the composition.

3. An electrophotographic element comprising an electrically conductive support bearing a layer of a photoconductive composition comprising an organic, electrically insulating, film-forming, polymeric binder having therein a compound of the formula:



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R⁵, R₁₀, R₁₁ and R₁₂ are each selected from the group consisting of a hydrogen atom, an alkyl radical having from 1 to about 2 carbon atoms, an alkoxy radical having from 1 to about 2 carbon atoms, a phenyl radical and a halogen atom.

4. An electrophotographic element as described in claim 3 wherein the photoconductive compound is 9,9'-bifulolyl.

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10

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