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3,485,625

PHOTOCONDUCTIVE ELEMENTS CONTAINING 2,3,4,5-TETRAARYL PYRROLE

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No Drawing. Filed June 9, 1966, Ser. No. 556,282

Int. Cl. G03g 5/06; C07d 27/22

U.S. Cl. 96—1.5

8 Claims

ABSTRACT OF THE DISCLOSURE

Electrophotographic elements containing a photoconductive composition comprising a 2,3,4,5-tetraaryl pyrrole photoconductor and a sensitizer for the photoconductive composition are described.

This invention relates to electrophotography, and in particular to organic photoconductor-containing elements having enhanced photosensitivity when electrically charged.

The process of xerograph, as disclosed by Carlson in U.S. 2,297,691, employed an electrophotographic element comprising a support material bearing a coating of a normally insulating material whose electrical resistance varies with the amount of incident actinic radiation it received during an imagewise exposure. The element, commonly termed a photoconductive element, is first given a uniform surface charge in the dark after a suitable period of dark adaptation. It is then exposed to a pattern of actinic radiation which has the effect of 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 may be selected to be electrostatically attracted to the surface in accordance with the charge pattern contained thereon. The imagewise deposited marking material may then be either permanently fixed to the surface of the sensitive element by known means such as heat, pressure, solvent vapor, or the like, or transferred to a second element to which it may similarly be fixed.

Various photoconductive insulating materials have been employed in the manufacture of electrophotographic elements. Selenium and selenium alloys vapor 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.

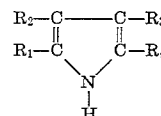
Recently, many organic compounds have demonstrated useful photoconduction. Some organic photoconductors can be especially useful in electrophotography because they can be uniformly coated in the form of an optically clear film. Many organic photoconductor compositions, when coated as a film or layer, on a suitable support 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 use of organic compounds in photoconductor compositions to form electrophotographic layers has proceeded on a compound by compound basis. Nothing has yet been discovered from the large number of different photoconductive substances which permits effective prediction and therefore selection of compounds which exhibit desirable electrophotographic properties.

It is an object of this invention to provide novel photoconductive elements containing at least one organic photoconductor in an amount sufficient to be useful in electrophotographic applications.

It is another object of this invention to provide novel photoconductive elements containing a particularly effective pyrrole photoconductor.

It is likewise an object of this invention to provide new photoconductive elements containing an organic photoconductor that can be effectively sensitized with pyrylium and thiapyrylium sensitizers.

These and further objects and advantages of this invention have been achieved by the discovery of the unusually advantageous photoconductive properties of the 2,3,4,5-tetraarylpyrroles. Compounds of this type correspond to the general formula:



in which R₁, R₂, R₃ and R₄ are aryl radicals such as phenyl and naphthyl radicals. Further, from one to four of such aryl radicals may be substituted at one or more of the available positions. For example, substituents for the aryl moieties R₁, R₂, R₃, or R₄ can include amino radicals and substituted amino radicals such as p-aryl-amino and p-alkylamino, halogen atoms, such as chlorine, bromine and iodine, and alkyl and methoxy radicals. The foregoing specific class of compounds includes compounds such as

- 2,3,4,5-tetra-p-diethylaminophenylpyrrole;
- 2,5-di-p-dimethylaminophenyl-3,4-diphenylpyrrole;
- 2,5-di-p-diphenylaminophenyl-3,4-diphenylpyrrole;
- 2,3,4,5-tetra-p-diphenylaminophenylpyrrole;
- 2,5-diphenyl-3,4-di-p-diphenylaminophenylpyrrole;
- 2,5-diphenyl-3,4-di-(4-dibutylaminophenyl)pyrrole;
- 2,5-di-(2,4-dimethylaminophenyl)-3,4-diphenylpyrrole;
- 2,5-di-(4-tolyl)-3,4-diphenylpyrrole;
- 2,5-diphenyl-3,4-di-(4-anisyl)pyrrole;
- 2,5-di-(4-chlorophenyl)-3,4-diphenylpyrrole;
- 2,3,4,5-tetra-(4-iodophenyl)pyrrole;
- 2,3,4,5-tetra-p-tolylpyrrole and
- 2,3,4,5-tetra-p-anisylpyrrole.

The compounds included are generally known and their derivatives can readily be synthesized. For example, the preparation of 2,3,4,5-tetra-p-tolylpyrrole and 2,3,4,5-tetra-p-anisylpyrrole are described in R. Kuhn and H. Kaines, *Biochem. and Biophys. Acta*, 12, 325 (1953) and F. E. King and B. D. Paterson, *J. Chem. Soc.*, 1936, 400, respectively.

A large number of pyrrole compounds, as well as most complex organic compounds, have shown a degree of photoconduction when incorporated into suitable structures and tested for their electrophotographic usefulness. In particular, some 2,3,5-triaryl pyrroles have shown useful photoconductive properties. 1,2,3,4,5-pentaryl pyrroles have also been prepared and tested in photoconductive compositions. Surprisingly, however, the electrophotographic response of the pyrroles is greatly enhanced when the 2, 3, 4 and 5 position carbon atoms of the pyrrole ring are aryl substituted. Conversely, when all five ring positions are aryl substituted, the resultant compounds generally are of marginal solubility, and give an insignificant electrophotographic response.

It was therefore not anticipated that the specific tetraaryl pyrrole compounds of this invention should provide an enhanced electrophotographic effectiveness over the triarylpyrroles. If any effect on the photoconduction of the compounds attributable to the aryl substitution of only the carbon atoms in the pyrrole ring could have been foreseen, such a prediction would probably have favored a

reduction in electrophotographic effectiveness by such substitution. As further described hereinafter, the substitution, contrary to what would be expected, produces a class of compounds exhibiting highly useful photoconductivity.

In preparing electrophotographic elements utilizing the photoconductor compounds of this invention, the photoconductive composition compounds may be formulated and coated with or without a binder. When a binder is employed, the compound is dissolved in a solution of binder and solvent and then after thorough mixing, the composition is coated on an electrically conducting support in a well-known manner, such as swirling, spraying, doctor-blade coating, and the like.

Preferred binders for use in preparing the photoconductive layers comprise polymers having fairly high dielectric strength and which are good electrically insulating film-forming vehicles. Materials of this type comprise styrene-butadiene copolymers; silicone resins; styrene-alkyd resins; silicone-alkyd resins; soya-alkyd resins; poly(vinyl chloride); poly(vinylidene chloride); vinylidene chloride; acrylonitrile copolymers; poly(vinyl acetate); vinyl acetate; vinyl chloride copolymers; poly(vinyl acetals), such as poly(vinyl butyral); polyacrylic and methacrylic esters, such as poly(methylmethacrylate), poly(n-butylmethacrylate), poly(isobutyl methacrylate), etc.; polystyrenes; nitrated polystyrene polymethylstyrene; isobutylene polymers; polyesters, such as poly(ethylenealkaryloxyalkylene terephthalate); phenol-formaldehyde resins; ketone resins; polyamide; polycarbonates; etc. Methods of making resins of this type have been described in the prior art, for example, styrene-alkyd resins can be prepared according to the method described in U.S. Patents 2,361,019 and 2,258,423. Suitable resins of the type contemplated for use in the photoconductive layers of the invention are sold under such trade names as Vitel PE-101, Cymac, Piccopale 100, and Saran F-220. Other types of binders which can be used in the photoconductive layers of the invention include such materials as paraffin, mineral waxes, etc.

Solvents of choice for preparing coating compositions of the present invention can include a number of solvents such as benzene, toluene, acetone, 2-butanone, chlorinated hydrocarbons, e.g., methylene chloride, ethylene chloride, etc., ethers, e.g., tetrahydrofuran, or mixtures of these solvents, etc.

In preparing the coating composition useful results were obtained where the photoconductor substance was present in an amount equal to at least about 1 weight percent of the coating composition. The upper limit in the amount of photoconductor substance present can be widely varied in accordance with usual practice. In those cases where a binder is employed, it is normally required that the photoconductor substance be present in an amount from about 1 weight percent of the coating composition to about 99 weight percent of the coating composition. A preferred weight range for the photoconductor substance 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 coating in the range of about 0.001 inch to about 0.01 inch before drying was useful for the invention. The preferred range of coating thickness was found to be in the range from about 0.002 inch to about 0.006 inch before drying.

Suitable supporting materials for coating the photoconductive layers of the present invention can include any of the electrically conducting supports, for example, paper (at a relative humidity above 20 percent); aluminum-paper laminates; metal foils such as aluminum foil, zinc foil, etc.; metal plates, such as aluminum, copper, zinc, brass, and galvanized plates; regenerated cellulose and cellulose derivatives; certain polyesters, especially polyesters having a thin electroconductive layer (e.g., cuprous iodide) coated thereon; etc. Suitable supporting

materials can also include the humidity-independent conducting layers of semiconductors dispersed in polymeric binders, as described in U.S. Patent No. 3,112,192.

The elements of 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 by the layer owing to 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 a 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, e.g., powder, a pigment in a resinous carrier, i.e., toner, or a liquid developer may 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. Patent 2,297,691, and in Australian Patent 212,315. In processes of electrophotographic reproduction such as in xerography, by selecting a developing particle which has as one of its components, a low-melting resin, it is possible to treat the developed photoconductive material with heat and cause the powder 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 United States and foreign patents, such as U.S. Patents 2,297,691 and 2,551,582, and in "RCA Review," vol. 15 (1954), pp. 469-484.

The photoconductive layers of the invention can also be sensitized to highly improved speed. Sensitizing compounds for use with the present photoconductive derivatives can include a wide variety of substances such as pyrylium and thiapyrylium salts of U.S. application Ser. No. 146,743, filed Oct. 23, 1961; fluorenes, such as 7, 12 - dioxo - 13 - oxo - dibenzo(a,h)fluorene, 5,10-dioxo-4a,11 - diazabenzob(b)fluorene, 3,13-dioxo-7-oxadibenzob(b,g) fluorene, and the like; aromatic nitro compounds of U.S. Patent 2,610,120; anthrones of U.S. Patent 2,670,285; quinones of U.S. Patent 2,670,286; benzophenones of U.S. Patent 2,670,287; thiazoles of U.S. Patent 2,732,301; mineral acids; carboxylic acids, such as maleic acid, dichloroacetic acid, and salicylic acid; sulfonic and phosphoric acids; and various dyes such as triphenylmethane, diarylmethane, thiazine, azine, oxazine, xanthene, phthalein, acridine, azo, and anthraquinone dyes. The preferred sensitizers of the invention, however, are pyrylium and thiapyrylium salts, fluorenes, carboxylic acids and the triphenylmethane dyes.

Where a sensitizing compound of the invention is to be used with a photoconductive layer of the invention, it is the usual practice to mix a suitable amount of the sensitizing compounds with the coating composition so that, after thorough mixing, the sensitizing compound is uniformly distributed in the coated element. In preparing

the photoconducting layers, no sensitizing compound is required to give photoconductivity in the layers which contain the photoconducting substances of the invention, so of course, the lower limit of sensitizer required in a particular photoconductive layer is zero. However, since relatively minor amounts of sensitizing compound give substantial improvement in speed in such layers, the sensitizer is preferred. 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 hydrophobic 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.

The invention will now be described by reference to the following examples.

EXAMPLE 1

A photoconductive layer of 2,3,4,5-tetraphenyl pyrrole was made for coating on a support material by mixing 0.15 part of the pyrrole photoconductor with 0.002 part of 2,6-(4-ethylphenyl)-4-(4-n-amyloxyphenyl) thiapyrylium perchlorate (hereinafter referred to as "Sensitizer A") and dissolving these together with 0.5 part by weight of a resinous polyester binder with suitable stirring in methylene chloride. The resultant mixture was then hand-coated on an aluminum-laminated paper support.

The polyester used is a copolymer of terephthalic acid and a glycol mixture comprising a 9:1 wt. ratio of 2,2-bis[4-(β -hydroxyethoxy)phenyl]propane and ethylene glycol. The coating thickness on the support was 0.004 inch thickness. After drying, the electrophotographic element was employed in a standard xerographic process which included charging under a positive corona and exposure from behind a transparency to a 3000° K. tungsten source of 20-foot-candle intensity at the point of exposure. The resulting electrostatic latent image on the element was rendered visible by dusting its exposed surface with an electrostatically attractable powder having optical density according to the method and materials described in U.S. Patent 2,297,691. According to the example, a high-quality positive image of the transparency was obtained.

EXAMPLE 2

The procedure of Example 1 was followed in preparing an electrophotographic element using 0.15 part 2,3,5-triphenyl pyrrole as the photoconductor in the coating composition. Exposure of the element and development by the method of Example 1 produced a visible image.

EXAMPLE 3

The procedure of Example 1 was followed in preparing an electrophotographic element using 0.15 part 1,2,3,4,5-pentaphenylpyrrole as the photoconductor in the coating composition. Exposure of the element and development produced a visible image.

EXAMPLE 4

The procedure of Example 1 was followed in preparing an electrophotographic element wherein the sensitizer used was 2,4-di(4-ethoxyphenyl)-6-(4-n-amyloxystyryl) pyrylium fluoroborate (hereinafter referred to as "Sensitizer B"). Testing by the method of Example 1 produced a visible image.

EXAMPLE 5

The procedure of Example 2 was followed in preparing an electrophotographic element wherein Sensitizer B was used.

EXAMPLE 6

The procedure of Example 3 was followed in preparing an electrophotographic element wherein the sensitizer used was Sensitizer B.

EXAMPLE 7

The elements prepared according to Examples 1-6 and an element not containing any photoconductor were tested by the following procedure: Each element was charged under positive corona source until the surface potential, as measured by an electrometer probe, reached 600 volts. It was then exposed to a light source in the manner of Example 1, with the exception that the negative transparency was replaced by a stepped density gray scale. The exposure caused 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 depended on the actual amount of exposure received by the area. The results of these measurements were then plotted on a graph of surface potential V vs. log exposure for each step. The actual speed of each element can then be expressed in terms of the reciprocal of the exposure required to reduce the surface potential to any fixed arbitrarily assigned value. The speeds thus obtained are tabulated below:

Photoconductor	Sensitizer	
	A	B
2,3,5-triphenylpyrrole.....	150	200
2,3,4,5-tetraphenylpyrrole.....	200	500
1,2,3,4,5-pentaphenylpyrrole.....	<1	<1
None.....	14	12

Comparable results were obtained as described in the above table when compounds such as 2,3,4,5-tetra-p-tolylpyrrole and 2,3,4,5-tetra-p-anisylpyrrole were substituted for the 2,3,4,5-tetraphenylpyrrole as photoconductors.

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 as described hereinabove and as defined in the appended claims.

I claim:

1. An organic photoconductor-containing electrophotographic element exhibiting photosensitivity when electrically charged comprising in a unitary structure a support material, an electrically conducting material and a photoconductive composition comprising a photosensitizing material and a photoconductive amount of a 2,3,4,5-tetraaryl pyrrole-containing composition in conducting relationship with the electrically conducting material.

2. The photoconductor-containing element of claim 1 wherein the aryl moieties of the pyrrole are phenyl radicals.

3. The photoconductor-containing element of claim 1 wherein the aryl moieties of the pyrrole contains substituents selected from the group of radicals consisting of an alkyl radical, a methoxy radical, an amino radical and a halogen atom.

4. The photoconductor-containing element of claim 1 wherein the photoconductive composition comprises at least about 1 percent by weight of 2,3,4,5-tetraphenylpyrrole, about 25 percent to about 99 percent by weight of a binder material and an amount of a photosensitizing material effective to enhance the photoconductivity of the photoconductor to actinic radiation.

5. The photoconductor-containing element of claim 1 wherein the photoconductive composition comprises at least about 1 percent by weight of 2,3,4,5-tetra-p-tolylpyrrole, about 25 percent to about 99 percent by weight of a binder material and an amount of a photosensitizing material effective to enhance the photoconductivity of the photoconductor to actinic radiation.

6. The photoconductor-containing element of claim 1 wherein the photoconductive composition comprises at least about 1 percent by weight of 2,3,4,5-tetra-p-anisyl-

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pyrrole, about 25 percent to about 99 percent by weight of a binder material and an amount of a photosensitizing material effective to enhance the photoconductivity of the photoconductor to actinic radiation.

7. The photoconductor-containing element of claim 1 wherein the photoconductive composition contains a photosensitizing material selected from compositions containing compounds selected from the group consisting of pyrylium and thiapyrylium compounds.

8. In an electrophotographic process wherein an electrostatic charge pattern is formed on a photoconductive element, the improvement characterized in that said comprising a photosensitizing material and a 2,3,4,5-tetra-aryl pyrrole as a photoconductive material.

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GEORGE F. LESMES, Primary Examiner

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U.S. Cl. X.R.

96—1; 260—313.1

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,485,625 Dated December 23, 1969

Inventor(s) Charles J. Fox

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

Column 7, line 12 after "said", the following should be inserted

---photoconductive element has a photoconductive layer---

SIGNED AND
SEALED
MAY 12 1970

(SEAL)

Attest:

Edward M. Fletcher, Jr.
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