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3,740,218

PHOTOCONDUCTIVE ELEMENTS CONTAINING COMPLEXES OF LEWIS ACIDS AND FORMALDEHYDE RESINS

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7 Claims

ABSTRACT OF THE DISCLOSURE

Certain formaldehyde resins are disclosed which form complexes with Lewis acids such as trinitrofluorenone to produce photoconductive compositions and elements of high speed and utility for electrostatic image formation.

This invention relates to electrophotography, and in particular to photoconductive compositions and elements.

The process of xerography, as disclosed by Carlson in U.S. 2,297,691, employs an electrophotographic element comprising a support material bearing a coating of a normally insulating material whose electrical resistance varies with the amount of incident electromagnetic radiation it receives during an imagewise exposure. The element, commonly termed a photoconductive element, is first given a uniform surface charge, generally 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 differentially reducing the potential of this 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 either the charge pattern or discharge pattern as desired. Deposited marking material can 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 can similarly be fixed. Likewise, the electrostatic charge pattern 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 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 the present-day document copying applications.

Since the introduction of electrophotography, a great many organic compounds have also been screened for their photoconductive properties. As a result, a very large number of organic compounds have been known to possess some degree of photoconductivity. Many organic compounds have revealed a useful level of photoconduction and have been incorporated into photoconductive compositions. 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

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

It is, therefore, an object of this invention to provide a novel class of photoconductors having useful photosensitivity when electrically charged.

It is another object to provide novel photoconductor-containing compositions which exhibit useful electrical speeds.

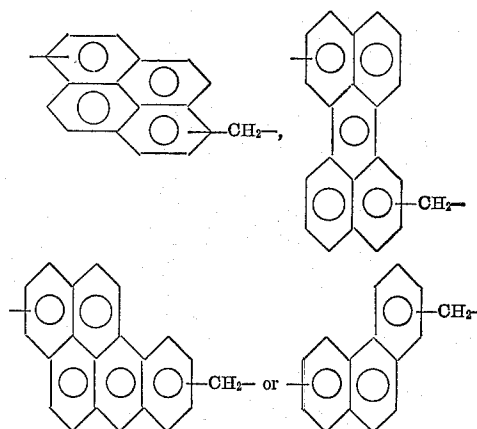
It is a further object of the invention to provide an improved process utilizing the novel photoconductors described herein.

These and other objects are accomplished by employing certain polynuclear aromatic materials condensed with formaldehyde to form a resin and forming a complex between the resin and certain Lewis acids such as

2,4,7-trinitro-9-fluorenone,
2,4,5,7-tetranitro-9-fluorenone,
2,6-dichloro-p-benzoquinone,
2,5-dinitro-9-fluorenone,
1,5-dichloro-2,4-dinitro-benzene,
2,5-dichloro-p-benzoquinone,
tetrachloroquinone,
2-chloro-3,5-dinitropyridine, and
2,4,5,7,9-pentanitro-indeno[2,1-a]-fluorene-11,12-dione,
2,5-diphenyl-p-benzoquinone,
2,3-dichloro-1,4-naphthoquinone,
9-dicyanomethylene-2,4,7-trinitrofluorene,

that are accompanied by spectral shifts. The photoconductive efficiency of said combinations is quite high and the observed photoconductivity can be further enhanced by employing additional sensitizers.

The compounds which form the complex of the present invention include resins which are formed by the condensation of phenanthrene or a polynuclear aromatic material having from 4 to 5 fused, carbocyclic, aromatic rings and containing from about 16 to about 20 carbon atoms with formaldehyde and which comprise units having the formula:



and an aforementioned Lewis acid such as 2,4,7-trinitro-9-fluorenone (TNF). The combination of such compounds as pyrene-formaldehyde, perylene-formaldehyde, benzo-pyrene-formaldehyde, and phenanthrene-formaldehyde as resins with TNF exhibit increased speed and efficiency over the combination of the aromatic materials alone complexed with TNF.

According to this invention, it has been found that the photoconductor complexes described herein have enhanced speed over those photoconductor complexes described in the prior art. In particular, substantial increases in speeds are obtained as compared to speeds attainable with many other closely related compounds. These increases in speed are observed when the coating accepts a

suitable potential (e.g., 500-600 volts) and the relative speed of the coating is determined on the basis of the reciprocal of the exposure required to reduce the potential of the surface charge by 100 volts (shoulder speed) or to 100 volts (toe speed). The terms "shoulder speed" and "toe speed" are terms known in the photographic art with reference to "H and D" curves. As used herein, such terms refer to corresponding curves resulting from exposure plotted against voltage. The reduction of the surface potential to 100 volts or below is significant in that it represents a requirement for suitable broad area development of an electrostatic image. The relative speed at 100 volts is a measure of the ability to produce and hence to develop or otherwise utilize the electrostatic image. When many conventional photoconductors are used, the surface potential frequently does not drop to or below 100 volts and therefore no speed can be assigned to such a composition. When most photoconductors are used in photoconductive compositions, the surface potentials of such resultant compositions usually drop below 100 volts and thus, a definite speed can be ascertained. However, these speeds are improved when the photoconductors' complexes of this invention are employed. The preparation of the complex is performed by simply mixing the constituents together when preparing a dope for the preparation of coatings.

Electrophotographic elements of the invention can be prepared to contain the photoconducting complexes of the present invention in the conventional manner, i.e. by blending a dispersion or solution of a photoconductive complex or the constituent compounds together with a binder, when necessary or desirable, and coating or forming a self-supporting layer with the materials. Likewise, other photoconductors known in the art such as those described in Light, Belgian Patent 705,117 dated Apr. 16, 1968, can be combined with the present photoconductors. In addition, supplemental materials useful for changing the spectral sensitivity or electrophotosensitivity of the element can be added to the composition of the element when it is desirable to produce the characteristic effect of such materials.

The photoconductive layers of the invention can also be sensitized by the addition of effective amounts of sensitizing compounds to exhibit improved electrophotosensitivity. Sensitizing compounds useful with the photoconductive compounds of the present invention can be selected from a wide variety of materials, including such materials as pyrylium dye salts including thiapyrylium dye salts and selanapyrylium dye salts disclosed in Van Allan et al., U.S. Patent 3,250,615; fluorenes, such as 7,12-dioxo - 13 - dibenzo(a,h)fluorene, 5,10-dioxo-4a,11-diazobenz(b)-fluorene, 3,13 - dioxo-7-oxadibenzo(b,g)-fluorene, and the like; aggregate-type sensitizers of the type described in Light, Belgian Patent 705,117, dated Apr. 16, 1968; aromatic nitro compounds of the kinds described in U.S. Patent 2,610,120; anthrones like those disclosed in U.S. Patent 2,670,284; quinones, U.S. Patent 2,670,286; benzophenones U.S. Patent 2,670,287; thiazoles U.S. Patent 2,732,301; 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 carboxycyanine), merocyanine, diarylmethanes, thiazine, axine, oxazine, xanthene, phthalein, acridine, azo, anthraquinone dyes and the like and mixtures thereof.

Where a sensitizing compound is employed with an organic photoconductor complex to form a sensitized electrophotographic element, it is the normal practice to mix a suitable amount of the sensitizing compound with the coating compound 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 con-

sistent with the practice of this invention. In preparing the photoconductive layers, no sensitizing compound is required to give photoconductivity in the layers which contain the photoconducting substances, therefore, no sensitizer is required in a particular photoconductive layer. 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 photoconductive layer to give the 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.

While the Lewis acid and the condensation resin in combination according to the invention may be used together without additional binder materials, it is sometimes desirable for binders to be employed. Preferred binders would then include materials compatible with the Lewis acid and condensation resin which are film-forming and exhibit fairly high dielectric strength.

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, etc., including substituted aromatic hydrocarbons such as toluene, xylene, mesitylene, 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, dioxane;

(5) Mixtures of the above.

In preparing the photoconductive coating compositions of the present invention useful results are obtained where the photoconductive complex is present in an amount equal to at least about 0.1 weight percent of the coating composition. The upper limit in the amount of photoconductive material present can be widely varied to at least 90% by weight in accordance with usual practice.

Coating thicknesses of the photoconductive layer on a support can vary widely. Normally, a wet coating thickness in the range of about 0.001 inch to about 0.01 inch is useful in the practice of the invention. A preferred range of coating thickness is from about 0.002 inch to about 0.006 inch 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 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 supports.

An especially useful 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. 3,007,901, 3,245,833 and 3,267,807.

The compositions of the present invention can be employed in photoconductive elements useful 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, 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 owing to 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 imagewise 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 reflex or bireflex 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 by virtue of the fact that light energy striking the photoconductor causes the electrostatic charge in the light struck 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 there, i.e., either the charged or uncharged areas rendered visible, by treatment with a medium comprising electrostatically responsive particles having optical density. The developing electrostatically responsive particles can be in the form of a dust, or powder and generally comprise a pigment in a resinous carrier called a toner. 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 described in the following U.S. Pats. 3,040,704; 2,786,439; 2,786,440; 2,786,441; 2,811,465; 2,874,063; 2,984,163; 3,117,884 and reissue Re. 25,779. Liquid development of the latent electrostatic image may also be used. In liquid development the developing 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, U.S. Pat. 2,297,691 and in Australian Pat. 212,315. In dry developing processes the most widely used method of obtaining a permanent record is achieved by selecting a developing particle which has as one of its components a low-melting resin. Heating the powder image then causes the resin to melt or fuse into or on the element. The powder is, therefore, caused to adhere permanently to the surface of the photoconductive layer. In other cases, a transfer of the charge image or powder 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 fusing or fusing respectively. 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.

An increasing use of electrophotographic elements has occurred in the field of recording data displayed on a cathode ray tube (CRT). Advantages gained through such use include attractive high photographic speed and short time of access to a visible recorded image. One difficulty often encountered in such recording is that the electrophotographic element utilized does not have proper response to the emission of the CRT phosphors utilized. In addition, the element itself is often so highly colored as to result in a developed image having essentially no contrast. Such a condition would make visible observa-

tion difficult or impossible and would also prevent or make difficult the production of further copies of original image.

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

Forty grams of pyrene, 9.0 g. of paraformaldehyde were combined in a flask with 0.2 g. of anhydrous zinc chloride. The mixture was heated for six hours at 225° C. A first dope (A) is prepared containing the following components:

Poly [4,4'-isopropylidenebis (phenyleneoxyethylene)-coethylene terephthalate] -----g--	0.75
Pyrene-formaldehyde resin -----g--	0.75
2,4,7-trinitro-9-fluorenone (TNF) -----g--	0.50
Dichloromethane -----ml--	11.7

A second dope (B), similar to the first, is prepared, in which the pyrene-formaldehyde resin is replaced with an equimolar portion of pyrene. Each dope is coated at a wet thickness of 150 microns on a suitable conductive support such as a film of poly(ethylene terephthalate) bearing a layer of evaporated nickel. The combination of TNF and the resin in dope A produces a complex as evidenced by a shift in the spectral absorption pattern. The speed of the element is 1000 with positive charging and 400 with negative charging, measured at 100 volts below the 600 volt surface potential to which the element is initially charged. The color of the coated layer is brownish, compared with the light yellow color of pyrene alone. The speed of the control element, when measured as indicated previously, is 55 for both positive and negative polarity of initial charging.

EXAMPLE 2

To a boiling solution of 3.0 g. (0.10 mole) of paraformaldehyde in 100 ml. of formic acid is added 17.8 g. (0.10 mole) of phenanthrene. After six hours of reflux, the liquid is decanted from the solid which separates, and the solid is dissolved in dichloromethane. The residual formic acid is removed by extraction with aqueous potassium carbonate. Evaporation of the dichloromethane gives the resinous product, phenanthrene-formaldehyde. Two photoconductive coating dopes are prepared, one containing the phenanthrene-formaldehyde resin and the other containing monomeric phenanthrene. The dopes have the following composition:

Poly(4,4'-isopropylidenediphenylene carbonate) -----g--	0.75
Resin or monomer -----g--	0.50
2,4,7-trinitro-9-fluorenone (TNF) -----g--	0.42
Dichloromethane -----ml--	11.7

Coating conditions are the same as in Example 1. When tested according to the procedure outlined in Example 1, the negative and positive speeds of the element containing

the resin complex are 560 and 170, respectively, while the corresponding speeds for the element containing monomeric phenanthrene are too low to be measured. The spectral absorption extension of the element containing the phenanthrene-formaldehyde resin is to a wavelength of 700 nm., while that of the control element is 530 nm. The combinations of perylene or benzo[a]pyrene condensed with formaldehyde similarly give complexes with TNF which are detectable by analogous spectral shifts.

EXAMPLE 3

An anthracene-formaldehyde resin is prepared using the general procedure of Example 2 substituting anthracene for phenanthrene. Next, two photoconductive coating dopes are prepared, each containing 1.2 g. of poly-(4,4'-isopropylidenephenylene carbonate), 0.8 g. of a combined formaldehyde resin and 0.67 g. of trinitrofluorenone in dichloromethane solvent. The dopes are then coated on a conducting support as in Example 1 to form electrophotographic elements. The first element is prepared using a dope of the above composition containing the anthracene-formaldehyde resin. A second element is prepared using a dope prepared as above and which contains the phenanthrene-formaldehyde resin of Example 2. Coating conditions used in forming these elements are as described in Example 1. Next, the elements are measured for electrophotographic speed as in Example 1 only using as the exposure source a 3000° K. tungsten light modulated with a filter pack to simulate the wavelength distribution of the emission spectrum of a P-11 phosphor. A P-11 phosphor is a standard phosphor used in cathode ray tubes. This phosphor has an emission peak at 460 nm. (λ max.). The speeds obtained using the anthracene-formaldehyde control coating are 4.5 and 10 for positive and negative charging, respectively. The element representing this invention exhibited positive and negative shoulder speeds of 9 and 23, respectively. A further advantage of the element of this invention is that the color of the coating is orange which does not tend to unduly obscure the visibility of black toner which is imagewise deposited thereon. On the other hand, the anthracene-formaldehyde resin containing coating resulted in a dark red to brown coating which obscures the visibility of black toner deposited thereon.

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

We claim:

1. An electrophotographic element comprising a conductive support having coated thereon a photoconductive composition comprising a polymeric film-forming binder and from about 0.01 to about 90 percent by weight of a photoconductive material, said material being formed by an amount of a Lewis acid and an amount of a resin effective to form a complex of the Lewis acid with the

resin, said Lewis acid selected from the group consisting of

2,4,7-trinitro-9-fluorenone,
2,4,5,7-tetranitro-9-fluorenone,
2,6-dichloro-p-benzoquinone,
2,5-dinitro-9-fluorenone,
1,5-dichloro-2,4-dinitrobenzene,
2,5-dichloro-p-benzoquinone,
tetrachloroquinone,
2-chloro-3,5-dinitro pyridine,
2,4,5,7,9-pentanitroindene[2,1-a]-fluoren-11,12-dione,
2,5-diphenyl-p-benzoquinone,
2,3-dichloro-1,4-naphthoquinone,
9-dicyanomethylene-2,4,7-trinitrofluorene,

said resin formed by the condensation of formaldehyde with phenanthrene or a polynuclear aromatic material selected from the group consisting of carbocyclic aromatic hydrocarbons having from 4 to 5 fused rings and containing from 16 to 20 carbon atoms.

2. The invention of claim 1 wherein said resin is a phenanthrene-formaldehyde resin.

3. The invention of claim 1 wherein said resin is a pyrene-formaldehyde resin.

4. The element of claim 1 wherein said photoconductive composition contains a sensitizer for said photoconductive complex.

5. The element of claim 1 wherein the photoconductive complex is formed from pyrene-formaldehyde resin and 2,4,7-trinitrofluorenone.

6. The element of claim 1 wherein the photoconductive complex is formed from phenanthrene-formaldehyde resin and 2,4,7-trinitrofluorenone.

7. The invention of claim 1 wherein said photoconductive composition comprises from about 0.005% to about 5% by weight of a sensitizer for said photoconductive composition.

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