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[54] POLYARYLALKANE-TERMINATED, SOLVENT-RESISTANT POLYCARBONATE RESINS AS PHOTOCONDUCTORS

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[52] **U.S. Cl.** ..... **96/1.5,** 96/1 PC, 260/47 XA, 117/37 LE

[51] **Int. Cl.** **G03g 5/02**

[58] **Field of Search** ..... 96/1.5, 1.6; 252/501; 260/47 XA, 390, 391, 393

[56] **References Cited**

UNITED STATES PATENTS

3,542,547	11/1970	Wilson	96/1.6
2,999,750	9/1961	Miller et al.	252/501 X
3,408,186	10/1968	Mammino	96/1.5
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3,567,686	3/1971	White et al.	260/47 XA

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[57] **ABSTRACT**

Polyarylalkane-terminated polycarbonate resins are disclosed which when utilized in photoconductive layers and elements show superior stability and resistance to lixiviation by the carrier liquid of liquid xerographic developers.

2 Claims, No Drawings

POLYARYLALKANE-TERMINATED, SOLVENT-RESISTANT POLYCARBONATE RESINS AS PHOTOCONDUCTORS

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

The process of xerography, as disclosed by Carlson in U.S. Pat. No. 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 expose 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. In particular liquid developers have found wide acceptance for such elements because of the high resolution images they make possible. Unfortunately the carrier liquid of conventional liquid developers attacks most known photoconductor systems and by a process called lixiviation leaches or otherwise removes photoconductor compounds, binders, sensitizers and the like from the element. Further the element can be softened and then mechanically injured during use.

Thus far, the selection of various compounds suitable for incorporation into photoconductive compositions to form electrophotographic layers has proceeded on a compound-by-compound basis. Effective prediction of the types of compounds which will exhibit desired properties from among the large number of different photoconductive substances available is difficult.

It is, therefore, an object of this invention to provide novel binder-photoconductors containing elements which exhibit high photosensitivity when electrically charged and are resistant to attack by conventional carrier liquids.

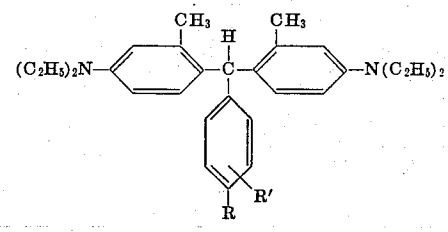
It is another object to provide photoconductor-containing compositions which in addition exhibit high electrical speeds.

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

Also, it is yet another object of this invention to provide solvent resistant electrophotographic elements.

These and other objects of the invention are accomplished by providing certain polycarbonate resins with photoconductive substituents generally selected from moieties of substituted triarylmethane compounds. Such a binder-photoconductor compound resists lixiviation when utilized in electrophotographic elements used with liquid development. Lixiviation of the photoconductor out of the photoconductive element and into the liquid developer has produced erratic results such as non-uniform development, contamination of the developer, and limited the useful life of the photoconductor element to extremely short run cycles which could be as low as 1 or 2 cycles depending on the rate of extraction of the photoconductor from the light-sensitive element.

The preferred polymer-photoconductor compositions or oligomers of the present invention are generally isopropylidenediphenol polycarbonate polymers terminated with photoconductor moieties characterized by the following general formula:



wherein R is selected from the group consisting of a hydroxyl group, a carboxy group, an hydroxy-alkoxy group or an amino group and R′ is hydrogen, alkyl or alkoxy or the like.

Electrophotographic elements prepared with the oligomers of the present invention can be prepared in a conventional manner such as, for example, by blending a dispersion of solution of the oligomer and additional photoconductor or binder when necessary or desirable together with other addenda and coating or forming a self-supporting layer with the oligomer containing material. Addenda useful in the practice of the present invention are generally supplemental materials added, i.e., dyes and the like which are useful for changing the spectral sensitivity or electrophotosensitivity of the element prepared therefrom where particular effects are desired.

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 oligomers 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 selenapyrylium dye salts disclosed in VanAllen et al. U.S. Pat. No. 3,250,615; fluorenes, such as 7,12-dioxo-13-dibenzo(a,h)fluorene, 5,10-dioxo-4a,11-diazabenzo(b)fluorene, 3,13-dioxo-7-oxadibenzo(b,g)fluorene, and the like; aggregate-type sensitizers of the type described in Belgian Pat. No. 705,117 dated Apr. 16, 1968; aromatic nitro compounds of the kind described in U.S. Pat. No. 2,610,120; anthrones like those disclosed in U.S. Pat. No. 2,670,284; quinones, U.S. Pat. No. 2,670,286; benzophenones U.S. Pat. No. 2,670,287; thiazoles U.S. Pat. No. 2,732,301; mineral acids; carboxylic acids, such as maleic acid, di- and tri-chloroacetic acids, and salicyclic acid; sulfonic and phosphoric acids; and various dyes, such as cyanine (including carbocyanine), merocyanine, diarylmethane, thiazine, azine, oxazine, xanthene, phthalein, acridine, azo, anthraquinone dyes and the like and mixtures thereof. The sensitizers preferred for use with the oligomers of this invention are selected from pyrylium salts including selenapyrylium

salts and thiapyrylium salts, and cyanine dyes including carbocyanine dyes.

Where a sensitizing compound is employed with the oligomer 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 element. 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, 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 photoconductor-incorporating layer to give effective increases in speed can vary widely. The optimum concentration in any given case will vary with the specific oligomer 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 polycarbonate resins utilized or useful in the preparation of the oligomers of the present invention include 4,4'-isopropylidenediphenol polycarbonate.

Solvents useful for preparing coating compositions with the oligomers of the present invention can include a wide variety of organic solvents for the components of the coating composition. For example, benzene; toluene; acetone; 2-butanone; chlorinated hydrocarbons such as methylene chloride; ethylene chloride; and the like; ethers, such as tetrahydrofuran and the like, or mixtures of such solvents can advantageously be employed in the practice of this invention.

In preparing the coating compositions utilizing the oligomers 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 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 galvinized plates, vapor deposited metal layer 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 carboxyester lactone of a maleic anhydride-vinyl acetate copolymer, cuprous iodide and the like. Such conducting layers and method for their optimum preparation and use are disclosed in U.S. Pat. Nos. 3,007,901, 3,245,833 and 3,267,807.

The oligomer 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 are 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 a latent 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. Pat. Nos.: 2,786,439; 2,786,440; 2,786,441; 2,811,465; 2,874,063; 2,984,163; 3,040,704; 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. No. 2,297,691 and in Australian Pat. No. 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. Pat. Nos. 2,297,691 and 2,551,582, and in "RCA Review," Vol. 15 (1954) pages 469–484.

The oligomer 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

In this example photoconductors were made wherein polycarbonate oligomers were terminated with a photoconductor molecule having a single hydroxyl group. Specifically, a short (average length, four units) isopropylidenediphenol polycarbonate was terminated with bis(4-diethylamino-2-methyl-phenyl)-[3-methoxy-4-(2-hydroxyethoxy)phenyl]methane in the following manner: to a solution of 5.0 g. (0.010 mole) of bis (4-diethylamino-2-methyl-phenyl)-[3-methoxy-4-(2-hydroxyethoxy) phenyl]methane and 4.6 g. (0.020 mole) of 4,4'-isopropylidenediphenol in 10 ml of dry methylene chloride and 10 ml of dry pyridine was added dropwise 2.6 g. (0.026 mole) of phosgene in 20 ml of dry methylene chloride with stirring at 25°. This mixture was then extracted successively with excess dilute hydrochloric acid, three portions of water, 5 percent aqueous sodium bicarbonate and water again. The product was precipitated by pouring the organic solution into isopropyl alcohol. When tested in the photoconductor system disclosed in Light et al, British Pat. No. 1,153,506 , i.e. Lexan polycarbonate plus photoconductor plus 4-(4-dimethylaminophenyl)-2,6-diphenyl thiapyrylium perchlorate 2%) the following data were obtained:

Photoconductor	Conc. (percent of total composition)	"H and D" electrical speed, shoulder/toe +	"H and D" electrical speed, shoulder/toe −	Leach-out test (percent photoconductor extracted [2]) In 1 hr.	Leach-out test (percent photoconductor extracted [2]) In 4 hrs.
Control [3]	20	6,100/768	5,230/990	0.4	[4] 2.0
Oligomer of Ex. 1	[1] 40	4,000/340	4,000/1,300	0.1	0.1

[1] The oligomer contains only 50 percent effective photoconductor.
[2] Extraction rate was determined from a static soaking of one square inch of sample film in 10 ml. of Isopar G followed by ultraviolet absorption spectroscopical analysis of the supernatant liquid.
[3] Bis(4-diethylamino-2-methylphenyl)phenylmethane.
[4] 3 hours.

EXAMPLE 2

To increase the photoconductor content in the oligomer, a single bisphenol unit was coupled through carbonate groups with a similar monohydroxy compound, bis (4-diethylamino-2-methyl-phenyl)-4-(2-hydroxyethoxy)phenylmethane in the following manner:

To a solution of 10 g. (.021 mole) of bis(4-diethyl-amino-2-methyl-phenyl)-[4-(2-hydroxyethoxy)phenyl]methane in 10 ml of dry methylene chloride and 5 ml of dry pyridine was added over several minutes a solution of 3.8 g. (0.011 mole) of 4,4'-isopropylidenediphenyl bischloroformate in 10 ml of dry methylene chloride. After the mixture was stirred an hour it was extracted with aqueous sodium bicarbonate and the organic layer was poured into ethanol to precipitate the crude product. This material, in 40 ml of methylene chloride, was extracted with aqueous sodium bicarbonate then shaken with 1 percent aqueous sodium dithionite to discharge the green color. After extraction with two portions of water the organic solution was poured into isopropyl alcohol to precipitate an amorphous solid which softens at about 105°.

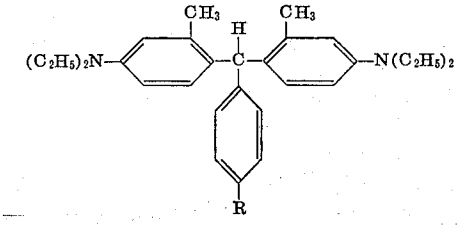
Anal. Calculated for $C_{79}H_{96}N_4O_8$: C, 77.2; H, 7.8; N, 4.6
found: C, 76.9; H, 7.8; N, 4.7

When tested as described in Example 1 the following results were obtained:

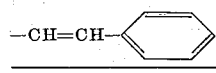
Photoconductor	Conc., percent of total composition	Electrical "H and D" speeds [1] shoulder/toe +	Electrical "H and D" speeds [1] shoulder/toe −	Leach-out test, percent OP extracted in 4 hrs.
Control (see Example 1)	20	6,100/768	5,230/990	[2] 2.0
Control	50			5.0
Oligomer of Ex. 2 [3]	20	2,500/100	2,000/330	0.1
Oligomer of Ex. 2 [3]	50	12,000/1,000	8,000/800	0.1

[1] The sensitizer utilized in this case was 4-(4-dimethylamino-phenyl)-2,6-diphenyl thiapyrylium fluoroborate.
[2] 3 hours.
[3] The oligomer contains 77 percent effective photoconductive.

It will be thus noted that the oligomer photoconductors appear to offer both low leachability and good electrophotographic speeds. Furthermore, it should be noted that merely adding high molecular weight groups to the photoconductor does not necessarily decrease its leachability. Thus in the following table it will be noted that merely increasing the size of R in the general structure does not necessarily decrease the leachability of the photoconductor.



PERCENT PHOTOCONDUCTOR EXTRACTED BY ISOPAR G

R	0.8M OP percent extracted after— 1 hr.	0.8M OP percent extracted after— 4 hrs.
$-CH_2CH_2CH_3$	0.1	0.1
	0.3	2.0

In addition to the foregoing oligomer precursors other bisphenols and glycols other than 4,4'-isopropylidenediphenyl may be used. Additionally other triphenylmethane derivatives have demonstrated utility in the preparation of the oligomers.

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.

We claim:

1. An electrophotographic element resistant to lixiviation by liquid developers, said element comprising a conductive support having thereon a photoconductive composition comprising an oligomeric isopropylidene diphenol polycarbonate terminated with bis(4-diethylamino-2-methyl)-(4-substituted phenyl)methane photoconductor moieties.

2. In an electrophotographic process wherein a photoconductive element is charged, imagewise exposed, and liquid developed, the improvement wherein said element is comprised of a conductive support having thereon a photoconductive composition comprising an oligomeric isopropylidene diphenol polycarbonate terminated with bis(4-diethylamino-2-methyl)-(4-substituted phenyl)methane photoconductor moieties.

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