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[54] **PHOTOCONDUCTIVE COMPOSITIONS AND ELEMENTS**
33 Claims, No Drawings

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[50] Field of Search 96/1.5-1.7;
260/429, 448, 45.75; 252/501

[56]

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ABSTRACT: Photoconductive compositions and elements containing as photoconductors organometallic compounds derived from Group III a metals are described.

PHOTOCONDUCTIVE COMPOSITIONS AND ELEMENTS

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 in the absence of charge 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 latent image can be transferred to a second element and developed there.

Various photoconductive insulating materials have been employed in the manufacture of electrophotographic elements. For example, vapors of selenium 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 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 photoconductors having high photosensitivity when electrically charged.

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

It is also an object to provide novel photoconductor-containing compositions which can be positively and negatively charged.

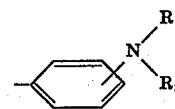
It is another object to provide novel transparent electrophotographic elements having high-speed characteristics.

It is a further object of this invention to provide novel electrophotographic elements useful for producing images electrophotographically by reflex or bireflex processes.

These and other objects of this invention are accomplished with electrophotographic elements having coated thereon photoconductive compositions containing as photoconductors organometallic compounds having at least one amino-aryl substituent attached to a Group IIIa metal atom.

The metallic substituents of these organometallic photoconductors are Group IIIa metals in accordance with the Periodic Table of the Elements (Handbook of Chemistry and Physics, 38th edition, pp. 394-95) and include boron, aluminum, gallium, indium and thallium. The organometallic photoconductors of this invention can be substituted in the metallo nucleus with a wide variety of substituents but at least one of the substituents should be an amino-aryl radical. The amino radical can be positioned anywhere on the aromatic nucleus, but best results are obtained if the aryl moiety is a phenyl radical having the amino group in the 4 or para position. Typical substituents attached to the metal nucleus include the following:

- a. a hydrogen atom;
- b. an alkyl group including substituted alkyl groups such as an aralkyl group e.g., benzyl, a halo-alkyl group e.g., a chloromethylene group, and aminoalkyl group e.g., $-\text{CH}_2-\text{N}(\text{Et})_2$, etc.;
- c. an aryl group such as phenyl, naphthyl, etc.; including substituted aryl groups such as aminoaryl e.g.,



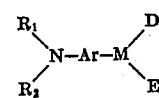
wherein R_1 , R_2 are each a hydrogen atom, an alkyl group including a substituted alkyl group such as an aralkyl group or an aryl group including a substituted aryl group such as an alkaryl group or a haloaryl group;

- d. an oxygen-containing group such as an alkoxy or aryloxy group;
- e. an amino group e.g., $-\text{NH}_2$ including substituted amino groups such as dialkylamino, diphenylamino, alkylamino, phenylamino, etc.; and
- f. a Group IIIa organometallic group e.g.,



M being a Group IIIa metal and R_9 and R_{10} being any of the substituents set forth in a. through e. above.

Illustrative photoconductors of this invention preferably have the following structure:



wherein:

D and E can be either

- a. a hydrogen atom;
- b. an aryl group including unsubstituted and substituted aryl groups such as phenyl, naphthyl, dialkylaminophenyl, dialkylaminonaphthyl, etc.;
- c. an alkyl group having 1 to 8 carbon atoms;
- d. an alkoxy group having 1 to 8 carbon atoms;
- e. an aryloxy group such as a phenoxy group or;
- f. an amino group e.g.,



R_3 and R_4 each being a hydrogen atom, an alkyl group or an aryl group;

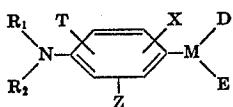
Ar is an arylene group including a substituted arylene group e.g., a phenylene group, a naphthylene group, an alkylphenylene group, a halophenylene group, etc.;

M is a Group IIIa metal;

R₁ and R₂ can be either

- a. a hydrogen atom,
- b. an alkyl group having 1 to 8 carbon atoms or
- c. an aryl group such as a phenyl or naphthyl group

Particularly improved results are obtained when those photoconductors having the following structure are used:



wherein:

M, D, E, R₁ and R₂ are the same as defined above and T, X and Z can be either

- a. a hydrogen atom,
- b. an alkyl group having 1 to 8 carbon atoms,
- c. an aryl group including a substituted aryl group e.g., phenyl, naphthyl, tolyl halophenyl, aminophenyl, etc.,
- d. an alkoxy group having 1 to 8 carbon atoms,
- e. an aryloxy group such as a phenoxy group,
- f. a halogen atom such as chlorine, bromine or iodine or,
- g. an amino group e.g.,



R₇ and R₈ each being a hydrogen atom, an alkyl group having 1 to 8 carbon atoms or an aryl group such as phenyl or naphthyl. X, T and Z can be the same or different and can be positioned in the 2, 3, 5 or 6 positions on the phenylene ring.

Some typical organometallic photoconductors of this invention include:

TABLE I

1. Tri-p-diethylaminophenylborane
2. Tri-p-diphenylaminophenylborane
3. Tri-p-methylaminophenylgallium
4. Methyl-phenyl-p-diethylaminophenylborane
5. 2 Naphthyl-p-dimethylaminophenylborane
6. p-Diisopropylaminophenylborane
7. Di-p-diethylaminophenylborane
8. Ethoxy-p-dimethylaminophenyl aluminum hydride
9. Diphenoxy-p-dibutylaminophenyl aluminum
10. Tri-(2,b-dimethyl4-diethylaminophenyl)indium
11. 2-chloro-4-dimethylaminophenyl gallium hydride
12. Tri-(2,6-diphenoxo-4-diethylaminophenyl)thallium
13. Tri-(2,6-dimethoxy-4-dimethylaminophenyl)thallium
14. Diphenylamino-p-diethylaminophenylborane
15. Dimesityl-4-dimethylaminophenylborane
16. Dimesityl-4-dimethylaminophenylborane
17. Dimesityl-(3,5-dimethyl-4-methoxyphenyl)borane
18. Dimesityl-4-diphenylaminophenylborane
19. 1,2Bis(p-diethylaminophenyl)diborane
20. 1-Phenyl-2-methyldiborane

Electrophotographic elements of the invention can be prepared with the photoconducting compounds of the invention in the usual manner, i.e., by blending a dispersion or solution or a photoconductive compound together with a binder, when necessary or desirable, and coating or forming a self-supporting layer with the photoconductor-containing material. Mixtures of the photoconductors described herein can be employed. Likewise, other photoconductors known in the art 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.

Sensitizing compounds useful with the photoconductive

- 5 compounds of the present invention can include a wide variety of substances such as pyrylium salts including thiapyrylium and selenapyrylium salts of U.S. Pat. No. 3,250,615, issued May 10, 1966; fluorenes, such as 7,12-dioxo-13-dibenz(a,h)flourene, 5,10-dioxo-4a,11 3,13-dioxo-7-ox-adibenz(a,g)fluorene, trinitrofluorenone, tetranitrofluorenone and the like; aromatic nitro compounds of U.S. Pat. No. 2,610,120; anthrones of U.S. Pat. No. 2,670,285; quinones of U.S. Pat. No. 2,670,286; benzophenones of U.S. Pat. No. 2,670,287; thiazoles of U.S. Pat. No. 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, anthraquinone dyes and many other suitable sensitizing dyes. The preferred sensitizers for use with the compounds of this invention are pyrylium salts including selenapyrylium and thiapyrylium salts, fluorenes, carboxylic acids, and triphenylmethane dyes.
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- 15
- 20
- 25

Where a sensitizing compound is to be used within a photoconductive layer as disclosed herein it is conventional practice to mix a suitable amount of the sensitizing compound with the coating composition so that, after thorough

- 30 mixing the sensitizing compound is uniformly distributed throughout the desired layer of the coated element. In preparing the photoconducting layers, no sensitizing compound is needed for the layer to exhibit photoconductivity. The lower limit of sensitizer required in a particular photoconductive 35 layer is, therefore, zero. However, since relatively minor amounts of sensitizing compound give substantial improvement in the electrophotographic speed of such layers, the use of some sensitizer is preferred. The amount of sensitizer that can be added to a photoconductor incorporating layer to give 40 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 45 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.

- 50 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. Materials of this type comprise styrene-butadiene copolymers; silicone resins; styrene-alkyd resins; silicone-alkyd resins; soy-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.; polystyrene; nitrated polystyrene; polymethylstyrene; isobutylene polymers; polyesters, such as poly (ethylenealkaryloxyalkylene terephthalate); phenoformaldehyde resins; ketone resins; polyamides; polycarbonates; polythiocarbonates; poly(ethyleneglycol-co-bishydroxyethoxyphenol propane terephthalate); copolymers of vinyl haloarylates and vinyl acetate such as poly(vinyl-m-bromobenzoate-covinylacetate); 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. Pat. Nos. 2,361,019 and 2,258,423. Suitable resins of the type contemplated for use in the photoconductive layers of the invention 75 are sold under such tradenames as Vitel PE-101, Cymac, Pic-

copale 100, Saran F-220, Lexan 105 and Lexan 145. 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 are obtained where the photoconductor 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 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 is useful for the practice of this 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 although useful results can be obtained outside of this range.

Suitable supporting materials for coating the photoconductive layers of the present invention can include any of a wide variety of electrically conducting supports, for example, paper (at a relative humidity above 20 percent); aluminum-paper laminates; metal foil 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 or aluminum and the like. An especially useful conducting support can be prepared by coating a support material such as polyethylene terephthalate with a layer containing a semiconductor dispersed in a resin. Such conducting layers both with and without insulating barrier layers are described in U.S. Pat. No. 3,245,833. Likewise, a suitable conducting coating can be prepared from the sodium salt of a carboxyester lactone maleic anhydride and a vinyl acetate polymer. Such kinds of conducting layers and methods for their optimum preparation and use are disclosed in U.S. Pat. Nos. 3,007,901 and 3,267,807.

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 aforementioned xerographic process. As previously explained, 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 attractive particles having optical density. The developing electrostatically attractive particles can be in the form of a dust, e.g., powder, 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. Pat. No. 2,297,691 and in Australian Pat. 212,315. In processes of electrophotographic reproduction such as in xerography, by selecting a developing particle which has 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 U.S. and foreign patents, such as U.S. Pats. Nos. 2,297,691 and 2,551,582, and in "RCA Review," vol. 15 (1954), pages 469-484.

10 The present invention is not limited to any particular mode of use of the new electrophotographic materials, and the exposure technique, the charging method, the transfer (if any), the developing method, and the fixing method as well as the 15 materials used in these methods can be selected and adapted to the requirements of any particular technique.

20 Electrophotographic materials according to the present invention can be applied to reproduction techniques wherein different kinds of radiations, i.e., electromagnetic radiations 25 as well as nuclear radiations, can be used. For this reason, it is pointed out herein that although materials according to the invention are mainly intended for use in connection with methods comprising an exposure, the term "electrophotography" wherever appearing in the description and the claims, is to be interpreted broadly and understood to comprise both xerography and xeroradiography.

25 The invention is further illustrated by the following examples which include preferred embodiments thereof.

EXAMPLE I

Tri-p-diethylaminophenylborane is separately incorporated into a coating dope have the following composition:

- 40 a. 0.25 gram of Lexan 145 (trade name of General Electric Company for poly(4,4'-isopropylidenediphenylcarbonate as a binder
- b. 0.25 gram of tri-p-diethylaminophenylborane as a photoconductor
- c. 4.5 grams of a 0.0029 g./ml. solution of [4-(p-dimethylaminophenyl)-2,6-diphenylthiapyrylium perchlorate] in methylene chloride as a sensitizer for the photoconductor
- d. 7.7 grams of a composition *

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55 *Prepared by the method described in U.S. Ser. No. 674,005 filed Oct. 9, 1967 by W. A. Light containing 3.92 grams of Lexan 145, 0.008 g. of [4-(p-dimethylaminophenyl)-2,6-diphenylthiapyrylium perchlorate] and 26.8 ml. of methylene chloride. The resulting composition is handcoated at a wet thickness of 0.006 inch on a conducting layer comprising the sodium salt of a carboxyester lactone, such as described in U.S. Pat. No. 3,120,028, which in turn is coated on a cellulose acetate film base. The coating blocks are maintained at a temperature of 90° F. These electrophotographic elements are charged under a positive or negative corona source until the surface potentials, as measured by an electrometer probe, reach about 600 volts. They are then subjected to exposure from behind a stepped density gray scale to a 3000° K. tungsten source. The exposure causes reduction of the surface potentials of the elements under each step of the gray scale from their initial potential, V_0 to some lower potential, V whose exact value depends on the actual amount of exposure in meter-candle-seconds received by the areas. The results of the measurements are plotted on a graph of surface potential V vs. log exposure for each step. The shoulder speed 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 by 100 volts. The toe speed 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 above composition has positive and negative shoulder speeds of 2,500 and 3,400 respectively. Positive and negative toe speeds are 250 and 900 respectively.

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EXAMPLE II

Example I is repeated except the sensitizer is replaced by 75 2,6-bis(4-ethylphenyl)-4-(amyloxyphenyl)thiapyrylium

19. An electrophotographic element comprising a support having coated thereon a composition comprising a photoconductor which is a Group III α organometallic compound having at least one amino-aryl group attached to a Group III α metal atom.

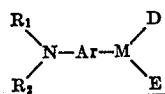
20. An electrophotographic element comprising a support having coated thereon a composition comprising a photoconductor which is a Group III α organometallic compound having attached to a Group III α metal atom (1) at least one amino-aryl group and (2) at least one substituent selected from the group consisting of a hydrogen atom, an alkyl group, an aryl group, a Group III α organometallic group, an alkoxy group, an aryloxy group and an amino group.

21. The electrophotographic element as defined in claim 20 wherein the Group III α organometallic compound is borane.

22. The electrophotographic element as defined in claim 20 wherein the Group III α organometallic compound is a *p*-dialkylaminophenylborane.

23. The electrophotographic element as defined in claim 20 wherein the Group III α organometallic compound is *p*-diethylaminophenylborane.

24. An electrophotographic element comprising a support having coated thereon a composition comprising a photoconductor represented by the formula:



wherein:

Ar is an arylene group;

D and E are each selected from the group consisting of an aryl group, an alkyl group, a hydrogen atom, an alkoxy group, an aryloxy group and an amino group;

M is a Group III α metal; and

R₁ and R₂ are each selected from the group consisting of an alkyl group, and aryl group and a hydrogen atom.

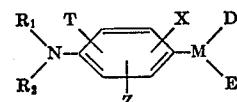
25. The electrophotographic element as defined in claim 24 wherein M is boron.

26. The electrophotographic element as defined in claim 24 wherein R₁ and R₂ are each an alkyl group.

27. The electrophotographic element as defined in claim 24 wherein D and E are each a *p*-dialkylaminophenyl group.

5 28. The electrophotographic element as defined in claim 24 wherein Ar is a phenylene group.

10 29. An electrophotographic element comprising a support having coated thereon a composition comprising a photoconductor represented by the formula:



wherein:

R₁ and R₂ are each selected from the group consisting of an alkyl group, an aryl group and hydrogen;

D and E are each selected from the group consisting of an aryl group, an alkyl group, hydrogen, an alkoxy group, an aryloxy group and an amino group;

M is a Group III α metal; and

20 X, T and Z are each selected from the group consisting of hydrogen, an alkyl group, an aryl group, an alkoxy group, an aryloxy group, a halogen atom and an amino group.

25 30. The electrophotographic element as defined in claim 29 wherein M is boron.

30 31. The electrophotographic element as defined in claim 30 wherein D and E are each a *p*-dialkylaminophenyl group.

32. The electrophotographic element as defined in claim 30 wherein R₁ and R₂ are each an alkyl group.

33. An electrophotographic element comprising a support having coated thereon a photoconductive composition comprising 10 to about 60 weight percent of tri-*p*-diethylaminophenylborane as a photoconductor, 0.005 to about 5.0 weight percent of [4-(*p*-diethylaminophenyl)-2,6-diphenylthiapyrylium perchlorate] as a sensitizer and a polymeric binder for said photoconductor.