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3,567,450
PHOTOCONDUCTIVE ELEMENTS CONTAINING SUBSTITUTED TRIARYLAMINE PHOTOCONDUCTORS

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ABSTRACT OF THE DISCLOSURE

Triarylamines having at least one of the aryl radicals substituted by either a vinyl radical or a vinylene radical 15 having at least one active hydrogen-containing group are good organic photoconductors in electrophotographic systems.

This invention relates to electrophotography, and in ²⁰ 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 actinic 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 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, 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 the discharge pattern as desired. The deposited marking material can then be either permanently fixed to the surface of the sensitve 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 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 are known to possess some 60 degree of photoconductivity. Many organic compounds have revealed a useful level of photoconduction and have been incorporated into photoconductive compositions. Optically clear organic photoconductor-containing elements having desirable electrophotographic properties can 65 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 70 element which is reusable; that is, it can be used to form subsequent images after residual toner from prior images

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has been removed by transfer and/or cleaning. Thus far, the selection of organic compounds for incorporation into photoconductive 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 tested which permits effective prediction and therefore selection of particular compounds exhibiting the desired electrophotographic properties.

It is, therefore, an object of this invention to provide photoconductive elements for use in electrophotography containing a novel class of organic photoconductors having enhanced photosensitivity when electrically charged.

It is also an object to provide electrophotographic elements having a layer of a novel photoconductive composition which can be positively or negatively charged. It is another object to provide novel transparent electro-

photographic 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 organic photoconductive compositions containing a triarylamine photoconductor wherein at least one of the aryl radicals is substituted by either a vinyl radical or a vinylene radical having at least one active hydrogencontaining group. The phrase "vinylene radical" includes substituted as well as unsubstituted vinylene radicals and also includes those radicals having at least one and as many as three repeating units of vinylene groups such as $(CH=CH)_n$ wherein n is an integer of from one to three. Groups which contain active hydrogen are well known in the art, the definition of this term being set forth in several textbooks such as "Advanced Organic Chemistry," R. C. Fuson, pp. 154–157, John Wiley & Sons, 1950. The term "active hydrogen-containing group" as used herein includes those compounds encompassed by the discussion in the textbook cited above and in addition includes those compounds which contain groups which are hydrolyzable to active hydrogen-containing groups. Typical active hydrogen-containing groups substituted on the vinylene radical of the triarylamine according to this invention include:

- (a) carboxy radicals,
- (b) hydroxy radicals,
- (c) ethynyl radicals including substituted ethynyl radicals such as hydroxy ethynyl radicals, aryl ethynyl radicals and alkyl ethynyl radicals,
- (d) ester radicals (e.g.,

wherein R is alkyl or aryl) including cyclic ester radicals e.g.,

wherein R is a cyclic alkylene radical connected to a vinylene combination such as is found in coumarin derivatives.

- (e) carboxylic acid anhydride radicals,
- (f) semicarbazono radicals,
- (g) cyano radicals,
- (h) acyl halide radicals (e.g.,

etc.), and

(i) amido radicals (e.g.,

wherein R is a hydrogen atom, an alkyl group or an aryl group).

Other active hydrogen-containing groups include sub- 10 stituted and unsubstited alkylidyne oximido radicals.

The preferred photoconductors of this invention are represented by the following structure:

$$\begin{array}{c} Ar_1 \\ N-Ar_3-\begin{pmatrix} C=C \\ \mid & \mid \\ R_1 & R_2 \end{pmatrix}_n -X \end{array}$$

wherein:

(a) Ar_1 and Ar_2 are each a phenyl radical including 20a substituted phenyl radical such as a halophenyl radical, an alkyl phenyl radical or an aminophenyl radical;

(b) Ar₃ is an arylene radical including a substituted arvlene radical such as a phenylene radical or a naphthylene radical,

(c) R₁ and R₂ are each hydrogen, a phenyl radical including a substituted phenyl radical or a lower alkyl radical preferably having 1-8 carbon atoms;

(d) X is either (1) an active hydrogen-containing group such as a carboxy radical, an acyl halide radical, an amido radical, a carboxylic acid anhydride radical, an ester radical, a cyano radical, a hydroxy radical, a semicarbazono radical, an ethynyl radical, or a methylidyne oximido radical or (2) hydrogen, provided that when X is hydrogen R₁ and R₂ are also hydrogen; and

(e) n is an integer of one to three.

The vinyl or vinylene radical can be substituted in any position on the arylene nucleus. However, when Ar₃ is phenylene, particularly good results are obtained if the substitution occurs in the para position.

The organic photoconductors of this invention exhibit substantial improvements in speed over comparable photoconductors which do not have both an active hydrogencontaining group (including groups hydrolyzable to active hydrogen-containing groups) and a vinyl or vinylene 45 group. Also, those compounds having an unsubstituted vinyl radical show improvements in electrical speed as organic photoconductors when compared to similar compounds which lack such a group. Thus, a compound according to the above formula when n is zero and X is 50an active hydrogen-containing group would not exhibit the higher speeds attainable when compared to a compound where n is 1, 2, or 3. Furthermore, if X is a group other than an active hydrogen-containing group or hydrogen (and n is 1, 2 or 3), the photoconductivity of the resulting compound is generally lower than that attainable if such groups are present. Finally, if X is a group other than an active hydrogen-containing group or hydrogen and n in the above formula is zero, the resultant speeds attainable from such compounds when used as organic photoconductors are somewhat lower than those attainable from comparable compounds according to this invention.

Those compounds in which Ar₁ and Ar₂ in the above formula are phenyl radicals generally have improved 65 photo-conducting properties over those which are substituted by one or two alkyl or benzyl radicals. Thus, pdiphenyl amino-cinnamic acid and methyl p-diphenylaminocinnamate display improved electrical speeds over p-(N-methyl, N-phenylamino) cinnamic acid, methyl p- 70 (N-methyl, N-phenylamino) cinnamate or methyl p-dibenzylaminocinnamate. Also, ethyl p-diphenylaminophenylvinylacrylate has enhanced electrical speed properties compared to ethyl p-dimethylaminophenylvinylacrylate.

Some typical photoconductors of this invention are:

Table I

(I) 4-(p-diphenylaminophenyl)-3-buten-1-yne

(II) p-diphenylaminostyrene

(III) ethyl p-diphenylaminocinnamate

(IV) methyl p-diphenylaminocinnamate

(V) p-diphenylaminocinnamoyl chloride

(VI) p-diphenylaminocinnamic acid N,N-diphenylamide

(VII) p-diphenylaminocinnamic acid anhydride

(VIII) 3-(p-diphenylaminophenyl)-2-butenoic acid

(IX) bis(p-diphenylaminobenzal)succinic acid (X) 4-N,N-bis(p-bromophenyl)aminocinnamic acid

(XI) 1-(4-diphenylamino)naphthacrylic acid

(XII) p-diphenylaminocinnamic acid

(XIII) p-diphenylaminocinnamonitrile (XIV) 7-diphenylamino coumarin

(XV) p-diphenylaminophenylvinylacrylic acid

(XVI) p-diphenylaminobenzyl p'-diphenylaminocin-

namate

(XVII) 7-(p-diphenylaminostyryl)coumarin

(XVIII) p-diphenylaminocinnamyl alcohol

(XIX) 4-diphenylaminocinnamaldehyde semicarbazone (XX) O-p-diphenylaminocinnamoyl p'-diphenylaminobenzaldehyde oxime

(XXI) p-diphenylaminocinnamaldehyde oxime, and

(XXII) 1,3-bis(p-diphenylaminophenyl)-2-propen-1-ol

These compounds can be prepared by the methods set forth in a copending application filed concurrently herewith entitled "Novel Substituted Triarylamines, Serial Number 706,799, filed Feb. 20, 1968."

Electrophotographic elements of the invention can be prepared with these photoconducting compounds in the usual manner, i.e., by blending a dispersion or solution of a photoconductive compound together with a binder, when necessary or desirable, and coating or forming a self-supporting layer with the photoconductor-containing materials. Mixtures of the photoconductors described herein can be employed. Likewise, other photoconductors known in the art 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 compounds of the present invention can include a wide variety of substances such as pyrylium, thiapyrylium, and selenapyrylium salts of U.S. Patent 3,250,615, issued May 10, 1966; fluorenes, such as 7,12-dioxo-13-dibenzo(a,h) fluorene, 5,10 - dioxo-4a,11-diazabenzo(b)fluorene, 3,13dioxo-7-oxadibenzo-(b,g)fluorene, trinitrofluorenone, tetranitrofluorenone 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, anthraquinone dyes and many other suitable sensitizing dyes. The preferred sensitizers for use with the compounds of this invention are pyrylium and thiapyrylium salts, fluorenes, carboxylic acids, and triphenylmethane dyes.

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 compounds with the coating composition so that, after thorough mixing, the sensitizing compound is uniformly distributed throughout the desired layer of the coated element. In preparing the photoconducting layers, no 75 sensitizing compound is needed for the layer to exhibit

photoconductivity. The lower limit of sensitizer required in a particular photoconductive 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 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. Generally, a sensitizer is added to the coating composition in an amount by weight from about 0.005 to about 5.0 percent by weight of the total coating composition.

Preferred binders for use in preparing the present photoconductive layers are film-forming polymeric binders having fairly high dielectric strength which are good 20 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; 25 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); phenol-formaldehyde resins; ketone resins; polyamides; polycarbonates; polythiocarbonates; poly(ethylene-glycol-cobishydroxyethoxy-phenyl propane terephthalate); nuclear substituted vinyl haloarylates such as poly(vinyl metabromobenzoate-co-vinyl acetate); 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 40 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, Saran F-220 and Lexan 105. 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 photo- 75 particular technique.

conductive 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 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 and the like. Metal (e.g., nickel, etc.) conducting layers deposited by high vacuum deposition techniques can be coated at low coverages so as to be substantially transparent to facilitate image exposure through the support. An especially useful conducting support can be prepared by coating a support material such as poly(ethylene terephthalate) with a layer containing a semiconductor dispersed in a resin. Suitable conducting layers both with and without insulating barrier layers are described in U.S. Patent 3,245,833. Other suitable conducting layers are described in U.S. Patent 3,120,-028. Likewise, a suitable conducting coating can be prepared from the sodium salt of a carboxyester lactone of 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. 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 blank electrostatic charge by placing 30 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 techniques, 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 charge 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, 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 to 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. Patents 2,297,691 and 2,551,582, and in "RCA Review," vol. 15, (1954) pages 469-484.

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 materials used in these methods can be selected and adapted to the requirements of any

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Electrophotographic materials according to the present invention can be applied to reproduction techniques wherein different kinds of radiations, i.e., electromagnetic radiations 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 xeroradiog-

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

EXAMPLE 1

Organic photoconductors of the type described herein are separately incorporated into a coating dope having the following composition:

Organic photoconductor: 0.5 g. Polymeric binder: 1.05 g.

Sensitizer: 0.02 g.

Methylene chloride: 11.7 ml.

The resulting compositions are coated at a wet thickness of 0.004 inch on a conducting layer comprising the sodium salt of a carboxyester lactone, such as described in U.S. 3,120,028, which in turn is coated on a cellulose acetate film base. The coating blocks are maintained at a tem- 30 perature 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 between about 500 and 600 volts. They are then subjected to exposure from behind a stepped density 35 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, Vo, to some lower potential, V whose exact value depends on the actual amount of exposure in meter-candle- 40 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 speed is the numerical expression of 104 multiplied by the reciprocal of the exposure in meter-candle-seconds required to reduce the 500 45 to 600 volt charged surface potentials to 100 volts above 0 volt. 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 a latent image. This speed at 100 volts is a measure of the ability to pro- 50 duce and hence forth to develop or otherwise utilize the latent image, higher speeds requiring less illumination to produce a latent image. When the photoconductor is absent from the coating, the surface potential does not drop to, or below, 100 volts and no speed value can be assigned. 55 This is also the case when a compound is present in the composition but is ineffective as a photoconductor. The speeds of the various photoconductive compositions are shown in Table II below. The sensitizers used are referred to below as follows:

- (B) 2,6-(4-ethylphenyl)-4-(4-amyloxyphenyl)thiapyrylium perchlorate
- (F) 2,4-bis(4-ethoxyphenyl)-6-(4-n-amyloxystyryl)pyrylium fluoborate
- (G) 2,4-bis(4-ethylphenyl)-6-(4-styrylstyryl)-
- pyrylium perchlorate
 (H) 2,6-bis(4-ethoxyphenyl)-4-(4-n-amyloxy-phenyl)
 thiapyrylium perchlorate

The data in the following Table II represents the positive speeds at 100 volts of various compositions prepared as described above containing several of the organic photoconductors set forth in Table I. The binder employed is poly(vinyl meta-bromobenzoate-co-vinyl acetate).

8 TABLE II

| | Speed at 100 volts Sensitizer | | |
|---------------------------|--|--------------------------|--|
| | | | |
| Photoconductor | F | G | H |
| IIIVIIIVIIIVIIIVIIIVIIIVI | 250 400 - 230 400 230 - 250 | 360 320 420 230 | 280 360 250 320 120 195 |

The latent electrostatic images in each instance developed with conventional electrophotographic liquid developers (e.g., U.S. Patent 2,907,674) to form sharp dense images.

EXAMPLE 2

Example 1 is repeated except that the binder employed is a film-forming polycarbonate resin sold commercially as "Lexan" by General Electric Co. The photoconductor employed in the photoconductive composition is p-diphenylaminocinnamoyl chloride (Compound V). The positive speed at 100 volts for compositions containing sensitizer F is 260 and for sensitizer G the speed is 220.

EXAMPLE 3

In order to show the efficacy of the vinylene moiety in the photoconductors of this invention, two closely related compounds are tested for their electrophotographic speeds at 100 volts positive. The first compound, p-diphenylaminocinnamic acid (Compound XII) has a vinylene moiety while the second, 4-carboxytriphenylamine, is the same as compound XII but lacks a vinylene moiety. Two photoconductive compositions are prepared and tested according to Example 1 except the following composition is used:

Photoconductor: 0.15 g. Binder Vitel 1011: 0.50 g. Sensitizer F: 0.002 g. Dichloromethane: 5.0 ml.

 1 A polyester of terephthalic acid and a mixture of ethylene glycol (1 part by weight) and 2,2-bis[4-(\$\beta\$-hydroxyethoxy) phenyl]propane (9 parts by weight).

The speed of 4-carboxytriphenylamine is 50. The speed of Compound XII is 160.

EXAMPLE 4

In this example p-diphenylaminocinnamic acid is compared to 4-diphenylaminocinnamaldehyde to show the effectiveness of the active hydrogen-containing group as opposed to a compound having none. Two compositions containing these compounds are prepared and tested according to Example 3 except 0.8% of sensitizer B and 20% photoconductor are used. The positive 100 volt speed of 4-diphenylaminocinnamaldehyde is 21. The positive 100 volt speed of compound XII is 105. This represents a five-fold increase in speed which is attributable to the presence of the active hydrogen-containing group.

EXAMPLE 5

This example demonstrates the increases in speed attainable with a photoconducting compound having both a vinylene moiety and an active hydrogen-containing group such as compound XII as opposed to a photoconducting compound having neither moiety present such as triphenylamine. Thus, photoconducting compositions containing the above photoconductors are prepared and tested according to Example 1 except the following composition is used:

Photoconductor: 1.0 g.

Binder, poly(vinyl meta-bromo-benzoate-co-vinyl ace-

tate): 1.0 g. Sensitizer G: 0.02 g.

75 Dichloromethane: 11.7 ml.

The positive 100 volt speed of the composition containing triphenylamine is 130. The positive 100 volt speed of the composition containing compound XII is 630.

The importance of having two phenyl radicals attached to the nitrogen atom of the photoconducting compounds of this invention was discussed earlier. Thus, in the general formula set forth above, it is preferable that Ar₁ and Ar₂ are phenyl radicals or substituted phenyl radicals. In this example the photoconducting properties of pdiphenylaminocinnamic acid are compared to the properties of p-(N-methyl, N-phenylamino) cinnamic acid in accordance with the procedure used in Example 1. The sensitizer is F. p-(N-methyl, N-phenylamino)cin- 15 namic acid has a positive 100 volt speed of 30 compared to 320 for p-diphenylaminocinnamic acid.

EXAMPLE 7

The 100 volt positive speed of p-diphenplaminocin- 20 haloarylate. namonitrile is determined according to Example 1 using the following composition:

Photoconductor: 0.15 g. Vitel 101: 0.50 g. Sensitizer G: 0.002 g. Dichloromethane: 5.0 ml. The resultant speed is 110.

EXAMPLE 8

Coating dopes prepared in the manner set forth in Example 1 containing the compounds in Table I are coated in the manner described in Example 1. In a darkened room, the surface of each of the photoconductive layers so prepared is charged to a potential of about +600 volts under a corona charger. The layer is then covered with a transparent sheet bearing a pattern of opaque and light transmitting areas and exposed to the radiation from an incandescent lamp with an illumination intensity of about 75 meter-candles for 12 $_{40}$ seconds. The resulting electrostatic latent image is developed in the usual manner by cascading over the surface of the layer a mixture of negatively charged black thermoplastic toner particles and glass beads. A good reproduction of the pattern results in each instance.

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 hereinbefore and as defined in the appended claims.

1. An electrophotographic element comprising a conductive support having coated thereon a photoconductive composition comprising a photoconductor having the 55 structure:

$$\begin{array}{c}
Ar_1 \\
N-Ar_3-\begin{pmatrix} C=C \\ | & | \\ R_1 & R_2 \end{pmatrix}_n -X
\end{array}$$

wherein:

(a) Ar₁ and Ar₂ are phenyl radicals;

- (b) Ar₃ is an arylene radical selected from the group consisting of:
 - (1) a phenylene radical and
 - (2) a naphthylene radical;
- (c) R_1 and R_2 are each selected from the group consisting of:
 - bon atoms,
- (2) a phenyl or a substituted phenyl radical, and (3) a hydrogen atom;
- (d) X is selected from the group consisting of hydrogen, a carboxylic ester radical, a carboxy radical, 75

an ethynyl radical, an acyl halide radical, a cyano radical, a carboxylic acid anhydride radical, a hydroxy radical, a semicarbazono radical, an oximido radical and an amido radical; and

(e) n is an integer of 1 to 3.

- 2. A photoconductive element as defined by claim 1 wherein the photoconductive composition contains a sensitizer for said photoconductor.
- 3. An electrophotographic element as defined in claim wherein the photoconductive composition is sensitized with a compound selected from the group consisting of:
 - (a) a pyrylium salt,
 - (b) a thiapyrylium salt,
 - (c) a selenapyrylium salt,
 - (d) a fluorenone, and
 - (e) a triphenylmethane dye.
- 4. An electrophotographic element as defined in claim 4 wherein a binder is utilized for the photoconductor, said binder being a polymer of a nuclear substituted vinyl

5. An electrophotographic element as defined in claim 4 wherein a poly(ethylenealkaryloxykylene terephthalate) binder is utilized for the photoconductor.

6. An electrophotographic element comprising an elec-25 trically conductive support having coated thereon a photoconductive composition comprising a polymeric binder and a photoconductor selected from the group consisting

(a) ethyl p-diphenylaminocinnamate,

- (b) methyl p-diphenplaminocinnamate,
- (c) p-diphenylaminocinnamoyl chloride,
- (d) p-diphenylaminocinnamic acid N,N diphenyl-

(e) p-diphenylaminocinnamic acid,

- (f) p-diphenylaminocinnamic acid anhydride,
- (g) 3-(p-diphenylaminophenyl)-2-butenoic acid,
- (h) 4-N,N-bis(p-bromophenyl)aminocinnamic acid,
- (i) bis(p-diphenylaminobenzal) succinic acid,
- (j) 1-(4-diphenylamino) naphthacrylic acid,
- (k) p-diphenylaminocinnamonitrile,
- (1) p-diphenylaminostyrene,
- (m) p-diphenylaminophenylvinylacrylic acid, and (n) 7-diphenylamino coumarin.
- 7. A photoconductive element for use in electrophotography comprising a conductive support having coated thereon a photoconductive composition comprising:
 - (a) about 10 to 60% by weight based on said photoconductive composition of methyl p-diphenylaminocinnamate as a photoconductor, and
 - (b) a film-forming polymeric binder for said photoconductor.
- 8. A photoconductive element for use in electrophotography comprising a conductive support having coated thereon a photoconductive composition comprising:
 - (a) about 10 to 60% by weight based on said photoconductive composition of p-diphenylaminocinnamic acid anhydride as a photoconductor, and
 - (b) a film-forming polymeric binder for said photoconductor.
- 9. A photoconductive element for use in electrophotography comprising a conductive support having coated thereon a photoconductive composition comprising:
 - (a) about 10 to 60% by weight based on said photoconductive composition of 3-(p-diphenylaminophenyl)-2-butenoic acid as a photoconductor, and
 - (b) a film-forming polymeric binder for said photoconductor.
- 10. A photoconductive element for use in electrophotography comprising a conductive support having (1) a lower alkyl radical having from 1 to 8 car- 70 coated thereon a photoconductive composition comprising:
 - (a) about 10 to 60% by weight based on said photoconductive composition of p-diphenylaminocinnamic acid as a photoconductor, and
 - (b) a film-forming polymeric binder for said photoconductor.

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11. A photoconductive element for use in electrophotography comprising a conductive support having coated thereon a photoconductive composition comprising:

(a) about 10 to 60% by weight based on said photoconductive composition of ethyl p-diphenylamino-

cinamate as a photoconductor, and

(b) a film-forming polymeric binder for said photoconductor.

12. A photoconductive element for use in electrophotography comprising a conductive support having coated thereon a photoconductive composition comprising:

(a) about 10 to 60% by weight based on said photoconductive composition of methyl p-diphenylamino-15

cinnamate as a photoconductor,

(b) about 0.005 to 5.0% by weight based on said photoconductive composition of a pyrylium salt as a sensitizer, and

(c) poly(vinyl meta-bromobenzoate-co-vinyl acetate) 20

as a binder for said photoconductor.

- 13. A photoconductive element for use in electrophotography comprising a conductive support having coated thereon a photoconductive composition comprising:
 - (a) about 10 to 60% by weight based on said photoconductive composition of p-diphenylaminocinnamic acid anhydride as a photoconductor,
 - (b) about 0.005 to 5.0% by weight based on said photoconductive composition of a pyrylium salt as 30 a sensitizer, and
 - (c) poly(vinyl meta bromobenzoate-co-vinyl acetate) as a binder for said photoconductor.
- 14. A photoconductive element for use in electrophotography comprising a conductive support having 35 coated thereon a photoconductive composition comprising:
 - (a) about 10 to 60% by weight based on said photoconductive composition of 3-(p-diphenylaminophenyl)-2-butenoic acid as a photoconductor,
 - (b) about 0.005 to 5.0% by weight based on said photoconductive composition of a pyrylium salt as a sensitizer, and
 - (c) poly(vinyl meta-bromobenzoate-co-vinyl acetate) as a binder for said photoconductor.

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- 15. A photoconductive element for use in electrophotography comprising a conductive support having coated thereon a photoconductive composition comprising:
 - (a) about 10 to 60% by weight based on said photoconductive composition of p-diphenylaminocinnamic acid as a photoconductor,
 - acid as a photoconductor,
 (b) about 0.005 to 5.0% by weight based on said photoconductive composition of a pyrylium salt as a sensitizer, and
 - (c) poly(vinyl meta-bromobenzoate-co-vinyl acetate) as a binder for said photoconductor.
- 16. A photoconductive element for use in electrophotography comprising a conductive support having coated thereon a photoconductive composition comprising:
 - (a) about 10 to 60% by weight based on said photoconductive composition of ethyl p-diphenylaminocinnamate as a photoconductor,
 - (b) about 0.005 to 5.0% by weight based on said photoconductive composition of a pyrylium salt as a sensitizer, and
 - (c) poly(vinyl meta-bromobenzoate-co-vinyl acetate) as a binder for said photoconductor.
- 17. In an electrophotographic process wherein an electrostatic charge pattern is formed on an electrophotographic element, the improvement characterized in that the charge pattern is formed on the electrophotographic element of claim 4.

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