United States Patent [19]
Shea

[11] **3,765,884**
[45] **Oct. 16, 1973**

[54] **1-SUBSTITUTED-2-INDOLINE HYDRAZONE PHOTOCONDUCTORS**

[75] Inventor: **Michael D. Shea,** Rochester, N.Y.

[73] Assignee: **Eastman Kodak Company,**
Rochester, N.Y.

[22] Filed: **July 6, 1971**

[21] Appl. No.: **160,064**

[52] **U.S. Cl.** .... **96/1.6,** 96/1.5, 260/298, 260/304, 260/307 D, 260/309.2, 260/326.11, 260/326.12, 260/326.15
[51] **Int. Cl.** **G03g 5/06**
[58] **Field of Search** .... 96/1 R, 1 PC, 1.5; 260/240 G

[56] **References Cited**

UNITED STATES PATENTS

3,417,082	12/1968	Taylor	260/240 G
2,872,449	2/1959	Baumann et al.	260/240 G
3,499,902	3/1970	Coles et al.	260/240 G
3,149,990	9/1964	Coles et al.	260/240 G
3,290,147	12/1966	Mattor et al.	96/1.5
3,230,081	1/1966	Tomanek et al.	96/1.5

FOREIGN PATENTS OR APPLICATIONS

641,983	5/1962	Canada	96/1 PC

Primary Examiner—Roland E. Martin, Jr.
Attorney—Robert W. Hampton et al.

[57] **ABSTRACT**

1-Substituted-2-indoline hydrazones are useful as photoconductors.

6 Claims, No Drawings

1-SUBSTITUTED-2-INDOLINE HYDRAZONE PHOTOCONDUCTORS

This invention relates to electrophotography and more particularly to a novel class of photoconductive materials and compositions and elements produced therefrom.

Electrophotographic processes employ an electrophotographic or photoconductive element comprising a coating of a photoconductive insulating material on a conductive support. The element is given a uniform surface charge in the dark and then is exposed to an image pattern of activating electromagnetic radiation such as light or x-rays. The charge on the photoconductive element is dissipated in the illuminated area to form an electrostatic charge pattern which is then developed by contact with an electroscopic marking material. The marking material or toner, as it is also called, whether carried in an insulating liquid or in the form of a dry powder, deposits on the exposed surface in accordance with either the charge pattern or the discharge pattern, as desired. Then, if the photoconductive element is of the non-reusable type, the developed image is fixed by fusion or other means to the surface of the photoconductive element. If the element is of the reusable type, e.g., a selenium-coated drum, the image is transferred to another surface such as paper and then fixed to provide a copy of the original.

All of this is well-known and has been described in many patents and other literature, for example, in the patent of Carlson, U.S. Pat. No. 2,297,691, and in more recent works such as "Electrophotography" by R. M. Schaffert, published by Focal Press Ltd., 1965.

The photoconductive compounds that have been used in electrophotographic processes have included both organic and inorganic compounds. The organic photoconductors have been desirable for a number of reasons. For instance, the organics are less abrasive than the inorganics. They can be charged to high negative or positive potential while the inorganics often saturate at low potential and accept only a positive or a negative charge. In addition, the organics usually offer greater exposure latitude, can be spectrally sensitized more effectively and offer a number of other advantages over zinc oxide and other inorganics.

However, the selection of photoconductive compounds for incorporation into electrophotographic compositions 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 which compounds will exhibit desirable electrophotographic properties.

It is, therefore, an object of this invention to provide a novel class of photoconductive compounds.

It is another object of this invention to provide a novel class of photoconductors having high photosensitivity when electrically charged.

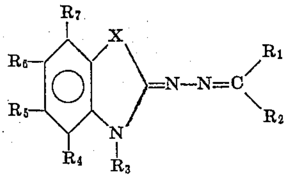
It is yet another object of this invention to provide novel photoconductor-containing compositions which exhibit useful electrical speeds when positively or negatively charged.

It is still another object of this invention to provide novel transparent electrophotographic elements having useful electrophotographic speeds.

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

These and other objects are accomplished by employing 1-substituted-2-indoline hydrazones as photoconductors. These materials can be substituted in various positions by any one or more of several substituents. Typically, the phenyl nucleus can be substituted with lower alkyl, aryl, halogen, alkoxy, aryloxy, amino or cyano groups, the nitrogen of the indole nucleus can be substituted with lower alkyl or aryl, and the terminal carbon atom can similarly be substituted with lower alkyl or aryl, all as hereinafter set forth with greater particularity.

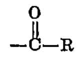
The 2-indoline hydrazones having utility according to the present invention are those corresponding to the following formula:



wherein:

R_1, R_2 and R_3 can be the same or different substituents each representing any of the following:

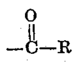
1. an alkyl radical having one to eight carbon atoms e.g., methyl, ethyl, propyl, butyl, isobutyl, octyl, etc, including a substituted alkyl group having one to eight carbon atoms such as
   - *a.* alkoxyalkyl, e.g., ethoxypropyl, methoxybutyl, propoxymethyl, etc,
   - *b.* aryloxyalkyl, e.g., phenoxyethyl, naphthoxymethyl, phenoxypentyl, etc,
   - *c.* aminoalkyl, e.g., aminobutyl, aminoethyl, aminopropyl, etc,
   - *d.* hydroxyalkyl, e.g., hydroxypropyl, hydroxyoctyl, etc,
   - *e.* aralkyl, e.g., benzyl, phenethyl, etc,
   - *f.* alkylaminoalkyl, e.g., methylaminopropyl, methylaminoethyl, etc, and also including dialkylaminoalkyl, e.g., diethylaminoethyl, dimethylaminopropyl propylaminooctyl, etc,
   - *g.* arylaminoalkyl, e.g., phenylaminoalkyl, diphenylaminoalkyl, N-phenyl-N-ethylaminopentyl, N-phenyl-N-ethylaminohexyl, naphthylaminomethyl, etc,
   - *h.* nitroalkyl, e.g., nitrobutyl, nitroethyl, nitropentyl, etc,
   - *i.* cyanoalkyl, e.g., cyanopropyl, cyanobutyl, cyanoethyl, etc,
   - *j.* haloalkyl, e.g., chloromethyl, bromopentyl, chlorooctyl, etc,
   - *k.* alkyl substituted with an acyl group having the formula



$$-\overset{\displaystyle O}{\overset{\|}{C}}-R$$

wherein R is hydroxy, hydrogen, aryl, e.g., phenyl, naphthyl, etc., lower alkyl having one to eight carbon atoms, e.g., methyl, ethyl, propyl, etc, amino, including substituted amino, e.g., diloweralkylamino, lower alkoxy having one to eight carbon atoms, e.g., butoxy, methoxy, etc, aryloxy, e.g., phenoxy, naphthoxy, etc;

2. an aryl group, e.g., phenyl, naphthyl, nathryl, fluorenyl, etc, including a substituted aryl group such as
   - *a.* alkoxyaryl, e.g., ethoxyphenyl, methoxyphenyl, propoxynaphthyl, etc,
   - *b.* aryloxyaryl, e.g., phenoxyphenyl, naphthoxyphenyl, phenoxynaphthyl, etc,
   - *c.* aminoaryl, e.g., aminophenyl, aminonaphthyl, aminoanthryl, etc,
   - *d.* hydroxyaryl, e.g., hydroxyphenyl, hydroxynaphthyl, hydroxyanthryl, etc,
   - *e.* biphenylyl,
   - *f.* alkylaminoaryl, e.g., methylaminophenyl, methylaminonaphthyl etc, and also including dialkylaminoaryl, e.g., diethylaminophenyl, dipropylaminophenyl, etc,
   - *g.* arylaminoaryl, e.g., phenylaminophenyl, diphenylaminophenyl, N-phenyl-N-ethylaminophenyl, naphthylaminophenyl, etc,
   - *h.* nitroaryl, e.g., nitrophenyl, nitronaphthyl, nitroanthryl, etc,
   - *i.* cyanoaryl, e.g, cyanophenyl, cyanonaphthyl, cyanoanthryl, etc,
   - *j.* haloaryl, e.g., chlorophenyl, bromophenyl, chloronaphthyl, etc,
   - *k.* aryl substituted with an acyl group having the formula



$$-\overset{O}{\overset{\|}{C}}-R$$

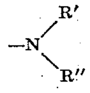
wherein R is hydroxy, hydrogen, aryl, e.g., phenyl, naphthyl, etc, amino, including substituted amino, e.g., diloweralkylamino, lower alkoxy having one to eight carbon atoms, e.g., butoxy, methoxy, etc, aryloxy, e.g., phenoxy, naphthoxy, etc, lower alkyl having one to eight carbon atoms, e.g., methyl, ethyl, propyl, butyl, etc,

   - *l.* alkanyl, e.g., tolyl, ethylphenyl, propyl, naphthyl, etc,

3. hydrogen:

R_4, R_5, R_6 and R_7 each represents any of the substituents set forth above for R_1, R_2 and R_3 and also can be any of the following:

1. an alkoxy group having 1 to 8 carbon atoms, e.g., methoxy, ethoxy, propoxy, butoxy, etc;
2. an aryloxy group, e.g., phenoxy, naphthoxy, etc;
3. halogen, e.g., chlorine, fluorine, bromine or iodine;
4. amino having the formula



$$-N\begin{matrix}R'\\R''\end{matrix}$$

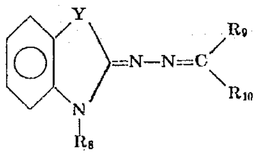
wherein R′ and R″ are the same or different including hydrogen, lower alkyl having one to eight carbon atoms such as ethyl, propyl, butyl, etc, aryl such as phenyl, naphthyl, etc, halogen, e.g., chlorine, bromine, etc,

5. cyano; or

any of R_4, R_5, R_6 and R_7 may be taken with an adjacent substituent to represent the number of atoms to complete a fused carbocyclic or heterocyclic ring system containing up to about **19** carbon atoms, which may in turn carry substituents such as those set forth hereinbefore.

X is an oxygen atom, a sulfur atom, a selenium atom, an imino group including a substituted imino group, or a methylene group including a substituted methylene group.

Preferred photoconductors of the invention ar those corresponding to the formula:

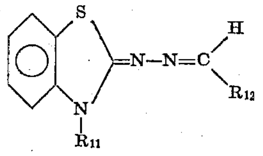


wherein:

R_8, R_9 and R_{10} each represents a hydrogen atom, a lower alkyl radical having from 1 to about 4 carbon atoms, e.g., methyl, ethyl, isopropyl, tert-butyl, etc, or an aryl radical including a substituted aryl radical, preferably an amino-substituted aryl radical; and

Y is an oxygen atom, a sulfur atom or an imino radical.

Particularly preferred photoconductors of the invention are those represented by the formula:



wherein:

R_{11} is a lower alkyl radical having from 1 to about 4 carbon atoms such as those set forth for R_8, R_9 and R_{10} above, and

R_{12} is a phenyl radical including a substituted phenyl radical, such as an amino-substituted phenyl radical including dialkylamino- and diarylamino-substituted phenyl radicals, or a naphthyl radical.

Typical compounds which belong to the herein described general class of photoconductive materials include the following listed in Table 1 below.

TABLE 1

I. N-isopropylidene-N′-(3-methyl-2-benzothiazal)hydrazine
II. N-benzylidene-N′-(3-methyl-2-benzothiazal)hydrazine
III. N-(p-diemthylaminobenzylidene)-N′-(3-methyl-2-benzothiazal)hydrazine
IV. N-(p-diethylaminobenzylidene)-N′-(3-methyl-2-benzothiazal)hydrazine
V. N-(p-diphenylaminobenzylidene)-N′-(3-methyl-2-benzothiazal)hydrazine
VI. N-(p-di-p-tolylaminobenzylidene)-N′-(3-methyl-2-benzothiazal)hydrazine
VII. N-(p-diethylamino-o-methoxybenzylidene)-N′-(3-methyl-2-benzothiazal)hydrazine
VIII. N-(4-diphenylamino-1-naphthylmethylene)-N′-(3-methyl-2-benzothiazal)hydrazine

According to this invention, it has been found that the photoconductors described herein yield compositions and elements which have enhanced electrophotographic properties when compared to those photoconductors described in the prior art. These enhanced properties are observed when the elements accept a suitable surface potential (e.g., 500–600 volts) and are subsequently exposed to actinic radiation. The relative electrophotographic speed of the element 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 is 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 toe speed can be assigned to such a composition. The photoconductive compositions disclosed herein do exhibit useful toe speeds.

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 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. 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 selenapyrylium dye salts disclosed in VanAllan et al, U.S. Pat. No. 3,250,615, issued May 10, 1966; hexaphenyl-p-rosaniline; fluorenes, such as 7,12-dioxo-13-dibenzo(a,h)fluorene, 5,-10-dioxo-4a,11-diazobenzo(b)fluorene, 3,13-dioxo-7-oxadibenzo(b,g)fluorene, and the like; aggregate-type sensitizers of the type described in Light, British Patent No. 1,153,506, dated May 29, 1969; aromatic nitro compounds of the kinds described in Minsk U.S. Pat. No. 2,610,120, dated Sept. 9, 1952; anthrones like those disclosed in Zvanut U.S. Pat. No. 2,670,284, dated Feb. 23, 1954; quinones as those in Minsk U.S. Pat. No. 2,670,286, dated Feb. 23, 1954; benzophenones as those in Minsk U.S. Pat. No. 2,260,287, dated Feb. 23, 1954; thiazoles as those of Robertson U.S. Pat. No. 2,732,301, dated Jan. 24, 1956; 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 carbocyanine and polycarbocyanine), merocyanine, diarylmethane, thiazine, azine, oxazine, xanthene, phthalein, acridine, azo, anthraquinone dyes and the like and mixtures thereof. The sensitizers preferred for use with the compounds of this invention are selected from pyrylium salts including selenpyrylium salts and thiapyrylium salts, and cyanine dyes including carboxyanine dyes.

Where a sensitizing compound is employed with the binder and organic photoconductor 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 layer.

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 requried 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 sensititizing compound give substantial improvement in speed in such layers, the sensitizer is preferred. The amount of sensitizer that can be added to a photoconductor-incorporating layer to give effective increases in speed can vary widely. The optimum concentration in any given case will vary with the specific photoconductor and sensitizing compound used. In general, substantial speed gains can be obtained where an appropriate sensitizer is added in a concentration range from about 0.0001 to about 30 percent by weight based on the weight of the film-forming coating composition. Normally, a sensitizer is added to the coating composition in an amount by weight from about 0.001 to about 30 percent and preferably 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 electrically insulating film-forming vehicles.

Typical of these materials are:

I. Natural resins including gelatin, cellulose ester derivatives such as alkyl esters of carboxylated cellulose, hydroxyethyl, cellulose, carboxy methyl cellulose, carboxy methyl hydroxy ethyl cellulose, etc;

II. Vinyl resins including:

a. polyvinyl esters such as a vinyl acetate resin, a copolymer of vinyl acetate and crotonic acid, a copolymer of vinyl acetate with an ester of vinyl alcohol and a higher aliphatic carboxylic acid such as aluric acid or stearic acid, polyvinyl stearate, a copolymer of vinyl acetate and maleic acid, a poly(-vinylhaloarylate) such as poly(vinyl-m-bromobenzoate-co-vinyl acetate), a terpolymer of vinyl butyral with vinyl alcohol and vinyl acetate, etc;

b. vinyl chloride and vinylidene chloride polymers such as a poly(vinylchloride), a copolymer of vinyl chloride and vinyl isobutyl ether, a copolymer of vinylidene chloride with acrylonitrile or vinyl chloride, a terpolymer of vinyl chloride, vinyl acetate and vinyl alcohol, poly(vinylidene chloride) a terpolymer of vinyl chloride, vinyl acetate and maleic anhydride, a copolymer of vinyl chloride and vinyl acetate, etc;

c. styrene polymers such as polystyrene, a nitrated polystyrene, a copolymer of styrene and minoisobutyl maleate, a copolymer of styrene acid polyvinyltoluene, a copolymer of styrene with methacrylic acid, a copolymer of styrene and butadiene, a copolymer of dimethylitaconate and styrene, polymethylstyrene, etc;

d. methacrylic acid ester polymers such as a poly-alkylmethacrylate), etc;

e. polyolefins such as chlorinated polyethylene, chlorinated polypropylene, poly(isobutylene), etc;

f. poly(vinyl acetals) such as poly(vinyl butyral), etc; and

g. poly(vinyl alcohol);

III. Polycondensates including:

a. a polyester of 1,3-disulfobenzene and 2,2-bis-(4-hydroxyphenyl)propane;

b. a polyester of diphenyl-p,p'-disulfonic acid and 2,-2-bis(4-hydroxyphenyl)propane;

c. a polyester of 4,4'-dicarboxyphenyl ether and 2,2-bis(4-hydroxyphenyl)propane;

d. a polyester of 2,2-bis(4-hydroxyphenyl)propane and fumaric acid;

e. polyester of pentaerythritol and phthalic acid;

f. resinous terpene polybasic acid;

g. a polyester of phosphoric acid and hydroquinone;

h. polyphosphites;

i. polyester of neopentylglycol and isophthalic acid;

j. polycarbonates including polythiocarbonates such as the polycarbonate of 2,2-bis(4-hydroxyphenyl)-propane;

k. polyester of isophthalic acid, 2,2-bis[4-(β-hydroxyethoxy)phenyl]propane and ethylene glycol;

l. polyester of terephthalic acid, 2,2-bis([4-(β-hydroxyethoxy)phenyl]propane and ethylene glycol;

m. polyester of ethylene, glycol, neopentyl, glycol, terephthalic acid and isophthalic acid;

n. polyamides;

o. ketone resins; and

p. phenolformaldehyde resins;

IV. Silicone resins;

V. Alkyd resins including styrene-alkyd resins, silicone-alkyd resins, soya-alkyd resins, etc;

VI. Paraffin; and

VII. Mineral waxes.

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, naphthalene, etc, including substituted aromatic hydrocarbons such as toluene, xylene, methylene, 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, ethylether;

5. mixtures of the above.

In preparing the coating compositions utilizing the photoconducting compounds 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 tht the photoconductive material be present in an amount ranging from about 1 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 2.5 microns to about 300 microns is useful in the practice of the invention. A preferred range of coating thickness is from about 50 microns to about 150 microns 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 alt 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 Minsk U.S. Pat. No. 3,007,901, dated Nov. 7, 1961, Trevoy U.S. Pat. No. 3,245,833, dated Apr. 12, 1966, and Sterman et al U.S. Pat. No. 3,262,807, dated July 26, 1966.

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 known in the art. e.g., Young U.S. Pat. No. 2,786,439, Giaimo U.S. Pat. No. 2,786,440 and Young U.S. Pat. No. 2,786,441, all dated Mar. 26, 1957. Liquid developemnt of the latent electrostatic image may also be used. liquid liauid 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, Metcalfe et al. U.S. Pat. No. 2,907,674, dated Oct. 6, 1959. 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 the literature, such as in "RCA Review," vol. 15 (1954) pages 469-484.

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 layers 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 ar included for a further understanding of the invention.

EXAMPLE 1

A composition in the form of a dope consisting of the following materials is coated at a wet thickness of 150 microns on a poly(ethylene terephthalate) film support bearing a conductive layer comprising vapor deposited nickel:

Photoconductor — see below — 0.25 g.
Binder — poly(4,4′-isopropylidene-bisphenyleneoxyethylene-co-ethylene terephthalate — 1.00 g.
Sensitizer — Rhodamine B, C.I 45170 — 0.01 g.
Dichloromethane — 9.60 g.

The support is held at a temperature of about 32°C during coating and until the solvent is removed. In a darkened room, the surface of the photoconductive layer 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 seconds. The resulting electrostatic charge pattern is developed by cascading over the surface of the layer negatively charged black thermoplastic toner particles on glass bead carriers. No image is reproduced on the element containing no photoconductor; however, a good quality image is produced on the elements containing photoconductors I through VIII.

EXAMPLE 2

The elements prepared in Example 1 are each recharged under a positive corona source until the surface potential, as measured by an electrometer probe, reaches V_{max}, which typically is about 600 volts. They are then exposed from behind a stepped density gray scale to a 3000°K. source. The exposure causes reduction of the surface potentials of the elements under each step of the gray scale from their initial potential, V_o, to some lower potential, V, whose exact value depends on the actual amount of exposure 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 104 multiplied by the reciprocal of the exposure in meter-candle-seconds required to reduce the surface potential V_{max} by 100 volts. The procedure is then repeated, using negative charging. The elements have speeds as thus determined as shown in Table 2 below.

TABLE 2

Photoconductor	Speed Positive	Negative
None	1	0
I	16	20
II	20	20
III	140	90
IV	340	140
V	400	270
VI	630	320
VII	250	140
VIII	170	100

EXAMPLE 3

Elements are prepared as in Example 1 using as the sensitizer one of the following Sensitizers A or B in place of Rhodamine B:

Sensitizer A — 2,6-bis(4-ethylphenyl)-4-(4-n-amyloxy-phenyl) thiapyrylium perchlorate
Sensitizer B — 4-n-butylamino-2-(4-methoxy-phenyl)benzo-(b) pyrylium perchlorate

When tested according to the procedure of Example 2, electrophotographic speeds as indicated in Table 3 are obtained.

TABLE 3

Photoconductor	Shoulder Speed Positive Charging Sensitizer None	A	B	Negative Charging Sensitizer None	A	B
I	0	80		0	63	
II	0	180	12	0	120	6
III	45	100		8	63	
IV	65	110		10	63	
V	68	320	550	14	100	20
VI	150	270	600	32	120	62
VII	85	200	200	11	80	15

VIII	65	160	160	10	90	32

EXAMPLE 4

A first dye-containing solution is prepared by dissolving 0.03 gram of dye 2,6-diphenyl-4-(4-dimethylaminophenyl)thiapyrylium perchlorate in 7.65 grams of dichloromethane. A second dye- and polymer-containing solution is prepared by dissolving 3.92 grams of poly(4-,4'-isopropylidenediphenylene carbonate) (Lexan 145, General Electric Co.) in 20.0 grams of dichloromethane which contains 0.08 gram of the above dye in solution. The second solution is subjected to shearing in a high-speed blender for a half-hour at room temperature. The two solutions are then incorportated into a photoconductor-containing coating solution to form a coating dope for each of the photoconductors listed in Table 4 below. The photoconductor-containing solution is prepared according to the following composition:

Lexan 145	0.25 g.
Photoconductor	0.25 g.
Solution 1	4.50 g.
Solution 2	7.70 g.

Each of the coating dopes thus produced is coated as in Example 1 to form photoconductive elements. Each element is then charged in turn positively and negatively and exposed as in Example 2 through a stepped density gray scale. Toe speeds obtained for both positive and negative charging at a voltage of 100 volts above zero volts are listed in Table 4.

TABLE 4

	Speed	
Photoconductor	Positive	Negative
None	25	21
I	71	190
II	80	71
III	40	80
V	900	310
VI	320	250
VIII	—	260

EXAMPLE 5

Three coating compositions in the form of a dope consisting of the following materials are prepared and coated according to the procedure of Example 1 to form an electrophotographic element:

Photoconductor — 0.5 g.
Sensitizer — Sensitizer B of Example 3 — 0.04 g.
Binder — poly(4,4'-isopropylidenebisphenyleneoxyethylene-co-ethylene isophthalate — 1.5 g.
Dichloromethane — 8.8 g.

Each of the elements thus produced is charged as in Example 1, and exposed to light from a xenon arc lamp which has been filtered in such a manner as to simulate as closely as possible the emission from a standard RETMA P-16 phosphor, which has an emission peak of about 385 nm. The time required to reduce the 600-volt charged surface potential to 50 volts is measured for each of the elements prepared. A control element contains 4,4'-benzylidenebis(N,N-diethyl-m-toluidine) as the photoconductor. The results of the measurements thus made are listed in Table 5.

TABLE 5

Photoconductor	Time Required
Control	26.3 sec.
V	24.8 sec.
VII	14.3 sec.

It is seen that the photoconductors of this invention give a desirable reduction in exposure time required when this mode of exposure is used.

EXAMPLE 6

Preparation of N-(p-diphenylaminobenzylidene-N'-(3-methyl-2-benzothiazal)hydrazine (Compound V)

A 6.65 gram portion of 3-methyl-2-benzothiazolinone hydrazone (0.0371 mole) and an 11.2 gram portion of p-diphenylaminobenzaldehyde (0.0410 mole) are suspended in 250 ml. of absolute ethanol and heated to reflux temperature, during which time the solids dissolve. The mixture is refluxed for 16 hours and allowed to cool to room temperature, whereupon a mass of yellow crystals precipitates. After filtering and washing with cold ethanol, there result 15.0 grams of product having a melting point range of 183°–185°C. Recrystallization from nitromethane yields 12.3 grams of yellow cubic crystals having a melting point range of 183.5°–184.5°C. The other photoconductive compounds according to the invention are prepared in an analogous manner from the same hydrazone and the appropriate aldehyde. The melting point, maximum absorption (λmax) in trichloromethane, and the extinction coefficient for each compound are summarized in Table 6 below. The extinction coefficient is represented by the expression ϵ=D/cl where D is the optical density of the solution, C is the concentration in moles/liter and l is the length (cm) of the cell holding the solution as measured along the optical path.

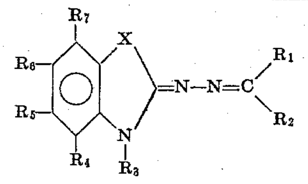
TABLE 6

Compound	Melting Point	$CHCL_3$ λmax	$\epsilon_{\lambda max}$ x 10^{-4}
I	111.0–112.5°	312 nm	1.98
II	163.0–165.0°	353 nm	3.08
III	176.0–178.0°	372 nm	4.60
IV	138.0–140.0°	375 nm	4.68
V	183.5–184.5°	385 nm	4.70
VI	199.5–201.0°	389 nm	4.90
VII	220.0–222.0°	392 nm	4.70
VIII	218.5–220.0°	384 nm	4.67

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.

I claim:

1. An electrophotographic element comprising a conductive support having thereon a layer of photoconductive composition comprising a photoconductor, a sensitizing amount of a sensitizer for said photoconductor and an electrically insulating polymeric film-forming binder, said photoconductor having the formula:



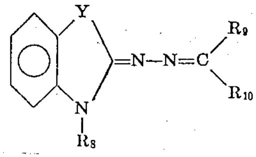
wherein:

R_1, R_2 and R_3 are each selected from the group consisitng of an alkyl radical having one to eight carbon atoms, a phenyl radical, a naphthyl radical and a hydrogen atom;

R_4, R_5, R_6 and R_7 are each selected from the group consisting of a cyano radical, a halogen atom, an alkyl radical having one to eight carbon atoms, an alkoxy radical having one to eight carbon atoms and a disubstituted amino radical wherein the substituents are the same or different and are selected from hydrogen, lower alkyl having one to eight carbon atoms, phenyl, naphthyl and halogen; and

X is selected from the group consisting of oxygen, sulfur, an imino group and a methylene group.

2. An electrophotographic element comprising a conductive support having thereon a layer of a photoconductive composition comprising a photoconductor, a sensitizing amount of a sensitizer for said photoconductor and an electrically insulating polymeric film-forming binder, said photoconductor having the formula:



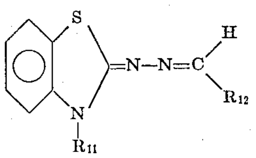
wherein:

R_8, R_9 and R_{10} are each selected from the group consisting of a hydrogen atom, a lower alkyl radical having one to about four carbon atoms, a phenyl radical and a naphthyl radical; and

Y is selected from the group consisting of oxygen, sulfur and an imino radical.

3. An element as described in claim 2 wherein said photoconductor is selected from the group consisting of N-isopropylidene-N'-(3-methyl-2-benzothiazal)hydrazine; N-benzylidene-N'-(3-methyl-2-benzothiazal)-hydrazine; N-(p-diethylaminobezylidene)-N'-(3-methyl-2-benzothiazal)hydrazine; N-(p-dimethylaminobenzylidene)-N'-(3-methyl-2-benzothiazal)-hydrazine; N-(p-diphenylaminobenzylidene)-N'-(3-methyl-2-benzothiazal)hydrazine; N-(p-di-p-tolylaminobenzylidene)-N'-(3-methyl-2-benzothiazal)-hydrazine; N-(p-diphenylamino-o-methoxybenzylidene)-N'-(3-methyl-2-benzothiazal)-hydrazine and N-(4-diphenylamino-1-naphthylmethylene)-N'-(3-methyl-2-benzothiazal)hydrazine.

4. An electrophotographic element comprising a conductive support having thereon a layer of a photoconductive composition comprising a photoconductor, a sensitizing amount of a sensitizer for said photoconductor and an electrically insulating polymeric film-forming binder, said photoconductor having the formula:



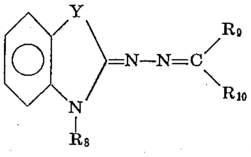
wherein:

R_{11} is a lower alkyl radical having one to about four carbon atoms; and

R_{12} is selected from the group consisting of a phenyl radical and a naphthyl radical.

5. An electrophotographic element as described in claim 4 wherein said sensitizer is selected from the group consisting of pyrylium dye salts and cyanine dyes.

6. In an electrophotographic process comprising the steps of (1) uniformly charging an electrophotographic element which comprises a conductive support having thereon a layer containing an organic photoconductor, a sensitizing amount of a sensitizer for said photoconductor and an organic film-forming polymeric binder, and (2) exposing the layer to a pattern of actinic radiation to selectively dissipate the charge in accordance with the radiation pattern, the improvement comprising using as the photoconductor an organic compound having the formula:



wherein:

R_8, R_9 and R_{10} are each selected from the group consisting of a hydrogen atom, a lower alkyl radical ving one to about four carbon atoms, a phenyl radical and a naphthyl radical; and

Y is selected from the group consisting of oxygen, sulfur and an imino radical.

* * * * *