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[54] CHARGE-TRANSFER COMPLEXES OF
DIBENZOFURAN-FORMALDEHYDE OR
DIBENZOTHIOPHENE-FO-
RMALDEHYDE RESINS AS PHOTO-
CONDUCTIVE MATERIALS

252/501

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[58] Field of Search 260/67 FP, 67 A; 96/1.5, 1;

[56]

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[57]

ABSTRACT

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

10 Claims, No Drawings

CHARGE-TRANSFER COMPLEXES OF DIBENZOFURAN-
FORMALDEHYDE OR DIBENZOTHIOPHENE-
FORMALDEHYDE RESINS AS PHOTOCONDUCTIVE
MATERIALS

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

The process of xerography, as disclosed by Carlson in U.S. Pat. No. 2,297,691, employs an electrophotographic element comprising a support material bearing a coating of a normally insulating material whose electrical resistance varies with the amount of incident electromagnetic radiation it receives during an imagewise exposure. The element, commonly termed a photoconductive element, is first given a uniform surface charge, generally in the dark after a suitable period of dark adaptation. It is then exposed to a pattern of actinic radiation which has the effect of differentially reducing the potential of this surface charge in accordance with the relative energy contained in various parts of the radiation pattern. The differential surface charge or electrostatic latent image remaining on the electrophotographic element is then made visible by contacting the surface with a suitable electroscopic marking material. Such marking material or toner, whether contained in an insulating liquid or on a dry carrier, can be deposited on the exposed surface in accordance with either the charge pattern or discharge pattern as desired. Deposited marking material can then be either permanently fixed to the surface of the sensitive element by known means such as heat, pressure, solvent vapor, or the like, or transferred to a second element to which it can similarly be fixed. Likewise, the electrostatic charge pattern can be transferred to a second element and developed there.

Various photoconductive insulating materials have been employed in the manufacture of electrophotographic elements. For example, vapors of selenium and vapors of selenium alloys deposited on a suitable support and particles of photoconductive zinc oxide held in a resinous, film-forming binder have found wide application in the present-day document copying applications.

Since the introduction of electrophotography, a great many organic compounds have also been screened for their photoconductive properties. As a result, a very large number of organic compounds have been known to possess some degree of photoconductivity. Many organic compounds have revealed a useful level of photoconduction and have been incorporated into photoconductive compositions. Typical of these organic photoconductors are the triphenylamines and the triarylmethane leuco bases. Optically clear photoconductor-containing elements having desirable electrophotographic properties can be especially useful in electrophotography. Such electrophotographic elements can be 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.

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

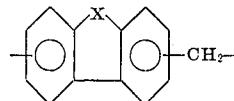
It is another object to provide novel photoconductor-containing compositions which exhibit high electrical speeds.

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

These and other objects are accomplished by employing certain dibenzofuran-formaldehyde resins or dibenzothiophene-formaldehyde resins which form a complex with certain Lewis acids such as 2,4,7-trinitro-9-fluorenone, 2,4,5,7-tetrinitro-9-fluorenone, 2,6-dichloro-p-benzoquinone, 2,5-dinitro-9-fluorenone, 1,5-dichloro-2,4-dinitrobenzene, 2,5-dichloro-p-benzoquinone, tetrachloroquinone, 2-chloro-3,5-dinitropyridine, and 2,4,5,7,9-pentanitro-indeno[2,1-a]fluoren-11,12-dione, 2,5-diphenyl-p-benzoquinone, 2,3-dichloro-1,4-naphthoquinone, 75

9-dicyanomethylene-2,4,7-trinitrofluorene, that are accompanied by spectral shifts. The photoconductive efficiency of said combinations is quite high and the observed photoconductivity can be further enhanced by employing additional sensitizers.

The compounds which form the complex of the present invention include resins which are formed by the condensation of dibenzothiophene with formaldehyde and dibenzofuran with formaldehyde and which comprise units having the formula



wherein X is an oxygen atom or a sulfur atom, and an aforementioned Lewis acid such as 2,4,7-trinitro-9-fluorenone (TNF). The combination of such compounds as dibenzothiophene-formaldehyde resin with TNF exhibits greatly increased speed and efficiency over the combination of dibenzothiophene itself complexed with TNF.

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

55 Electrophotographic elements of the invention can be prepared to contain the photoconducting complexes of the present invention in the conventional manner, i.e., by blending a dispersion or solution of a photoconductive complex or the constituent compounds together with a binder, when necessary or desirable, and coating or forming a self-supporting layer with the materials. Likewise, other photoconductors known in the art such as those described in Light, British Pat. No. 1,153,506 dated May 29, 1969, can be combined with the present photoconductors. In addition, supplemental materials 60 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 65 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 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-oxo-5-adibeno(b,g)fluorene, and the like; aggregate-type sensitizers of the type described in Light, British Pat. No. 1,153,506, dated May 29, 1969; aromatic nitro compounds of the kinds described in Minsk U.S. Pat. No. 2,610,120 issued Sept. 9, 1952; anthrones like those disclosed in Zvanut U.S. Pat. No. 2,670,284 issued Feb. 23, 1954; quinones, Minsk U.S. Pat. No. 2,670,286 issued Feb. 23, 1954; benzophenones, Minsk U.S. Pat. No. 2,670,287 issued Feb. 23, 1954; thiazoles Robertson U.S. Pat. No. 2,732,301 issued Jan. 24, 1956; mineral acids; carboxylic acids, such as maleic acid, dichloroacetic acid, trichloroacetic acid and salicylic acid; sulfonic and phosphoric acids; 2,7-dimethyl-9-(p-tolyl)-10-(p-tolyl)-9-acridinol; N-(p-diphenylaminobenzal)-N'-(3-methyl-2-benzothiazal)hydrazine; p-diphenylaminocinnamic acid; 4,4',4"-trimethoxyphenylamine; and various dyes, such as cyanine (including carbocyanine and polycarbocyanine, merocyanine, diarylmethane, thiazine, azine, oxazine, xanthene, phthalein, acridine, azo, anthraquinone dyes and the like; mixtures thereof.

When a sensitizing compound is employed with an organic photoconductor complex to form a sensitized electrophotographic element, it is the normal practice to mix a suitable amount of the sensitizing compound with the coating 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 required to give photoconductivity in the layers which contain the photoconducting substances, therefore, no sensitizer is required in a particular photoconductive layer. However, since relatively minor amounts of sensitizing compound give substantial improvement in speed in such layers, the sensitizer is preferred. As seen from the previous listing both spectral and chemical sensitizers can be used in this invention, either alone or in combination. The amount of sensitizer that can be added to a photoconductive 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 0.005 to about 5.0 percent by weight of the total coating composition.

While the Lewis acid and dibenzofuran-formaldehyde resin or dibenzothiophene-formaldehyde resin may be used together without additional binder materials, it is sometimes desirable for binders to be employed. Preferred binders include materials which are film-forming, hydrophobic 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, hydroxy ethyl 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 lauric acid or stearic acid, polyvinyl stearate, a copolymer of vinyl acetate and maleic acid, a poly(vinylhaloarylate) such as poly(vinyl-m-bromo-benzoate-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 and acrylonitrile, 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 monoisobutyl maleate, a copolymer of styrene with methacrylic acid, a copolymer of styrene and butadiene, a copolymer of dimethyl itaconate 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'-disulphonic 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(4hydroxyphenyl)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, etc., including substituted aromatic hydrocarbons, such as toluene, xylene, mesitylene, etc.;

2. Ketones, such as acetone, 2-butanone, etc.;

3. Halogenated aliphatic hydrocarbons, such as methylene chloride, chloroform, ethylene chloride, etc.;

4. Ethers including cyclic ethers such as tetrahydrofuran, dioxane; and

5. Mixtures of the above.

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

Coating thicknesses of the photoconductive layer on a support can vary widely. Normally, a wet coating thickness in the range of about 0.001 inch to about 0.01 inch is useful in the

practice of the invention. A preferred range of coating thickness is from about 0.002 inch to about 0.006 inch before drying although such thicknesses can vary widely depending on the particular application desired for the electrophotographic element.

Suitable supporting materials for the photoconductive layers of the present invention can include any of the electrically conducting supports, for example, various conducting papers; aluminum-paper laminates; metal foils, such as aluminum foil, zinc foil, etc.; metal plates such as aluminum, copper, zinc, brass, and galvanized plates; vapor deposited metal layers such as silver, nickel or aluminum on conventional film supports, such as cellulose acetate, poly(ethylene terephthalate), polystyrene and the like conducting supports.

An especially useful conducting support can be prepared by coating a transparent film support material such as poly(ethylene terephthalate) with a layer containing a semiconductor dispersed in a resin. A suitable conducting coating can be prepared from the sodium salt of a carboxy-ester lactone of a maleic anhydride-vinyl acetate copolymer, cuprous iodide and the like. Such conducting layers and methods for their optimum preparation and use are disclosed in U.S. Pat. No. 3,007,901 by Minsk issued Nov. 7, 1961; U.S. Pat. No. 3,262,807 by Sterman issued July 26, 1966, and U.S. at. No. 3,245,833 by Trevoy issued Apr. 12, 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 toner formed of a pigment in a resin binder. 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.: U.S. Patents No. 2,786,439 by Young issued Mar. 26, 1957; U.S. Pat. No. 2,786,440 by Giaimo issued Mar. 26, 1957; and U.S. Pat. No. 2,786,441 by Young issued Mar. 26, 1957. Liquid development of the latent electrostatic image may also be used. In liquid development the developing particles are carried to the image-bearing surface in an electrically insulating liquid carrier. Methods of development of this type are widely known and have been described in the patent literature, for example, U.S. Patent No. 2,907,674 by Metcalfe et al. issued 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 layer or sensitizing layer and the conducting layer. It is also possible to adjust the position of the support and the conducting layer by placing a photoconductor layer over a support and coating the exposed face of the support or the exposed or overcoated face of the photoconductor with a conducting layer. Configurations differing from those contained in the examples can be useful or even preferred for the same or different application for the electrophotographic element.

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

EXAMPLE 1

To a boiling solution of 3.0 grams (0.10 mole) of paraformaldehyde in 100 ml. of formic acid is added 16.8 grams (0.10 mole) of dibenzofuran. After 6 hours of reflux, the liquid is decanted from the solid which separates, and the solid is dissolved in dichloromethane. The residual formic acid is removed by extraction with aqueous potassium carbonate. Evaporation of the dichloromethane gives the resinous product, dibenzofuran-formaldehyde. The resinous dibenzothiophene-formaldehyde is prepared in the same manner using dibenzothiophene as the starting material in place of the dibenzofuran. A first dope (A) is prepared containing the following components:

poly(4,4'-isopropylidenediphenylene carbonate)	0.75 g.
dibenzofuran-formaldehyde resin	0.75 g.
2,4,7-trinitro-9-fluorenone (TNF)	0.50 g.
dichloromethane	11.7 ml.

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A second dope (B), similar to the first, is prepared, in which the dibenzofuran-formaldehyde resin is replaced with an equal weight of dibenzothiophene-formaldehyde resin. A third dope (C), similar to the first, is prepared as a control, in which the dibenzofuran-formaldehyde resin is replaced completely with an equal weight of the polycarbonate. A fourth dope (D), similar to the second, is prepared as a control, in which the dibenzothiophene-formaldehyde resin is replaced with an equal weight of dibenzothiophene. Each dope is hand coated at a wet thickness of 150 microns on suitable conductive support such as evaporated nickel on a poly(ethylene terephthalate) film support. The coating block is maintained at a temperature of about 32° C. 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. Each layer in turn is 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 illuminance of about 75 meter-candles for 12 seconds. Each of the resulting electrostatic charge patterns is developed by cascading over the surface of each layer a developer comprising negatively charged black thermoplastic toner particles on glass bead carriers. The quality of the images reproduced using the various photoconductors described herein is set forth in Table I.

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TABLE I

Element No.	Dope	Image Quality
1	A	Good
2	B	Good
3	C (control)	Poor
4	D (control)	No Image

EXAMPLE 2

Each of the electrophotographic elements prepared in Example 1 is charged under a positive or negative corona source until the surface potential, as measured by an electrometer probe, reaches about 600 volts. It is then exposed from behind a stepped density gray scale to a light source using either a 3000° K. tungsten source or a xenon arc. The exposure causes reduction of the surface potential of the element under each step of the gray scale from its initial value, V_0 , to some lower value V whose exact value depends on the actual amount of exposure received by the area under the step. 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. An apparatus for automatically measuring the potentials and recording them is described in Robinson et al. U.S. Pat. No. 3,449,658, issued June 10, 1969. The speeds obtained for the various elements tested are given in Table II below.

TABLE II.—ELECTROPHOTOGRAPHIC SPEEDS

Element No.	Dope	Absorption extends to—	Positive shoulder/ toe		Negative shoulder/ toe	Source
			Extends to—	Positive shoulder/ toe		
1	A	560 nm	2,500/100		5,000/450	Xenon.
2	B	590 nm	5,700/400		9,000/1,100	Do.
3	C	440 nm	20/6.3		1,200/25	Do.
4	D	540 nm	65/2.9		200/12	Tungsten.
2	B	590 nm	1,000/14		630/32	Do.

The combination of TNF and the resins in dopes A, B and D produce complexes evidenced by shifts in spectral absorption. Dopes C and D, in which the dibenzothiophene-formaldehyde resin is absent, produce elements having lower speeds than those obtained with dopes A and B. Similar results are obtained when the TNF is replaced with an equal weight of 2,4,5,7,9-pentanitroindeno[2,1-a]fluoren-11,12-dione and 9-dicyanomethylene-2,4,7-trinitrofluorene.

EXAMPLE 3

Coating compositions are made according to the procedure of Example 1 in which the polycarbonate binder is replaced in its entirety with an equal weight of the polymer poly(4,4'-isopropylidenebisphenyleneoxyethylene - co - ethylene terephthalate). One of the compositions contains no sensitizing dye, and serves as the control. Each of the remaining compositions contains one of the dye sensitizers listed hereinafter.

I. 3,3'-diethyl-9-methylthiobarboxyanine bromide

II. 3,3'-diethylthiadicarbocyanine bromide

III. 3,3'-diethylthiaticarbocyanine iodide

IV. 6-chloro-1'-methyl-1,2',3'-triphenylimidazo 4,5-b-quinoxalino-3'-indolocarbocyanine-p-toluenesulfonate

V. 6,6'-dichloro-1,1',3,3'-tetraphenylimidazo 4,5-b-quinoxalino carbocyanine p-toluenesulfonate

VI. Rhodamine B (C.I. 45,170)

VII. 2,6-bis(4-ethylphenyl)-4-(4-n-amyloxyphenyl)-thiapyrylium perchlorate

VIII. hexaphenyl-p-rosaniline disulfone Elements prepared

from each of these compositions are tested according to the procedures given in Examples 1 and 2 above. When tested according to the procedure of Example 1, each gives a visible image. When tested according to the procedure of Example 2, using tungsten exposure, speeds are obtained as summarized in Table III below.

Element No.:	Sensitizer	Speed (neg. 100 v. Toe)	Sensitization	
			Range, nm.	Peak, nm.
5	I	90	400-580	480-600
6	II	120	400->740	(¹)
7	III	36	600-550	680, 770, 800
8	IV	63	380-600	1480-560
9	V	80	380-680	500, 620
10	VI	100	400-620	1580
11	VII	43	400-600	510
12	VIII	80	400-580	
13	(²)	39	400-580	510

¹ Broad.

² None (control).

Each of the dyes is present in an amount of 1 percent of the total solids content, with the exception of Dyes III and VII, which are present at twice that concentration. Only negative toe speeds are measured. It is seen that the sensitizing dyes generally increase the speed or absorption range of the photoconductor-containing compositions and elements of the invention.

EXAMPLE 4

Coating compositions are made according to the control composition of Example 3, that is, containing no sensitizing dye. To each of these compositions is added an amount of one of chemical sensitizers E, F, G, H and J as indicated hereinafter.

E 2,7-dimethyl-9-(p-tolyl)-19-(p-tolyl)-9-acridinol

F N-(p-diphenylaminobenzal)-N'-(3-methyl-2-benzothiazol)hydrazine

G p-diphenylaminocinnamic acid

H 4,4',4''-tris(methoxyphenyl)amine

J tri-p-tolylamine

Certain of the compositions also contain a spectral dye sensitizer, as indicated in Table IV below.

TABLE IV

Element No.	Compound	Conc. (g)	Speed (Neg. toe)
14	None (control)	--	34
15	E	0.02	98
16	F	0.02	66
17	G	0.02	90
18	H	0.02	63
19	J	0.02	120
20	J + IV	0.02 + 0.02	140
21	J + V	0.02 + 0.02	225

It is seen that addition of chemical sensitizers as indicated herein markedly increases the electrophotographic response of the compositions and elements containing them.

EXAMPLE 5

Coating compositions are made according to the control composition of Example 3 but with varying concentrations of TNF. The concentration of TNF content is varied between about 12.5 percent and about 50 percent, based on the weight of the total solids. The compositions are coated to form electrophotographic elements in the manner hereinbefore indicated, and the elements thus formed are tested electrophotographically with both positive and negative polarities of initial charging. The toe and shoulder speeds, as hereinbefore defined, of these elements are given in Table V.

TABLE V

Weight Percent TNF	Positive Shoulder.	Speed			5
		Toe	Negative Shoulder	Toe	
12.5	250	3.2	450	7.8	
25.0	710	20	630	32	
37.5	630	18	790	32	
50.0	450	10	500	20	10

The speed figures given in Table V show that a concentration of as high as 50 percent of the weight of the total solids in the coating composition gives a decided improvement in electrophotographic response. This is seen to be true even though the concentration passes through an optimum for both positive and negative charging.

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

We claim:

1. An electrophotographic element comprising a conductive support having coated thereon a photoconductive composition comprising a complex formed by a resin selected from the group consisting of dibenzofuran-formaldehyde resins and dibenzothiophene-formaldehyde resins and a Lewis acid selected from the group consisting of 2,4,7-trinitro-9-fluorenone, 2,4,5,7-tetranitro-9-fluorenone, 2,6-dichloro-p-benzoquinone, 2,5-dinitro-9-fluorenone, 1,5-dichloro-2,4-dinitrobenzene, 2,5-dichloro-p-benzoquinone, tetrachloroquinone, 2-chloro-3,5-dinitropyridine, 2,4,5,7,9-pantanitroindene[2, 1]-fluoren-11, 12-dione, 2, 5-diphenyl-p-benzoquinone, 2,3-dichloro-1,4-naphthoquinone, 9-dicyanomethylene-2,4,7-trinitrofluorene.

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

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

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

5. The element of claim 1 wherein said photoconductive composition contains a film-forming polymeric binder for said complex.

6. An electrophotographic element comprising a conduc-

tive support having coated thereon a photoconductive composition comprising

a. from about 0.01 to about 90 percent by weight based on said photoconductive composition of a complex formed by a resin selected from the group consisting of dibenzofuran-formaldehyde resins and dibenzothiophene-formaldehyde resins and a compound selected from the group consisting of 2,4,7-trinitro-9-fluorenone, 2,4,5,7-tetranitro-9-fluorenone, 2,6-dichloro-p-benzoquinone, 2,5-dinitro-9-fluorenone, 1,5-dichloro-2,4-dinitrobenzene, 2,5-dichloro-p-benzoquinone, tetrachloroquinone, 2-chloro-3,5-dinitropyridine, 2,4,5,7,9-pantanitroindene[2, 1]-fluoren-11, 12-dione, 2, 5-diphenyl-p-benzoquinone, 2,3-dichloro-1,4-naphthoquinone, 9-dicyanomethylene-2,4,7-trinitrofluorene,

b. a film-forming polymeric binder for said complex and

c. from about 0.005 percent to about 5 percent by weight based on said photoconductive composition of a sensitizer for said photoconductive composition.

7. In an electrophotographic process wherein an electrostatic charge pattern is formed on an electrophotographic element, the improvement characterized in that said electrophotographic element has a photoconductive layer comprising a complex of a Lewis acid and a resin selected from the group consisting of dibenzofuran-formaldehyde resins and dibenzothiophene-formaldehyde resins.

8. The process of claim 7 wherein the photoconductive layer comprises a complex formed between dibenzofuran-formaldehyde resin and 2,4,7-trinitrofluorenone.

9. The process of claim 7 wherein the photoconductive layer comprises a complex formed between dibenzothiophene-formaldehyde resin and 2,4,7-trinitrofluorenone.

10. An electrophotographic element comprising a conductive support having coated thereon a photoconductive composition comprising

a. from about 0.01 to about 90 percent by weight based on said photoconductive composition of a complex formed by a resin selected from the group consisting of dibenzofuran-formaldehyde resins and dibenzothiophene-formaldehyde resins and 2, 4, 7-trinitro-9-fluorenone,

b. a film-forming polymeric binder for said complex, and

c. from about 0.005 percent to about 5 percent by weight based on said photoconductive composition of a sensitizer for said photoconductive composition.

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