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ELECTROPHOTOGRAPHIC MATERIALS AND METHOD EMPLOYING PHOTOCONDUCTIVE RESINOUS CHARGE TRANSFER COMPLEXES

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ABSTRACT OF THE DISCLOSURE

Photoconductive materials are prepared from polyurethane resins and Lewis acids. The materials are charge transfer complexes. The photoconductive materials are used to make electrophotographic plates. Methods of using the plates are also disclosed.

This invention relates to photoconductive materials, and more particularly, to their use in electrophotography.

It is known that images may be formed and developed on the surface of certain photoconductive materials by electrostatic means. The basic xerographic process, as taught by Carlson in U.S. Patent 2,297,691, involves uniformly charging a photoconductive insulating layer and then exposing the layer to a light-and-shadow image which dissipates the charge on the portions of the layer which are exposed to light. The electrostatic latent image formed on the layer corresponds to the configuration of the light-and-shadow image. This image is rendered visible by depositing on the image layer a finely divided developing material comprising a colorant called a toner and a toner carrier. The powder developing material will normally be attracted to those portions of the layer which retain a charge, thereby forming a powder image corresponding to the latent electrostatic image. This powder image may then be transferred to paper or other receiving surfaces. The paper then will bear the powder image which may subsequently be made permanent by heating or other suitable fixing means. The above general process is also described in U.S. Patents, 2,357,809; 2,891,011 and 3,079,342

That various photoconductive insulating materials may be used in making electrophotographic plates is known. Suitable photoconductive insulating materials such as anthracene, sulfur, selenium or mixtures thereof, have been disclosed by Carlson in U.S. Patent 2,297,691. These materials generally have sensitivity in the blue or near ultraviolet range, and all but selenium have a further limitation of being only slightly light sensitive. For this reason, selenium has been the most commercially accepted material for use in electrophotographic plates. Vitreous selenium, however, while desirable in most aspects, suffers from serious limitations in that its spectral response is somewhat limited to the ultraviolet, blue and green region of the spectrum, and the preparation of vitreous selenium plates requires costly and complex procedures, such as vacuum evaporation. Also, selenium plates require the use of a separate conductive substrate layer, preferably with an additional barrier layer deposited thereon before deposition of the selenium photoconductor. Because of these economical and commercial considerations, there have been many recent efforts towards developing photoconductive insulating materials other than selenium for use in electrophotographic plates.

It has been proposed that various two-component materials be used in photoconductive insulating layers used in electrophotographic plates. For example, the use of inorganic photoconductive pigments dispersed in suitable binder materials to form photoconductive insulating layers

is known. It has further been demonstrated that organic photoconductive insulating dyes and a wide variety of polycyclic compounds may be used together with suitable resin materials to form photoconductive insulating layers useful in binder-type plates. In each of these two systems, it is necessary that at least one original component used to prepare the photoconductive insulating layer be, itself, a photoconductive insulating material.

In a third type plate, inherently photoconductive polymers are used; frequently in combination with sensitizing dyes or Lewis acids to form photoconductive insulating layers. Again, in these plates at least one photoconductive insulating component is necessary in the formation of the layer. While the concept of sensitizing photoconductors is, itself, commercially useful, it does have the drawback of being limited to only those materials already having substantial photoconductivity.

The above discussed three types of known plates are further described in U.S. Patents 3,097,095; 3,113,022; 3,041,165; 3,126,281; 3,073,861; 3,072,479; 2,999,750; Canadian Patent 644,167 and German Patent 1,068,115.

The polymeric and binder-type organic photoconductor plates of the prior art generally have the inherent disadvantages of high cost of manufacture, brittleness, and poor adhesion to supporting substrates. A number of these photoconductive insulating layers have low temperature distortion properties which make them undesirable in an automatic electrophotographic apparatus which often includes powderful lamps and thermal fusing devices which tend to heat the xerographic plate. Also, the choice of physical properties has been limited by the necessity of using only inherently photoconductive materials.

Inorganic pigment-binder plates are limited in usefulness because they are often opaque and are thus limited to use in systems where light transmission is not required. Inorganic pigment-binder plates have the further disadvantage of being nonreusable due to high fatigue and rough surfaces which make cleaning difficult. Still another disadvantage is that the materials used have been limited to those having inherent photoconductive insulating properties.

It is therefore an object of this invention to provide a photoconductive insulating material suitable for use in electrophotographic plates devoid of the above noted disadvantages.

Another object of this invention is to provide an economical method for the preparation of photoconductive insulating materials wherein none of the required components is by itself substantially photoconductive.

Another object of this invention is to provide a photoconductive insulating material suitable for use in electrophotographic plates in both single use and reusable systems.

Yet another object is to provide a photoconductive insulating layer for an electrophotographic plate which is substantially resistant to abrasion and has a relatively high distortion temperature.

Yet a further object of this invention is to provide an electrophotographic plate having a wide range of useful physical properties.

A still further object of this invention is to provide photoconductive insulating layers which may be cast into self-supporting binder-free photoconductive films and structures.

Still another object of this invention is to provide a novel combination of initially nonphotoconductive insulating materials suitable for use in the manufacture of the photoconductive insulating layer of a xerographic plate which is easily coated on a desired substrate or combined with a conductive layer.

Another object is to provide a transparent self-supporting photoconductive film adapted for xerographic imaging which does not require a conductive backing.

A still further object of this invention is to provide a photoconductive insulating material which may be made substantially transparent and which is particularly adapted for use in systems where light transmission is required.

The foregoing objects and others are accomplished in accordance with this invention, generally speaking, by providing a photoconductive material adapted for use in electrophotographic plates which is obtained by complexing:

(A) A suitable Lewis acid with
(B) A polyurethane resin produced by the reaction of an aromatic di-isocyanate and an organic compound containing at least two active hydrogen containing groups as determined by the Zerewitinoff method.

It should be noted that neither of the above two components, (A) and (B) used to make the photoconductor of this invention is by itself photoconductive; rather, they are each nonphotoconductive.

After the above substantially nonphotoconductive Lewis acid is mixed or otherwise complexed with said substantially nonphotoconductive resinous material, the highly desirable photoconductive insulating material is obtained which may be either cast as a self-supporting layer or may be deposited on a suitable supporting substrate. Any other suitable method of preparing a photoconductive plate from the above photoconductive material may be used.

It has been found by the present invention that electron acceptor complexing may be used to render inherently nonphotoconductive electron donor type insulators photoconductive. This greatly increases the range of useful materials for electrophotography.

A Lewis acid is any electron acceptor relative to other reagents present in the system. A Lewis acid will tend to accept a pair of electrons furnished by an electron donor (or Lewis base) in the process of forming a chemical compound or, in the present invention, a charge transfer complex.

A "Lewis acid" is defined for the purposes of this invention as any electron accepting material relative to the polymer to which it is complexed.

A charge transfer complex may be defined as a molecular complex between substantially neutral electron donor and acceptor molecules, characterized by the fact that photoexcitation produces internal electron transfer to yield a temporary excited state in which the donor is more positive and the acceptor more negative than in the ground state.

It is believed that the donor-type insulating resins of the present invention are rendered photoconductive by the formation of charge transfer complexes with electron acceptors or Lewis acids and that these complexes, once formed, constitute the photoconductive elements of the plates.

Broadly speaking, charge transfer complexes are loose associations containing electron donors and acceptors, frequently in stoichiometric ratios which are characterized as follows:

(A) Donor-acceptor interaction is weak in the neutral ground state, i.e. neither donor nor acceptor is appreciably perturbed by the other in the absence of photoexcitation.
(B) Donor-acceptor interaction is relatively strong in the photoexcited state, i.e., the components are at least partially ionized by photoexcitation.
(C) When the complex is formed, one or more new absorption bands appear in the near ultraviolet or visible region (wave lengths between 3200–7500 angstrom units) which are present in neither donor alone nor acceptor alone, but are instead a property of the donor-acceptor complex.

It is found that both the intrinsic absorption bands of the donor and the charge transfer bands of the complex may be used to excite photoconductivity.

"Photoconductive insulator" for the purposes of this invention is defined with reference to the practical application in xerographic imaging. It is generally considered that any insulator may be rendered "photoconductive" through excitation by sufficiently intense radiation of sufficiently short wavelengths. This statement applies generally to inorganic as well as to organic materials, including the inert binder resins used in binder plates, and the electron acceptor type activators and aromatic resins used in the present invention. However, the short wavelength radiation sensitivity is not useful in practical imaging systems because sufficiently intense sources of wavelengths below 3200 angstrom units are not available, because such radiation is damaging to the human eye and because this radiation is absorbed by glass optical systems. Accordingly, for the purposes of this application, the term "photoconductive insulator" includes only those materials which may be characterized as follows:

(1) They may be formed into continuous films which are capable of retaining an electrostatic charge in the absence of actinic radiation.
(2) These films are sufficiently sensitive to illumination of wavelengths longer than 3200 angstrom units to be discharged by at least one half by a total flux of at most 10^{14} quanta/cm.^{2} of absorbed radiation.

This definition excludes the resins and Lewis acids of our disclosure when used individually from the class of "photoconductive insulators."

The polyurethane resins used in the present invention are obtained by reacting an aromatic polyisocyanate with an organic compound containing at least two active hydrogen containing groups as determined by the Zerewitinoff method. Best results are obtained when using Bisphenol-A (2,2-(4-bis-hydroxy-phenol)-propane) in the preparation of the resin, and this is considered to be the preferred active hydrogen containing compound. Other active hydrogen containing compounds such as resorcinol, hydroquinone glycols, glycerol, and mixtures thereof may be used in mixture with or in lieu of the hydroxy alkanes if desired. The di(mono-hydroxyaryl)-alkanes, however, are preferred; with, as noted above, Bisphenol-A (2,2-(4-bis-hydroxy phenyl)-propane) being the most preferred embodiment.

Any suitable organic compound containing at least two active hydrogen containing groups may be used in accordance with the process of the present invention for reaction with either an excess or a deficiency of an aromatic polyisocyanate. These compounds preferably have terminal —OH or —NH_2 groups. Any suitable hydroxyl polyester, polyhydric polyalkalene ether, polyhydric polythioethers polyacetal, polyhydric alcohol, polycarboxylic acid, alkylene oxide, or polyalkylene ether glycol. Typical are:

1,4-butene diol;
1,4-butine diol;
3,3'-dichloro diamino diphenyl methane;
1,3-propylene glycol;
1,4-butane diol;
o-dichlorobenzidine;
N-dioxyethyl-B-naphthylamine;
1,6-hexane diol;
bis-hydroxy methyl cyclohexane;
4,4'-dihydroxy chalcone;
4,4'-dihydroxy-3-methoxy chalcone;
trimethylol propane;
sorbitol;
1,4-phenylene-bis-hydroxy ethyl ether;
1,2-diphenyl propane-4,4'-bis-hydroxy ethyl ether
(4,4-dihydroxy-diphenyl)-methane,
2,2-(4-bis-hydroxy-phenyl)propane,
1,1-(4,4'-dihydroxy-diphenyl) cyclohexane,
1,1-(4,4'-dihydroxy-3,3'-dimethyl-diphenyl) cyclohexane,

1,1-(4,4'-dihydroxy-3,3'-dimethyl-diphenyl) cyclohexane,
1,1-(2,2'-dihydroxy-4,4'-dimethyl-diphenyl)-butane,
2,2-(2,2'-dihydroxy-4,4'-di-tert-butyl-diphenyl)-propane,
1,1'-(4,4'-dihydroxy-diphenyl)-1-phenyl-ethane,
2,2-(4,4'-dihydroxy-diphenyl)butane,
2,2-(4,4'-dihydroxy-diphenyl)pentane,
3,3-(4,4'-dihydroxy-diphenyl)pentane,
2,2-(4,4'-dihydroxy-diphenyl)hexane,
3,3-(4,4'-dihydroxy-diphenyl)hexane,
2,2-(4,4'-dihydroxy-diphenyl-4-methyl)-pentane (dihydroxy-diphenyl)-heptane,
4,4-(4,4'-dihydroxy-diphenyl)-heptane,
2,2-(4,4'-dihydroxy-diphenyl)-tridecane,
2,2-(,4'-dihydroxy-3'-methyl diphenyl)-propane,
2,2-(4,4'-dihydroxy-3-methyl-3'-isopropyl-diphenyl)-butane,
2,2-(3,5,3',5'-tetra-chloro-4,4'-dihydroxy-diphenyl)-propane,
2,2-(3,5,3',5'-tetrabromo-4,4'-dihydroxy-diphenyl)-propane,
(3,3'-dichloro-4,4'-dihydroxy-diphenyl)-methane and
2,2'-(dihydroxy-5,5'-difluoro-diphenyl)methane,
(4,4'-dihydroxy-diphenyl)-phenyl-methane and
1,1-(4,4'-dihydroxy-diphenyl-1-phenyl)-ethane,
and mixtures thereof.

Any suitable aromatic polyisocyanate may be used, but it is preferred to employ an aromatic diisocyanate with the above mentioned difunctional compounds. Typical polyisocyanates are

polymethylene polyphenyl isocyanate;
diphenyl methane-4,4'-diisocyanate;
2,4-toluylene diisocyanate;
2,6-toluylene diisocyanate;
1-naphthalene diisocyanate;
hexamethylene diisocyanate;
p-phenylene diisocyanate;
m-phenylene diisocyanate;
diphenyl sulphone-4,4'-diisocyanate;
3,3'-dimethyl-4,4'-biphenylene diisocyanate;
3,3'-dimethoxy-4,4'-biphenylene diisocyanate;
3,3'-diphenyl-4,4'-biphenylene diisocyanate;
3,3'-dichloro-4,4'-biphenylene diisocyanate;
1,5-naphthalene diisocyanate;
furfurylidene diisocyanate;
p,p'-diphenyl-methane diisocyanate;
3-nitrophenylene diisocyanate;
p,p'p''-tri-phenyl methane triisocyanate; and the like.

Any suitable Lewis acid can be complexed with the above-noted resins to form the desired photoconductive material. While the mechanism of the complex chemical inter-reaction involved in the present process is not completely understood, it is believed that a "charge transfer complex" is formed having absorption bands characteristic of neither of the two components considered individually. The mixture of the two non-photoconductive components seems to have a synergistic effect which is much greater than additive.

Best results are obtained when using these preferred Lewis acids: 2,4,7-trinitro-9-fluorenone, 4,4-bis-(dimethyl-amino) benzophenone, tetrachlorophthalic anhydride, chloranil, picric acid and benz(a)anthracene-7,12-dione, 1,3,5-trinitrobenzene.

Other typical Lewis acids are: quinones, such as

p-benzo-quinone,
2,5-dichlorobenzoquinone,
2,6-dichlorobenzoquinone,
chloranil,
naphthoquinone-(1,4),
2,3-dichloronaphthoquinone-(1-4),
anthraquinone,
2-methylanthraquinone,
1,4-dimethyl-anthraquinone,

1-chloroanthraquinone,
anthraquinone-2-carboxylic acid,
1,5-dichloroanthraquinone,
1-chloro-4-nitroanthraquinone,
phenanthrenequinone,
acenaphthenequinone,
pyranthrenequinone,
chrysenequinone,
thio-naphthene-quinone,
anthraquinone-1,8-disulfonic acid

and anthraquinone - 2- aldehyde, triphthaloyl-benzene-aldehydes such as bromal, 4-nitrobenzaldehyde, 2,6-dichlorobenzaldehyde - 2 - ethoxy-1-naphthaldehyde, anthracene-9-aldehyde, pyrene-3-aldehyde, oxindole-3-aldehyde, pyridine - 2,6 - dialdehyde, biphenyl-4-aldehyde, organic phosphonic acids such as 4-chloro-3-nitro-benzene-phosphonic acid; nitrophenols, such as 4-nitrophenol, and picric acid; acid anhydrides, for example, acetic-anhydride, succinic anhydride, maleic anhydride, phthalic anhydride, tetrachlorophthalic anhydride, perylene-3,4,9,10-tetracarboxylic acid and chrysene-2,3,8,9-tetracarboxylic anhydride, di-bromo maleic acid anhydride; metal-halides of the metals and metalloids of the Groups IB, II through to Group VIII of the Periodic System, for example: aluminum chloride, zinc chloride, ferric chloride, tin tetrachloride, (stannic chloride), arsenic trichloride, stannous chloride, antimony pentachloride, magnesium chloride, magnesium bromide, calcium bromide, calcium iodide, strontium bromide, chromic bromide, manganous chloride, cobaltous chloride, cobaltic chloride, cupric bromide, ceric chloride, thorium chloride, arsenic triiodide; boron halide compounds, for example: boron trifluoride, and boron trichloride; and ketones, such as actophenone, benzo-phenone, 2-acetyl-naphthalene, benzil, benzoin, 5-benzoyl acenaphthene, biacene-dione, 9-acetyl-anthracene, 9 - benzoyl-anthracene, 4-(4-dimethyl-amino-cinnamoyl)-1-acetylbenzene, acetoacetic acid anilide, indandione - (1,3), (1,3 - diketo-hydrindene), acenaphthene quinone-dichloride, anisil, 2,2-pyridil and furyl.

Additional Lewis acids are mineral acids such as the hydrogen halides, sulphuric acid and phosphoric acid; organic carboxylic acids, such as acetic acid and the substitution products thereof,

monochloro-acetic acid,
dichloroacetic acid,
trichloro-acetic acid,
phenylacetic acid, and
6-methyl-coumarinyl-acetic acid (4);
maleic acid,
cinnamic acid,
benzoic acid,
1-(4-diethyl-amino-benzoyl)-benzene-2-carboxylic acid,
phthalic acid, and
tetra-chlorophthalic acid,
alpha-beta-di-bromo-beta-formyl-acrylic acid (mucobromic acid),
dibromo-maleic acid,
2-bromo-benzoic acid,
gallic acid,
3-nitro-2-hydroxyl-1-benzoic acid,
2-nitrophenoxy-acetic acid,
2-nitro-benzoic acid,
3-nitro-benzoic acid,
4-nitro-benzoic acid,
3-nitro-4-ethoxy-benzoic acid,
2-chloro-4-nitro-1-benzoic acid,
2-chloro-4-nitro-1-benzoic acid,
3-nitro-4-methoxy-benzoic acid,
4-nitro-1-methyl-benzoic acid,
2-chloro-5-nitro-1-benzoic acid,
3-chloro-6-nitro-1-benzoic acid,
4-chloro-3-nitro-1-benzoic acid,
5-chloro-3-nitro-2-hydroxy-benzoic acid,
4-chloro-2-hydroxy-benzoic acid,

2,4-dinitro-1-benzoic acid,
2-bromo-5-nitro-benzoic acid,
4-chlorophenyl-acetic acid,
2-chloro-cinnamic acid,
2-cyano-cinnamic acid,
2,4-dichlorobenzoic acid,
3,5-dinitro-benzoic acid,
3,5-dinitro-salycylic acid,
malonic acid,
mucic acid,
acetosalycylic acid,
benzillic acid,
butane-tetracarboxylic acid,
citric acid
cyano-acetic acid,
cyclo-hexane-dicarboxylic acid,
cyclo-hexane-carboxylic acid,
9,10-dichloro-stearic acid,
fumaric acid,
itaconic acid,
levulinic acid, (levulic acid),
malic acid,
succinic acid,
alpha-bromo-stearic acid,
citraconic acid,
dibromo-succinic acid,
pyrene-2,3,7,8-tetra-carboxylic acid,
tartaric acid;

organic sulphonic acids, such as

4-toluene sulphonic acid, and
benzene sulphonic acid,
2,4-dinitro-1-methyl-benzene-6-sulphonic acid,
2,6-dinitro-1-hydroxy-benzene-4-sulphonic acid,
2-nitro-1-hydroxy-benzene-4-sulphonic acid,
4-nitro-1-hydroxy-2-benzene-sulphonic acid,
3-nitro-2-methyl-1-hydroxy-benzene-5-sulphonic acid,
6-nitro-4-methyl-1-hydroxy-benzene-2-sulphonic acid,
4-chloro-1-hydroxy-benzene-3-sulphonic acid,
2-chloro-3-nitro-1-methyl-benzene-5-sulphonic acid and
2-chloro-1-methyl-benzene-4-sulphonic acid.

The following examples will further define the specifics of the present invention. Parts and percentages are by weight unless otherwise indicated. The examples below should be considered to illustrate various preferred embodiments of the present invention:

Test procedures for determining photoconductivity as indicated in Table I

The substance to be evaluated is coated by suitable means onto a conductive substrate and dried. The coated plate is connected to ground and the layer is electrically charged in the dark by a corona discharge device (positive or negative) to saturation potential using a needlepoint scorotron powered by a high voltage power supply manufactured by High Volt Power Supply Company, Condenser Products Division, Model PS–10–1M operating at 7 kilovolts while maintaining the grid potential at 0.9 kilovolts using a Kepco, Incorporated regulated D.C. supply (0–1500 volts). Charging time is 15 seconds.

The electrostatic potential due to the charge is then measured with a transparent electrometer probe without touching the layer or affecting the charge. The signal generated in the probe by the charged layer is amplified and fed into a Moseley Autograf recorder, Model 680. The graph directly plotted by the recorder indicates the magnitude of the charge on the layer and rate of decay of the charge with time. After a period of about 15 seconds, the layer is illuminated by shining light onto the layer through the transparent probe using an American Optical Spence microscope illuminator having a G.E. 1493 medical type incandescent lamp operating at 2800° K. color temperature. The illumination level is measured with a Weston Illumination Meter, Model No. 756, and is recorded in the table. The light discharge rate is measured for a period of 15 seconds or until a steady residual potential is reached.

The numerical difference in the rate of discharge of the charge on the layer with time in the light minus the rate of discharge of the charge on the layer in the dark is considered to be a measure of the light sensitivity of the layer.

A practical test is also made on each material under study which shows photoconductivity. An electrophotographic image is produced by charging the material by corona discharge, exposing the material by projecting to a light-and-shadow image and developing the electrostatic latent image by cascading using a commercial developer, depending on the polarity of the initial corona charge given to the photoconductive material. Details of this procedure are given in Example I.

EXAMPLE I

About 2 grams of polymethylene polyphenylisocyanate (PAPI, available from the Carwin Company) is dispersed in a solvent blend consisting of about 10 g. of methyl ethyl ketone and about 20 g. of cyclohexanone contained in a 100 ml. Pyrex beaker. About 1.5 g. of Bisphenol-A is added to the above prepared solution and the mixture is agitated by means of a stirrer until solution of the Bisphenol-A is achieved. About 0.7 g. of 2,4,7-trinitrofluorenone is added to the above prepared solution and stirred as before to achieve solution.

The solution is applied onto an aluminum plate (0.005 x 11" x 16" flat rectangular sheet of bright finished 1145–H19 aluminum foil made by the Aluminum Company of America) by suitable means such as by a wire wound rod, dip coated, flow coated, whirler coated, etc. and the coating is dried. The solution is applied onto the plate until the thickness of the dried layer amounts to about 5 microns. The coating is cured for 30 minutes at 200° C.

A 6" x 6" portion of the above plate is negatively charged to about 400 volts by means of a corona discharge, exposed for about 15 seconds by projection using a Simmon Omega D3 enlarger equipped with an *f*4.5 lens and a tungsten light source operating at 2950° K. color temperature. The illumination level at the exposure plane is four foot-candles as measured with a Weston Illumination Meter Model No. 756. The plate is then developed by cascade using Xerox Corporation 1824 developer. The developed image is electrostatically transferred to a receiving sheet and fused. The image on the receiving sheet corresponds to the original projected image. The plate is cleaned of residual toner and is reused as by the above described process.

Another 6" x 6" portion of the above plate is electrometered as previously described and the results are tabulated. See Table I.

EXAMPLE II

A coating solution is prepared as described in Example I above and about 0.2 g. of p,p'-diaminodiphenylmethane is added. The mixture is stirred until solution is achieved. The solution is applied onto an aluminum plate as before and cured in an oven for 30 minutes at 200° C.

The plate is charged, exposed and developed and the image is fused onto the plate surface. The image developed on the plate corresponds to the original projected image.

Another portion of the above plate is electrometered as previously described and the results tabulated. See Table I.

EXAMPLE III

A coating solution is prepared as described in Example I above and about 0.05 g. of Brilliant Green dye is added. The mixture is stirred until solution is achieved. The solution is applied onto a conductive substrate and cured for 30 minutes at 200° C. in an oven.

The plate is charged, exposed and developed and the image is electrostatically transferred to a receiving sheet. The plate is cleaned of residual toner and reused as by the

above described process. Another portion of the plate is electrometered and the results are tabulated. See Table I.

EXAMPLE IV

About 0.05 g. of Brilliant Green dye is added to and dissolved in a coating solution prepared as described in Example II above. The solution is applied onto a conductive substrate and cured for 30 minutes at 200° C. in an oven.

The plate is charged, exposed and developed and the image is electrostatically transferred to a receiving sheet. The plate is cleaned of residual toner and reused as in the above described process. Another plate is prepared and electrometered as described and the results are tabulated in Table I.

Examples III and IV show that increased visible light sensitivity may be obtained by the addition of a sensitizing dye to the composition.

EXAMPLE V

A coating solution is prepared as described in Example I but without the addition of 2,4,7-trinitrofluorenone. An aluminum plate is coated with the solution and cured in an over for 30 minutes at 200° C. The coating is electrometered and the data are tabulated. See Table I.

EXAMPLE VI

A coating solution is prepared as described in Example II but without the addition of 2,4,7-trinitrofluorenone. An aluminum plate is coated with the solution and the coating is cured in an oven for 30 minutes at 200° C. The coating is electrometered and the data are tabulated. See Table I.

Examples V and VI show that the urethane resin coatings are nonphotoconductive in themselves.

EXAMPLE VII

About 2 grams of Lucite 2042, an ethyl methacrylate resin manufactured by E. I. duPont de Nemours and Co. (Inc.), is dissolved in 10 ml. of methyl ethyl ketone. The solution is applied onto an aluminum plate and dried. The plate is electrometered and the results are tabulated. See Table I.

This plate is used as a control.

EXAMPLE VIII

About 0.2 grams of p,p'-diaminodiphenylmethane is added to a resin coating solution prepared as described in Example VII above. The solution is applied onto a conductive base and dried. The plate is electrometered and the results are tabulated. See Table I.

EXAMPLE IX

About 0.5 grams of 2,4,7-trinitrofluorenone is added to a coating solution prepared as described in Example VIII above. The solution is applied onto a conductive base and dried. The plate is electrometered and the results are tabulated. See Table I.

The data of Examples VIII and IX show that p,p'-diaminodiphenylmethane and 2,4,7-trinitrofluorenone are non-photoconductive in an inert binder. See Table I.

TABLE I.—ELECTROMETER DATA ON POLYURETHANE PHOTOCONDUCTORS

Example	Initial Potential (Volts)	Light Discharge (Volts/Sec.)	Dark Discharge (Volts/Sec.)	Residual Potential Volts After 15 Secs.	Illumination Level (Foot Candles C 2,800° K.)	Sensitivity[1] (Volts/100 F.C., Sec.)
I	+355	14.0	8	190	32	20
	−440	23.0	2	250		70
II	+435	32.0	6	205	32	80
	−475	28.0	4	250		70
III	+390	27.0	6	170	32	60
	−470	80.0	1	190		300
IV	+380	71.0	3	125	32	220
	−430	133.0	3	120		410
V	+490	0.0	0	490	300	0
	−480	0.0	0	480		0
VI	+380	1.1	1.1	350	300	0
	−420	1.2	1.2	405		0
VII	+460	4.4	4.4	394	300	0
	−500	5.3	5.3	420		0
VIII	+420	0.0	0.0	420	260	0
	−450	0.0	0.0	450		0
IX	+425	3.0	2.0	380	260	0
	−440	3.0	2.0	390		0

[1] Figure of Merit is initial discharge rate upon illumination in volts/ft.-candle second, corrected for rate of dark discharge.

While a useful photoconductor will result from mixtures comprising from about 1 to about 100 parts of resin for each one part Lewis acid, for optimum sensitivity and reusability it is preferred that from about 1 to about 5 parts of resin be mixed with each one part Lewis acid.

Although specific materials and conditions were set forth in the above examples, these were merely illustrative of the present invention. Various other compositions, such as the typical materials listed above and various conditions where suitable, may be substituted for those given in the examples with similar results. For example, the polyurethane resin may be in the form of a continuous coating, as in the above examples, or in the form of a sponge or foam-like layer. The photoconductive composition of this invention may have other materials mixed therewith to enhance, sensitize, synergize or otherwise modify the photoconductive properties of the composition.

Many other modifications of the present invention will occur to those skilled in the art upon a reading of this disclosure. These are intended to be encompassed within the spirit of this invention.

What is claimed is:

1. A photoconductive charge transfer complex material comprising a mixture of a Lewis acid and a polyurethane resin which comprises the reaction product of an aromatic diisocyanate and an organic compound containing at least two active hydrogen containing groups said photoconductive charge transfer complex material having at least one new absorption band within a range of from about 3200 to about 7500 angstrom units.

2. The photoconductive material of claim **1** comprising from about 1 to about 100 parts of said resin for every one part of said Lewis acid.

3. The photoconductive material of claim **1** comprising from about 1 to about 4 parts of said resin for every one part of said Lewis acid.

4. The photoconductive material of claim **1** wherein said resin comprises the reaction product of polymethylene polyphenyl isocyanate and 2,2-bis(4-hydroxyphenyl) propane.

5. The photoconductive material of claim **4** comprising from about 1 to about 100 parts of said resin for every one part of said Lewis acid.

6. The photoconductive material of claim **4** comprising from about 1 to about 4 parts of said resin for every one part of Lewis acid.

7. The photoconductive charge transfer complex material of claim 1 wherein said Lewis acid comprises at least one member of the group consisting of 2,4,7-trinitro-9-fluoronone, 4,4-bis (dimethylamino) benzophenone, tetrachlorophthalic anhydride, chloranil, picric acid, 1,3,5-trinitrobenzene and benz(a) anthracene-7,12-dione.

8. The photoconductive charge transfer complex material of claim 7 wherein said Lewis acid comprises 2,4,7-trinitro-9-fluoronone.

9. A process for the preparation of a photoconductive charge transfer complex material which comprises mixing a Lewis acid and a polyurethane resin comprising the reaction product of an aromatic diisocyanate and an organic compound containing at least two active hydrogen containing groups said photoconductive charge transfer complex material having at least one new absorption band within a range of from about 3200 to about 7500 angstrom units.

10. The process of claim 9 wherein from about 1 to about 100 parts of said resin are mixed for about every one part of said Lewis acid.

11. The process of claim 9 wherein from about 1 to about 4 patrs of said resin are mixed for every one part of said Lewis acid.

12. The process as disclosed in claim 9 wherein said Lewis acid comprises at least one member of the group consisting of 2,4,7-trinitro-9-fluoronone, 4,4-bis (dimethylamino) benzophenone, tetrachlorophthalic anhydride, chloranil, picric acid, 1,3,5-trinitrobenzene and benz(a) anthracene-7,12-dione.

13. The process as disclosed in claim 12 wherein said Lewis acid comprises 2,4,7-trinitro-9-fluoronone.

14. The process of claim 9 wherein said resin comprises the reaction product of polymethylene polyphenyl isocyanate and 2,2-bis-(4-hydroxyphenyl) propane.

15. The process as disclosed in claim 14 wherein from about 1 to about 100 parts of said resin are mixed for about one part of said Lewis acid.

16. The process of claim 14 wherein from about 1 to about 4 parts of said resin are mixed for about one part of said Lewis acid.

17. An electrophotographic plate comprising a support substrate having fixed to the surface thereof a photoconductive charge transfer complex material comprising a mixture of a Lewis acid and a polyurethane resin which comprises the reaction product of an aromatic diisocyanate and an organic compound containing at least two active hydrogen containing groups, said photoconductive charge transfer complex material having at least one new absorption band within the range of from about 3200 to about 7500 angstrom units.

18. The electrophotographic plate of claim 17 wherein said polyurethane resin comprises the reaction product of polymethylene polyphenyl isocyanate and 2,2-bis-(4-hydroxyphenyl) propane.

19. The electrophotographic plate of claim 17 wherein said Lewis acid comprises at least one member of the group consisting of 2,4,7-trinitro-9-fluoronone, 4,4-bis(dimethylamino) benzophenone, tetrachlorophthalic anhyhydride, chloranil, picric acid, 1,3,5-trinitrobenzene and benz(a) anthracene-7,12-dione.

20. The plate of claim 19 wherein said Lewis acid comprises 2,4,7-trinitro-9-fluoronone.

21. An electrophotographic process wherein the plate of claim 17 is uniformly electrically charged, exposed to a light image pattern to be reproduced and developed with electrically attractable marking particles.

22. An electrophotographic process wherein the plate of claim 17 is charged in an image pattern and developed with electrically attractable marking particles.

23. A method of forming a latent electrostatic charge pattern by the process of uniformly charging the electrophotographic plate of claim 17 and exposing said plate to a pattern of activating electromagnetic radiation.

24. A method of forming a latent electrostatic charge pattern by the process wherein the plate of claim 17 is electrostatically charged in an image pattern.

25. The process as disclosed in claim 21 further including the steps of transferring said marking particles to a receiving sheet, and recharging, exposing and developing said plate to produce at least more than one copy of the original.

26. The process as disclosed in claim 22 further including the steps of transferring said marking particles to a receiving sheet and recharging and developing said plate to produce at least more than one copy of the original.

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