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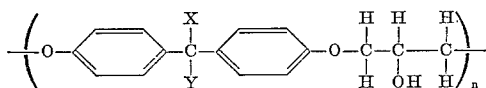
3,408,182

ELECTROPHOTOGRAPHIC MATERIALS AND METHODS EMPLOYING PHOTO- CONDUCTIVE RESINOUS CHARGE TRANSFER COMPLEXES

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ABSTRACT OF THE DISCLOSURE

Photoconductive materials are prepared from thermoplastic phenoxy resins having a repeating unit



plus a Lewis acid. The materials are charge transfer complexes. The photoconductive materials are used to make electrophotographic plates. Methods of using the plates are 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. Alternatively, a latent electrostatic image may be formed on the plate by charging said plate in image configuration. 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 ultra-violet, 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 economic and commercial considerations, there have been many recent efforts towards de-

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veloping 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 powerful 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 non-reusable 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 an electrophotographic plate 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.

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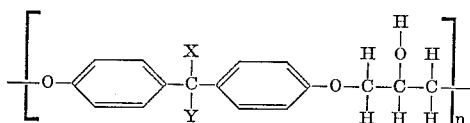
Still another object of this invention is to provide a novel combination of initially non-photoconductive insulating materials suitable for use in the manufacture of the photoconductive insulating layer of a xerographic plate which are easily coated on a desired substrate or combined with a conductive 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 thermoplastic phenoxy resin comprising recurring units having the formula:



wherein:

R₁ and R₂ are each selected from the group consisting of hydrogen and alkyl radicals, the total number of carbon atoms in X and Y being up to 12; and n is an integer having a value of at least two.

The above described complex may comprise from 1 to about 100 parts of resin for every one part of Lewis acid. About 1 to about 4 parts resin for each part Lewis acid is preferred as producing a plate with the most desirable combination of photoconductive sensitivity and reusability. Best results have been obtained when using a complex comprising 2,4,7-trinitro-9-fluoronone as the Lewis acid and the resin obtained by condensing epichlorohydrin with Bisphenol-A, [2,2-(4-bis-hydroxy phenol)-propane].

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 non-photoconductive.

After the above substantially non-photoconductive Lewis acid is mixed or otherwise complexed with said substantially non-photoconductive 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 non-photoconductive 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 photo-excitation 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.

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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 photo-excitation.
- (B) Donor-acceptor interaction is relatively strong in the photo-excited state, i.e., the components are at least partially ionized by photo-excitation.
- (C) When the complex is formed, one or more new absorption bands appear in the near ultra-violet or visible region (wave-lengths between 3200-7500 angstrom units) which are present in neither donor alone nor acceptor alone, but which 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 10¹⁴ 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 resins used in the present invention are obtained by condensing epichlorohydrin with a suitable dihydroxy organic compound. Best results are obtained when using bisphenol-A, [2,2-(4-bis-hydroxy-phenyl)-propane], in the preparation of the resin, and this is considered to be the preferred hydroxy compound. Other hydroxy-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.

An suitable di-(mono-hydroxy)alkane may be used in this invention. Typical alkanes are:

- (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-(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 (di-
 hydroxy-diphenyl)-heptane,
 4,4(4,4'-dihydroxy-diphenyl)-heptane,
 2,2-(4,4'-dihydroxy-diphenyl)-tri decane,
 2,2-(4,4'-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)-pro-
 pane,
 2,2-(3,5,3',5'-tetrabromo-4,4'-dihydroxy-diphenyl)-pro-
 pane,
 (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.

The basic chemical structure of phenoxy resins is similar to that of epoxy resins. Phenoxy resins, however, can be readily distinguished as a separate and unique resin class, differing from epoxides in several important characteristics. These important differences include:

- (1) Phenoxy resins do not have terminal, highly reactive epoxy groups and are stable materials which have infinite shelf life.
- (2) Phenoxy resins are thermoplastic with high molecular weights (about 30,000 compared to 340-4,000 for conventional epoxies) and are tough and ductile.
- (3) Phenoxy resins can be used as adhesives and coatings without further chemical conversion. They require no catalysts, curing agents or, "hardeners" to be useful.

A phenoxy resin prepared by the above method is then charge transfer complexed with a suitable Lewis acid to form the photoconductive material of this invention.

Any suitable Lewis acid can be complexed with the above noted phenoxy resins to form the desired photoconductive material. While the mechanism of the complex chemical interreaction 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 - fluoronone, 4,4-bis-(dimethylamino) 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-dimethylanthraquinone,
 1-chloroanthraquinone,
 anthraquinone-2-carboxylic acid,
 1,5-dichloroanthraquinone,
 1-chloro-4-nitroanthraquinone,
 phenanthrene-quinone,
 acenaphthenequinone,
 pyranthrenequinone,

chrysenequinone,
 thio-naphthene-quinone,
 anthraquinone-1,8-disulfonic acid and anthraquinone-2-aldehyde;

- 5 triphthaloylbenzene-aldehydes such as bromal,
 4-nitrobenzaldehyde,
 2,6-dichlorobenzaldehyde-2,
 ethoxy-1-naphthalidehyde,
 anthracene-9-aldehyde,
- 10 pyrene-3-aldehyde,
 oxindole-3-aldehyde,
 pyridine-2,6-dialdehyde,
 biphenyl-4-aldehyde;
- 15 organic phosphonic acids such as 4 - chloro - 3 - nitro-
 benzene-phosphonic acid nitrophenols, such as 4-nitro-
 phenol, and picric acid; acid anhydrides, for example,
 acetic-anhydride, succinic anhydride, maleic anhydride,
 phthalic anhydride, tetrachlorophthalic anhydride, peryl-
 ene 3,4,9,10-tetracarboxylic acid and chrysene-2,3,8,9-
 tetracarboxylic anhydride, di-bromo maleic acid an-
 hydride, metal halides of the metals and metalloids of
 20 the groups IB, II through to group VIII of the periodical
 system, for example: aluminum chloride, zinc chloride,
 ferric chloride, tin tetrachloride, (stannic chloride,)
 25 arsenic trichloride, stannous chloride, antimony penta-
 chloride, magnesium chloride, magnesium bromide, cal-
 cium bromide, calcium iodide, strontium bromide, chro-
 mic bromide, manganous chloride, cobaltous chloride,
 cobaltic chloride, cupric bromide, ceric chloride, thorium
 30 chloride, arsenic tri-iodide; boron halide compounds, for
 example: boron trifluoride, and boron trichloride; and
 ketones, such as acetophenone, benzophenone, 2-acetyl-
 naphthalene, benzil, benzoin, 5-benzoyl acenaphthene,
 35 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 furil.
- 40 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 sub-
 stitution products thereof, monochloro-acetic acid, di-
 chloroacetic acid, trichloro-acetic acid, phenylacetic acid,
 and 6-methylcoumarinylacetic acid (4);
- 45 maleic acid,
 cinnamic acid,
 benzoic acid,
 1-(4-diethyl-amino-benzoyl)-benzene-2-carboxylic acid,
 50 phthalic acid,
 and tetra-chlorophthalic acid,
 alpha-beta-dibromo-beta-formyl-acrylic acid (muco-
 bromic acid),
 dibromo-maleic acid,
 55 2-bromo-benzoic acid,
 gallic acid,
 3-nitro-2-hydroxyl-1-benzoic acid,
 2-nitro phenoxy-acetic acid,
 2-nitro-benzoic acid,
 60 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,
 65 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,
 70 4-chloro-3-nitro-1-benzoic acid,
 5-chloro-3-nitro-2-hydroxybenzoic acid,
 4-chloro-2-hydroxy-benzoic acid,
 2,4-dinitro-1-benzoic acid,
 2-bromo-5-nitro-benzoic acid,
 75 4-chlorophenyl-acetic acid,

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2-chloro-cinnamic acid,
2-cyano-cinnamic acid,
2,4-dichlorobenzoic acid,
3,5-dinitro-benzoic acid,
3,5-dinitro-salicylic acid,

malonic acid, mucic acid, acetosalicylic acid, benzilic acid, butane-tetra-carboxylic 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 procedure for determining photo-conductivity 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 needle-point 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 kilovolt using a Kepco, Incorporated regulated DC 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 Spencer microscope illuminator having a GE 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.

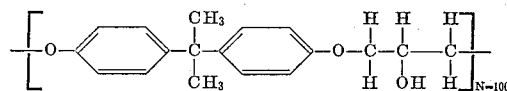
The numerical difference in the rate of discharge of the charge on the layer with time in the light minus the rate of discharge of the charge on the layer in the dark is considered to be a measure of the light sensitivity of the layer.

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 projection 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.

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EXAMPLE I

About 30 parts of Bakelite phenoxy resin PKDA-8500, (manufactured by the Union Carbide Corporation) which is obtained from the reaction of bisphenol-A and epichlorohydrin and has the following molecular structure:



is put into a Pyrex beaker containing a solvent blend consisting of about 80 parts ethyl Cellosolve, about 90 parts methyl ethyl ketone and about 30 parts toluene. The mixture is agitated by means of a stirrer until all of the resin is in solution.

About 0.1 part 2,4,7-trinitrofluoronone dissolved in a solvent blend consisting of about 3 parts cyclohexanone and about 3 parts toluene is added to about 10 parts of the phenoxy resin solution prepared above contained in a beaker. The mixture is agitated to insure complete mixing.

The above prepared solution is applied onto a conductive substrate, such as bright finished 1145-H19 aluminum foil made by the Aluminum Company of America, by suitable means such as wire wound bar, 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.

A 6 x 6 inch portion of the above prepared plate is negatively charged to about 450 volts by means of a corona discharge device, exposed for about 15 seconds by projection using a Simmons Omega D3 enlarger equipped with an f4.5 lens and a tungsten light source operating at 2950° K. color temperature. The illumination level at the plate is about four foot candles as measured with a Weston Illumination Meter Model No. 756. The plate is then developed by cascading Xerox Corporation 1824 developer over the plate. The developed image is then electrostatically transferred to a receiving sheet and fused. The image on the sheet is of good quality and corresponds to the projected image. The plate is then cleaned of residual toner and is reused as by the above described process.

Another portion of the above prepared 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 except that about 0.25 part 2,3-dichloro-1,4-naphthaquinone is added to the phenoxy resin solution rather than the Lewis acid of Example I. The above prepared solution is coated onto an aluminum substrate and dried. The coating is charged negatively by corona discharge, exposed and developed as previously described. The image developed on the plate is fused directly thereon. A direct image corresponding to the original is produced, having good density and contrast and resolution in excess of 20 line pairs/mm.

Another plate is prepared as described above and the plate is electrometered and the results are tabulated. See Table I.

EXAMPLE III

A coating solution is prepared as described in Example I above except that about 0.25 part of benz(a)-anthracene-7,12-dione is added to the phenoxy resin solution rather than the Lewis acid of Example I. The solution thus prepared is applied onto a conductive substrate as previously described and dried. A direct image corresponding to the original is produced, having good density and contrast and resolution in excess of 20 line pairs/mm. A coated plate is then electrometered as described and the data are tabulated. See Table I.

The data in Examples I to III show that the phenoxy

resin coatings are photoconductive when combined with a Lewis acid.

EXAMPLE IV

A coating solution is prepared as described in Example I above but without any Lewis acid. The resin solution is applied onto a conductive substrate and dried. The above prepared plate is electrometered and the results tabulated. See Table I. The phenoxy resin coating without Lewis acid is non-photoconductive.

EXAMPLE V

About 2 milligrams of Brilliant Green dye is added to a coating solution prepared as described in Example I above. The solution is applied onto a conductive substrate and dried. A xerographic image produced as in Example I

EXAMPLE IX

About 0.25 part of 2,3-dichloro,1,4-naphthoquinone is added to a coating solution prepared as described in Example VI above. The solution is applied onto a conductive substrate as described and dried. The plate is electrometered and the data are tabulated. See Table I.

EXAMPLE X

About 2 milligrams of Brilliant Green dye is added to a coating solution prepared as described in Example VI above. The solution is applied onto a conductive substrate and dried. The plate is electrometered and the results are tabulated. See Table I.

Examples VI to X show that the Lewis acids and sensitizing dyes tested are non-photoconductive in an inert binder, such as Lucite 2042. See Table I.

TABLE I.—ELECTROMETER DATA ON PHOTOCONDUCTIVE PHENOXY RESIN

Example	Initial Potential (Volts)	Light Discharge (Volts/Sec.)	Dark Discharge (Volts/Sec.)	Residual Potential Volts After 15 Secs.	Thickness, Microns	Illumination, Foot/Candles	Sensitivity (Volts/100 F.C. Sec.)
I.....	+430	20.0	5.6	250	5	136	10
	-460	21.3	0.0	265			20
II.....	+215	13.3	3.6	110	5	136	10
	-270	26.7	1.5	110			20
III.....	+395	9.7	0.0	310	10	136	10
	-400	8.4	0.0	310			10
IV.....	+450	0.0	0.0	450	5	136	0
	-450	0.0	0.0	450			0
V.....	+295	93.3	4.1	60	5	136	70
	-270	62.3	4.4	70			40
VI.....	+460	4.4	4.4	394	5	136	0
	-500	5.3	5.3	420			0
VII.....	+310	3.3	3.3	260	7	136	0
	-310	3.3	3.3	260			0
VIII.....	+380	3.0	3.0	335	7	136	0
	-470	4.0	4.0	410			0
IX.....	+320	1.6	1.6	290	5	136	0
	-300	4.5	4.5	225			0
X.....	+350	2.7	2.7	310	5	136	0
	-325	1	1	315			0

is of excellent quality. A plate is electrometered and the data are tabulated. See Table I.

This illustrates that increased visible light sensitivity may be obtained by the addition of sensitizing dyes to the composition.

EXAMPLE VI

About one gram of Lucite 2042, an ethyl methacrylate resin manufactured by E. I. du Pont de Nemours & Company, Inc., is dissolved in a solvent blend consisting of about 10 parts methyl ethyl ketone, about 1 part benzene, about 1 part acetone and about 2 parts diethyl ketone. The mixture is agitated by a stirrer until the resin is fully dissolved in the solvent blend.

The above solution is applied onto an aluminum plate by suitable means and dried.

The above plate is electrometered and the results are tabulated. See Table I. This plate is used as a control binder in Examples VII-X.

This indicates that Lucite 2042 is non-photoconductive.

EXAMPLE VII

About 0.25 part of 2,4,7-trinitrofluorone is added to a coating solution prepared as described in Example VI above. The solution is applied onto a conductive substrate as described and dried. The plate is electrometered and the data are tabulated. See Table I.

EXAMPLE VIII

About 0.25 part benz(a)anthracene 7,12-dione is added to a coating solution prepared as described in Example VI above. The solution is applied onto a conductive substrate as described and dried. The plate is electrometered and the data are tabulated. See Table I.

In the above table, sensitivity represents the initial discharge rate upon illumination in volts/100 foot candle seconds corrected for the rate of dark discharge. As shown by Examples I-III, a mixture of a phenoxy resin and a Lewis acid is photoconductive. Example IV shows that a phenoxy resin used alone, with no Lewis acid, is not photoconductive. Example V indicates that an epoxy resin-Lewis acid complex can be dye sensitized. As shown by Example VI, Lucite 2042, is not photoconductive. Examples VIII-X show that the Lewis acids and sensitizing dyes used in Examples I-V are not photoconductive in an inert Lucite binder.

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. The photoconductive composition of this invention may have other materials or colorants mixed therewith to enhance, sensitize, synergize or otherwise modify the photoconductive properties of the composition. The photoconductive compositions of this invention, where suitable, may be used in other imaging processes, such as those disclosed in copending applications Serial Nos. 384,737; 384,680 and 384,681, where their electrically photosensitive properties are beneficial.

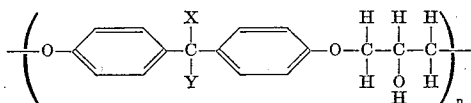
Many other modifications of the present invention will occur to those skilled in the art upon a reading of this disclosure. These are intended to be encompassed within the spirit of this invention.

What is claimed is:

1. A photoconductive charge transfer complex material comprising a mixture of a Lewis acid and a thermoplastic phenoxy resin, said phenoxy resin being void of ter-

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minal epoxy groups and having repeating units of the following general formula:



wherein:

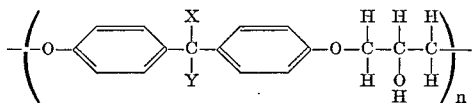
X and Y are each selected from the group consisting of hydrogen and alkyl radicals, and wherein the total number of carbon atoms in X and Y is up to 12; and n is an integer having a value of at least 2, and photoconductive charge transfer complex material having at least one new absorption band within 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 wherein said resin comprises the reaction product of epichlorohydrin and 2,2-bis-(4-hydroxy-phenyl) propane.

4. The photoconductive material of claim 3 comprising a mixture of from about 1 to about 100 parts of said resin for every one part of Lewis acid.

5. A process for the preparation of a photoconductive charge transfer complex material which comprises mixing a Lewis acid and a thermoplastic phenoxy resin, said phenoxy resin being void of terminal epoxy groups and having repeating units of the following formula:



wherein:

X and Y are each selected from the group consisting of hydrogen and alkyl radicals, and wherein the total number of carbon atoms in X and Y is up to 12; and n is an integer having a value of at least 2, said resulting photoconductive charge transfer complex material having at least one new absorption band within a range of from about 3200 to about 7500 angstrom units.

6. The process of claim 5 wherein from about 1 to about 100 parts of resin are mixed for every one part of Lewis acid.

7. The process of claim 5 wherein said resin comprises the reaction product of epichlorohydrin and 2,2-bis-(4-hydroxy-phenyl) propane.

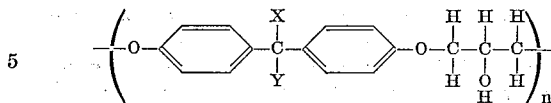
8. The process as disclosed in claim 5 wherein said Lewis acid is at least one member selected from the group consisting of 2,4,7-trinitro-9-fluoronone, 4,4-bis(dimethylamino) benzophenone, tetrachlorophthalic anhydride, chloranil, picric acid, 2,3-dichloro-1,4-naphthaquinone, benz(a)-anthracene-7,12-dione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

9. The process as disclosed in claim 8 wherein said Lewis acid comprises 2,4,7-trinitro-9-fluoronone.

10. 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 thermoplastic phenoxy resin, said phenoxy resin being void of terminal epoxy

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groups and having repeating units of the following general formula:



wherein:

X and Y are each selected from the group consisting of hydrogen and alkyl radicals, and wherein the total number of carbon atoms in X and Y is up to 12; and n is an integer having a value of at least 2, 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.

11. The plate as disclosed in claim 10 wherein said Lewis acid is selected from 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, 2,3-dichloro-1,4-naphthaquinone, benz(a)-anthracene-7,12-dione and 1,3,5-trinitrobenzene.

12. The plate as disclosed in claim 11 wherein said Lewis acid comprises 2,4,7-trinitro-9-fluoronone.

13. An electrophotographic process wherein the plate of claim 10 is electrically charged, exposed to an image pattern to be reproduced and developed with electrically attractable marking particles.

14. The process as disclosed in claim 13 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.

15. The process as disclosed in claim 11 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.

16. An electrophotographic process wherein the plate of claim 10 is electrically charged in an image pattern and developed with electrically attractable marking particles.

17. A method of forming a latent electrostatic charge pattern wherein the plate of claim 10 is uniformly electrically charged and exposed to a pattern of activating electromagnetic radiation.

18. A method of forming a latent electrostatic charge pattern wherein the plate of claim 10 is electrically charged in image configuration.

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

20. The charge transfer complex material of claim 19 wherein the Lewis acid is 2,4,7-trinitro-9-fluoronone.

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