United States Patent Office

3,408,184

Patented Oct. 29, 1968

3,408,184

ELECTROPHOTOGRAPHIC MATERIALS AND METHODS EMPLOYING PHOTOCONDUCTIVE RESINOUS CHARGE TRANSFERS COMPLEXES

Joseph Mammino, Penfield, N.Y., assignor to Xerox Corporation, Rochester, N.Y., a corporation of New York

No Drawing. Filed Jan. 18, 1965, Ser. No. 426,423

23 Claims. (Cl. 96—1.5)

ABSTRACT OF THE DISCLOSURE

Photoconductive materials are prepared from epoxy resins and 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 of 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 economic 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 material 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 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 are easily coated on a desired substrate or combined with a conductive layer.

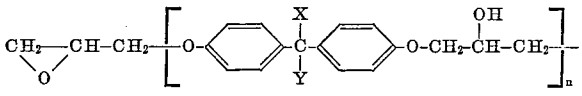
Another object is to provide a transparent self-supporting photoconductive film adapted for xerographic imaging which does not require a conductive backing.

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 composition having the following repeating units:



wherein:

X and Y are each selected from the group consisting of hydrogen, alkyl radicals wherein the total number of carbon atoms in X and Y is up to 12, and aralkyl radicals; 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-fluorenone as the Lewis acid and the resin obtained by condensing epichlorohydrin with Bisphenol-A, 2,2 - (4 bis - hydroxy phenyl)-propane.

It should be noted that neither of the above two components (A) and (B) used to make the photoconductor of 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 this 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 (wavelengths 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 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 resins used in the present invention are obtained by condensing epichlorohydrin with a suitable dyhydroxy organic compound. Best results are obtained when using Bisphenol-A (2,2-(4-bis-hydroxyphenyl)-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-hydroxyphenyl)-propane) being the most preferred embodiment.

Any suitable polyhydroxy organic compound may be used in this invention. Typical 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(dihydroxy diphenyl)-heptane,
4,4-(4,4'-dihydroxy-diphenyl)heptane,
2,2-(4,4'-dihydroxy-diphenyl)tridecane,
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)-propane,
2,2-(3,5,3',5'-tetra-bromo-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,
1,3-diphenyl-1,1,3,3-tetra-p-phenol propane,
1,1,3,3-tetra-p-phenol propane,
1,1,4,4-tetra-p-phenol butane,
and mixtures thereof.

An epoxy 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 epoxy 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-fluorenone, 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-benzoquinone, 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, chrysene-quinone, thio-naphthene-quinone, anthraquinone-1,8 disulfonic acid and anthraquinone-2-aldehyde, triphthaloyl-benzene-aldehydes such as bromal, 4-nitrobenzaldehyde, 2,6-di-chlorobenzaldehyde-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 periodical 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 acetophenone benzophenone, 2 - acetyl-naphthalene, benzil, benzoin, 5-benzoyl acenaphthene, biacene-dione, 9-acetyl-anthracene, 4-(4 - dimethylamino - cinnamoyl)-1-acetylbenzene, acetoacetic acid anilide, indandione-(1,3), (1 - 3 - diketo-hydrindene), acenaphthene quinone-dichloride, anisil, 2,2-pyridil and furil, 9-benzoyl-anthracene.

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 (muco-bromic acid), dibromo-maleic acid, 2-bromobenzoic acid gallic acid, 3-nitro - 2 - hydroxyl-1-benzoic acid, 2-nitro phenoxy-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-salicylic acid, malonic acid, mucic acid, acetosalicylic acid, benzilic acid, butane-tetracarboxylic acid, citric acid, cyano-acetic acid cyclo-hexane-dicarboxylic acid, cyclo-hexene-carboxylic acid, 9,10-dichloro-stearic acid, fumaric acid, itaconic acid, levulinic acid (levulic acid), maleic acid, succinic acid, alpha-bromo-stearic acid, citraconic acid, dibromo-succinic acid, pyrene-2,3,7,8-tetracarboxylic 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 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 kilovolt using a Kepco, Incorporated, regulated D.C. supply (0–1500 volts). Charging time is 15 seconds.

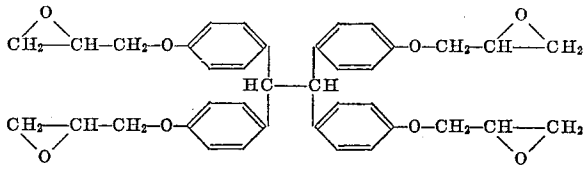
The electrostatic potential due to the charge is then measured with a transparent electrometer probe without touching the layer or affecting the charge. The signal generated in the probe by the charged layer is amplified and fed into a Moseley Autograf recorder, Model 680. The graph directly plotted 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 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.

EXAMPLE I

About one gram of an epoxy resin Epon 1031 (manufactured by the Shell Chemical Company) which consists of a mixture of isomers and homologues having an idealized structure as follows:



is dissolved in about 9 grams of a one-to-one solvent blend of acetone and toluene contained in a 50 ml. beaker. The mixture is agitated by means of a stirrer until all of the resin is fully dissolved in the solvent. About 0.5 gram of 2,4,7-trinitrofluorenone is added to the epoxy resin solution prepared above and the mixture stirred until solution of the 2,4,7-trinitrofluorenone is achieved.

The above prepared solution is applied onto a conductive substrate, for example, 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 aluminum plate 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" portion of the above prepared plate is negatively charged to about 300 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 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 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

About one gram of an epoxy resin Araldite 7097 manufactured by Ciba Products Company which is obtained by reacting Bisphenol-A with epichlorohydrin, is put into a 50 ml. Pyrex beaker containing about 2 g. of toluene and 7 g. of acetone. The mixture is agitated by means of a stirrer until all of the resin is in solution.

About 250 mg. of 2,4,7-trinitofluorenone is added to the above prepared solution and stirred as before until solution of the 2,4,7-trinitrofluorenone is achieved.

The above prepared solution is applied onto an aluminum substrate by means of a wire wound bar and dried. The coated sheet is then charged, exposed and developed as described in Example I above and the toner is fused directly onto the plate.

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

EXAMPLE III

A coating solution is prepared as described in Example II above except that about 250 mg. of benz(a)anthracene 7,12-dione is added to the Araldite 7079 epoxy resin solution instead of 2,4,7-trinitrofluorenone. The above prepared solution is applied onto an aluminum substrate and dried. The coated sheet is then electrometered as previously described and the data are tabulated. See Table I.

EXAMPLE IV

A coating solution is prepared as described in Example II above except that about 250 mg. of benzophenone tetracarboxylic acid dianhydride is added to the Araldite 7097 epoxy resin solution in place of 2,4,7-trinitrofluorenone. The above prepared solution is applied onto an aluminum substrate and dried. The coated sheet is then electrometered as previously described and the data are tabulated. See Table I.

EXAMPLE V

About 2 grams of an epoxy resin, Oxiron 2002 (manufactured by Food Machinery and Chemical Corporation) which is obtained by epoxidizing polybutadiene, is put into a 50 ml. Pyrex beaker containing a solvent mixture consisting of about 3 g. isobutanol, about 2 g. toluene and about 10 g. of acetone. The mixture is agitated by means of a stirrer until resin is fully dispersed. About one gram of phthalic anhydride and one gram of 2,4,7-trinitrofluorenone are added to the above prepared solution and stirred as before until solution is achieved.

The above prepared solution is applied onto an aluminum substrate by means of a No. 36 wire wound bar and cured in an oven maintained at 350° F. for 3 hours. The coating thus obtained is infusible and solvent resistant.

The above prepared plate is charged, exposed and developed as described in Example I above and the image obtained corresponded to the original projected image. The developed image is then fused directly onto the plate.

Another plate is prepared as described above and charged, exposed and developed as described. The image is then electrostatically transferred to a receiving sheet and fused. 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 VI

A coating solution is prepared consisting of about one gram of Epon 1031 epoxy resin (Shell Chemical Company) and discussed in Example I above is put into a 50 ml. beaker and dissolved in 4 g. of a one-to-one solvent

blend consisting of acetone and toluene. The solution is applied onto an aluminum substrate and dried.

The above plate is electrometered and the results tabulated. See Table I.

EXAMPLE VII

A coating solution is prepared consisting of about one gram of Araldite 7097 epoxy resin (Ciba Products Company) and is described above is put into a 50 ml. beaker containing 4 g. of a solvent blend consisting of 2 g. acetone and 2 g. toluene. The solution is applied onto an aluminum substrate and dried.

The above plate is electrometered and the results tabulated. See Table I.

EXAMPLE VIII

A coating solution is prepared consisting of about 2 g. of Oxiron 2002 epoxy resin and described above is put into a 50 ml. beaker containing 1 g. of phthalic anhydride dissolved in a solvent blend consisting of 10 g. acetone, 3 g. isobutanol and 2 g. toluene. The mixture is agitated by means of a stirrer until all of the materials are well dispersed. An aluminum substrate is coated with the above prepared solution by means of a wire wound bar and dried.

The above plate is electrometered and the results are tabulated. See Table I.

Tests on the coatings prepared as described in Example VI, Example VII, and Example VIII indicate that the epoxy resins are nonphotoconductive by themselves.

EXAMPLE IX

A coating solution is prepared consisting of about one gram of Araldite 7097 epoxy resin and described above dissolved in 4 g. of a one-to-one solvent blend of acetone and toluene contained in a 50 ml. beaker. About 12.5 cc. of a 2,4,7-trinitrofluorenone solution in toluene at a concentration of 0.02 g./cc. is added to the above prepared solution. About 0.013 g. of 2-p-iodophenyl-3-(-p-nitrophenyl)-5-phenyl tetrazolium chloride dissolved in a solvent blend of 2 cc. methanol, 5 cc. cyclohexanone and 5 cc. of acetone is added to the above prepared solution. The mixture is agitated by means of a stirrer to disperse the materials.

An aluminum substrate is coated with the above prepared solution by means of a wire wound bar and dried.

The above plate is electrometered and the results are tabulated. See Table I.

EXAMPLE X

A coating solution is prepared as described in Example IX above except that about 0.013 g. of Brilliant Green dye is added to the Araldite 7097 epoxy resin instead of 2 - p - iodophenyl - 3 - (- p - nitrophenyl) - 5 - phenyl tetrazolium chloride. The above prepared solution is applied onto an aluminum substrate by dip-coating techniques and dried.

The above prepared coating is electrometered and the results are tabulated. See Table I.

EXAMPLE XI

A coating solution is prepared as described in Example X above except that about 0.013 g. of Martius Yellow dye is added to the epoxy resin solution in place of Brilliant Green dye. Another coating is prepared in the same manner and electrometered. The results are tabulated. See Table I.

EXAMPLE XII

A coating solution is prepared as described in Example X above except that about 0.013 g. of Martius Yellow dye is added to the epoxy resin solution in place of Brilliant Green dye. Another coating is prepared in the same manner and electrometered. The results are tabulated. See Table I.

The above data of Examples IX to XII show that increased visible light sensitivity may be obtained by the addition of sensitizing dyes to the resin-Lewis acid composition.

EXAMPLE XIII

About one gram of Lucite 2042, an ethyl methacrylate resin manufactured by E. I. du Pont de Nemours and Company, Inc., is dissolved in a solvent blend consisting of 10 ml. of methyl ethyl ketone, 1 ml. of benzene, 1 ml. of acetone and 2 ml. of 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; in that Lucite 2042 is an inert, nonphotoconductive binder.

EXAMPLE XIV

About 250 mg. of 2,4,7-trinitrofluorenone is added to a coating solution prepared as described in Example XIII 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 XV

About 250 mg. of benz(a)anthracene 7,12-dione is added to a coating solution prepared as described in Example XIII 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 XVI

About 250 mg. of benzophenone tetracarboxylic acid dianhydride is added to a coating solution prepared as described in Example XII above. The solution is applied onto a conductive substrate as described and dried. The plate is electrometered and the data tabulated. See Table I.

EXAMPLE XVII

About 0.010 g. of 2 - p - iodophenyl - 3 - (p-nitrophenyl) - 5 - phenyltetrazolium chloride is added to a coating solution prepared as described in Example XIII above. The solution is applied onto a conductive substrate and dried. The plate is electrometered and the data are tabulated. See Table I.

EXAMPLE XVIII

About 0.010 g. of Brilliant Green dye is added to a coating solution prepared as described in Example XIII above. The solution is applied onto a conductive substrate and dried. The plate is electrometered and the results are tabulated. See Table I.

EXAMPLE XIX

About 0.010 g. of Rhodamine B base dye is added to a coating solution prepared as described in Example XIII above. The solution is applied onto a conductive substrate and dried. The plate is electrometered and the results are tabulated. See Table I.

EXAMPLE XX

About 0.010 g. of Martius Yellow dye is added to a coating solution prepared as described in Example XIII above. The solution is applied onto a conductive substrate and dried. The plate is electrometered and the results are tabulated. See Table I.

The data in Examples XIV to XX shows that the Lewis acids and sensitizing dyes tested are nonphotoconductive in an inert binder, and thus are not themselves photoconductive.

As shown in Examples I–V, a mixture of an epoxy resin and a Lewis acid is photoconductive. Examples VI–VIII show that epoxy resins are not photoconductive when used alone. That the sensitivity of an epoxy resin-Lewis acid plate can be increased by the addition of

resin having repeating units of the following general formula:

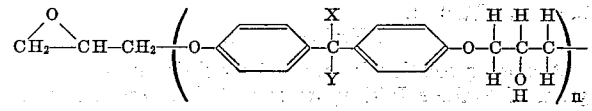


TABLE I.—ELECTROMETER DATA ON PHOTOCONDUCTIVE EPOXY RESINS

Example	Initial Potential (Volts)	Light Discharge (Volts/sec.)	Dark Discharge (Volts/sec.)	Volts Residual Potential After 15 Sec.	Thickness, Microns	Illumination, Foot Candles	Sensitivity (Volts/100 f.c. Sec.)*
I	+110	26.7	4.9	5	5	94	20
	−230	27.0	3.3	0			28
II	+130	21.3	2.2	35	15	94	20
	−100	26.7	0	5			30
III	+340	26.7	2	190	15	94	30
	−440	93.4	1	170			30
IV	+490	11.1	3.1	360	20	94	10
	−470	11.9	2.8	330			10
V	+370	44.4	6.7	145	5	94	40
	−470	160	6.7	110			160
VI	+180	1	1	165	5	94	0
	−150	2	2	120			0
VII	+175	0	0	175	10	94	0
	−150	0	0	150			0
VIII	+350	4.5	4.5	285	10	94	0
	−320	20	20	220			0
IX	+200	80	6.7	25	7	94	80
	−310	334	0	0			400
X	+155	53.4	2.2	0	7	94	50
	−165	133	0	0			140
XI	+130	4.5	1	0	10	94	10
	−170	93.4	1	0			100
XII	+90	26.7	1.9	10	5	94	30
	−150	133	0	0			140
XIII	+460	4.4	4.4	394	10	94	0
	−500	5.3	5.3	420			0
XIV	+310	3.3	3.3	260	13	94	0
	−310	3.3	3.3	260			0
XV	+320	1.6	1.6	290	10	94	0
	−300	4.5	4.5	225			0
XVI	+280	0	0	280	10	94	0
	−250	2	2	220			0
XVII	+200	5.3	5.3	90	5	94	0
	−180	8.9	8.9	50			0
XVIII	+350	2.7	2.7	310	15	94	0
	−325	0.7	0.7	315			0
XIX	+75	1.3	1.3	55	7	94	0
	−340	9.0	9.0	210			0
XX	+420	0	0	420	5	94	0
	−340	1.1	1.1	330			

*Sensitivity—Figure of Merit is initial discharge rate upon illumination in volts/ft. candle second, corrected for rate of dark discharge.

various sensitizing dyes is shown by Examples IX–XII. Example XIII shows that Lucite 2042 is nonphotoconductive. This resin is used as an inert binder resin in Example XIV to show that Lewis acids and sensitizing dyes are not in themselves, photoconductive.

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 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 Numbers 384,737; 384,680 and 384,681, where their electrically photosensitive properties are beneficial. While any suitable epoxy resin may be used, it is preferred that one having a molecular weight of from 700 to 1500 be used.

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 acid and an epoxy wherein:

X and Y are each selected from the group consisting of hydrogen, alkyl radicals wherein the total number of carbon atoms in X and Y is up to 12, and aralkyl radicals; 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 a range of from about 3200 to about 7500 angstrom units.

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

3. The photoconductive charge transfer complex material of claim **2** wherein said Lewis acid is 2,4,7-trinitro-9-fluorenone.

4. 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.

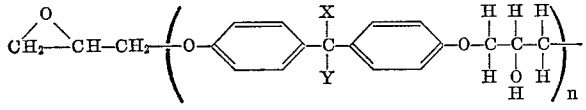
5. The photoconductive material of claim **1** comprising from about 1 to about 4 parts of said resin for every one part of said Lewis acid.

6. The photoconductive material of claim **1** wherein the molecular weight of the resin is from about 700 to about 1500.

7. The photoconductive material of claim 1 wherein said resin comprises the reaction product of epichlorohydrin and 1,1,3,3-tetra-p-phenol propane.

8. The photoconductive material of claim 1 wherein said resin comprises the reaction product of epichlorohydrin and 2,2-bis-(4-hydroxy-phenyl) propane.

9. A process for the preparation of a photoconductive charge transfer complex material which comprises mixing a Lewis acid and an epoxy resin having repeating units of the following formula:



wherein:

X and Y are each selected from the group consisting of hydrogen, alkyl radicals wherein the total number of carbon atoms in X and Y is up to 12, and aralkyl radicals; 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.

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

11. The process of claim 10 wherein said Lewis acid is 2,4,7-trinitro-9-fluorenone.

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

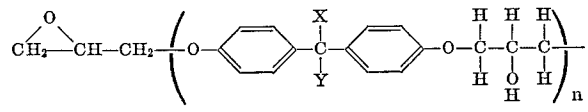
13. The process of claim 9 wherein from about 1 to about 4 parts of resin are mixed for every one part of Lewis acid.

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

15. The method of claim 9 wherein said resin and said Lewis acid are mixed while in a liquid carrier, and subsequently depositing the resulting liquid mixture on a supporting substrate and removing the liquid portion from said mixture.

16. 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 an epoxy resin having repeating units of the following general formula:



wherein:

X and Y are each selected from the group consisting of hydrogen, alkyl radicals wherein the total number of carbon atoms in X and Y is up to 12, and aralkyl radicals; 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.

17. The plate of claim 16 wherein said Lewis acid is selected from at least one member of the group consisting of 2,4,7-trinitro-9-fluorenone, 4,4-bis-(dimethylamino) benzophenone, tetrachlorophthalic anhydride, chloranil, picric acid, benz(a)anthracene-7,12-dione and 1,3,5-dinitrobenzene.

18. The plate of claim 17 wherein said Lewis acid is 2,4,7-trinitro-9-fluorenone.

19. An electrophotographic process wherein the plate of claim 16 is uniformly electrically charged, exposed to a pattern of activating electromagnetic radiation and developed with electrically attractable marking particles.

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

21. A method of forming a latent electrostatic charge pattern which comprises uniformly charging the electrophotographic plate of claim 16 and exposing said plate to a pattern of activating electromagnetic radiation.

22. The process as disclosed in claim 19 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.

23. The process as disclosed in claim 20 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.

References Cited

UNITED STATES PATENTS

2,752,269	6/1956	Condo et al.	117—139.4
3,037,861	6/1962	Hoegl et al.	96—1

OTHER REFERENCES

Sorensen, Wayne R. and Campbell, Tod W., Preparative Methods of Polymer Chemistry, 1961, p. 307.

NORMAN G. TORCHIN, *Primary Examiner.*

J. C. COOPER, *Assistant Examiner.*