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3,408,190

## ELECTROPHOTOGRAPHIC PLATE AND PROCESS EMPLOYING PHOTOCONDUCTIVE CHARGE TRANSFER COMPLEXES

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### ABSTRACT OF THE DISCLOSURE

Photoconductive materials are prepared from polysulfone 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 areas 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 the plate in image configuration. This image is rendered visible by depositing on the image layer a finely divided electroscopic marking material called a toner. 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 ultra-violet 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 regions 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 insulat-

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ing 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 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 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 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 film and structures.

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.

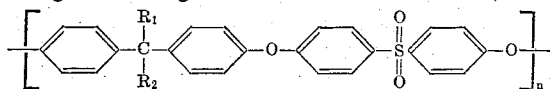
Another object is to provide a transparent self-support-

ing 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 polysulfone resin comprising recurring units having the formula



wherein:

- $R_1$  and  $R_2$  are each selected from the group consisting of hydrogen and alkyl radicals, the total number of carbon atoms in  $R_1$  and  $R_2$  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-fluorenone as the Lewis acid and the resin obtained by reacting the potassium or sodium salt of bisphenol-A with p,p'-dichlorodiphenylsulfone in dimethylsulfoxide and chlorobenzene. This synthesis is described in detail in Dutch Patent 6,408,130.

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 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 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 (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 electrophotographic 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.<sup>2</sup> of absorbed radiation.

This definition excludes the resins and Lewis acids of my disclosure, when used individually, from the class of "photo-conductive insulators."

The resins used in the present invention are obtained by condensing p,p'-dichlorodiphenylsulfone with a suitable salt of a dihydroxy organic compound. Best results are obtained when using salts of bisphenol-A, 2,2-(4 bis-hydroxy-phenyl)-propane, in the preparation of the resin and this is considered to be the preferred dihydroxy 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 being the most preferred embodiment.

Any 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'-dihydroxydiphenyl) 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'-dihydroxydiphenyl) 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)-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'-tetrachloro-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, and  
 1,1-(4,4'-dihydroxy-diphenyl-1-phenyl)-ethane,  
 and mixtures thereof.

Any suitable Lewis acid can be complexed with the above noted polysulfone resins to form the desired photo-conductive material. While the mechanism of the complex chemical interaction 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-photo-conductive 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, 9-(dicyanomethylene)-2,4,7-trinitrofluorene, 2,3-dichloro-1,4-naphthaquinone and mixtures thereof.

Other typical Lewis acids include: quinones, such as

p-benzo-quinone,  
 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;  
 triphthalolylbenzene-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-phosphoric 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,

metal halides of the metals and metalloids of the groups 1B, II through to Group VIII of the periodical system for example:

- 5 aluminum chloride,  
zinc chloride,  
ferric chloride tin tetrachloride (stannic chloride),  
arsenic trichloride,  
stannous chloride,  
antimony pentachloride,
- 10 magnesium chloride,  
magnesium bromide,  
calcium bromide,  
calcium iodide,  
strontium bromide,
- 15 chromic bromide,  
manganous chloride,  
cobaltous chloride,  
cobaltic chloride,  
cupric bromide,
- 20 ceric chloride,  
thorium chloride,  
arsenic tri-iodide;  
boron halide compounds, for example:
- 25 boron trifluoride, and  
boron trichloride;  
and ketones, such as  
acetophenone,  
benzophenone,
- 30 2-acetylnaphthalene,  
benzil  
benzoin,  
5-benzoyl acenaphthene,  
biacenedione,
- 35 9-acetyl-anthracene,  
9-benzoylanthracene,  
4-(4-dimethyl-amino-cinnamoyl)-1-acetylbenzene,  
acetoacetic acid anilide,  
indandione-(1,3),
- 40 (1-3-diketo-hydrindene) acenaphthene quinone-dichloride,  
anisil,  
2,2-pyridil, and  
fural.

Additional Lewis acids include 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,
- 50 dichloroacetic acid,  
trichloro-acetic acid,  
phenylacetic acid, and  
6-methylcoumarinylacetic acid (4);  
maleic acid,
- 55 cinnamic acid,  
benzoic acid,  
1-(4-diethyl-amino-benzoyl)-benzene-2-carboxylic acid,  
phthalic acid, and  
tetra-chlorophthalic acid,
- 60 alpha-beta-dibromo-beta-formyl-acrylic acid (muco-bromic acid),  
dibromomaleic acid,  
2-bromo-benzoic acid,  
gallic acid,
- 65 3-nitro-2-hydroxyl-1-benzoic acid,  
2-nitro phenoxy-acetic acid,  
2-nitrobenzoic acid,  
3-nitro-benzoic acid,  
4-nitro-benzoic acid,
- 70 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,
- 75 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,  
 benzoic acid,  
 butane-tetra-carboxylic acid,  
 citric acid,  
 cyano-acetic acid,  
 cyclo-hexane-dicarboxylic acid,  
 cyclo-hexane-carboxylic acid,  
 9,10-dichlorostearic 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 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:

In each of Examples I-XIII 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. Such corona charging is described in detail by Carlson in U.S. Patent 2,588,699.

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

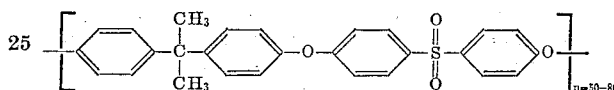
1493 medical type incandescent lamp operating at 2800° K. color temperature. The illumination level is measured with a Weston Illumination Meter, Model No. 756, and is recorded in the table. The light discharge rate is measured for a period of 15 seconds or until a steady residual potential is reached.

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.

Practical tests are also made on each material under study which shown 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 cascade using a commercial developer. Details of this procedure are given in Example I.

#### EXAMPLE I

About 10 parts of Bakelite Polysulfone P1700 (manufactured by the Union Carbide Corporation) which has the following molecular structure.



is dissolved in about 200 parts dichloromethone. To this solution is added a solution of about 3 parts 2,4,7-trinitro-9-fluorenone in about 50 parts cyclohexanone. The mixture is agitated to insure uniformity.

The above prepared solution is flow coated onto bright finished 1145-H19 aluminum foil made by the Aluminum Company of America and oven dried at about 150° C. for about 10 minutes. The dried coating thickness is 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 f/4.5 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 cascade as described by Walkup in U.S. Patent 2,618,551. The developed image is then electrostatically transferred to a receiving sheet and fused by the method described by Schaffert in U.S. Patent 2,576,047. 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 the polysulfone is Bakelite Polysulfone P2300 (Union Carbide). This polysulfone has a structure similar to that given in Example I, but has a higher molecular weight. The above prepared solution is coated onto an aluminum substrate and dried. The coating is charged negatively by corona discharge, exposed and developed as in Example I previously described. The image developed on the plate is fused directly thereon. A positive image corresponding to the original is produced, having good density and contrast.

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 the polysulfone is Bakelite Polysulfone P3500 (Union Carbide). This resin has a structure similar

to that shown in Example I, but has a still higher molecular weight. The solution thus prepared is applied onto a conductive substrate as previously described and dried. A positive 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.

#### EXAMPLE IV

A coating solution is prepared as described in Example I, except that about 3 parts 9-(dicyanomethylene)-2,4,7-trinitrofluorene is used in place of the 2,4,7-trinitro-9-fluorenone. The solution thus prepared is applied onto a conductive substrate as previously described and dried. A portion of the plate is exposed and developed as in Example I, producing a positive image of good quality. Another portion of the plate is then electrometered and the data tabulated in Table I.

#### EXAMPLE V

A plate is coated, dried, charged, exposed and developed as in Example IV, except that here the Lewis acid used is 2,3-dichloro-1,4-naphthoquinone. The image produced on this plate is of excellent quality. A portion of the plate is electrometered and the results recorded in Table I.

The data resulting from Examples I-V show that polysulfone resins are photoconductive where combined with Lewis acids.

#### EXAMPLE VI

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 polysulfone resin coating without Lewis acid is thus found to be non-photoconductive.

#### EXAMPLE VII

A coating solution is prepared as described in Example II above, but without any Lewis acid. The resin solution is applied onto a conductive substrate and dried. This plate is charged, exposed and electrometered as in Example II. As shown in Table I, this plate is non-photoconductive.

#### EXAMPLE VIII

A coating solution is prepared as described in Example III above, but with no Lewis acid. The resin solution is coated onto a conductive substrate and wired. This plate is charged, exposed and electrometered as in Example III. As shown by the results tabulated in Table I, the plate is non-photoconductive in the absence of Lewis acid.

#### EXAMPLE IX

About 2 milligrams of Brilliant Green Special dye, C.I. No. 662, a triphenyl methane (Allied Chemical) 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 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 X

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 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 XI

About 0.25 part of 2,4,7-trinitrofluorenone is added to a coating solution prepared as described in Example X 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 XII

About 0.25 part 9-(dicyanomethylene)-2,4,7-trinitrofluorenone is added to a coating solution prepared as described in Example X 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 XIII

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

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

TABLE I

Example	Initial Potential (volts)	Light Discharge (volts/sec.)	Dark Discharge (volts/sec.)	Residual Potential after 15 sec. (volts)	Illumination (foot candles)	Sensitivity volts/100 f.c.-sec.)
I.....	+500	24.0	4.0	+280	134	1.8
	-640	48.0	5.0	-295	134	3.2
II.....	+540	22.4	6.4	+310	134	1.2
	-550	32.0	4.4	-310	134	1.3
III.....	+480	32.0	4.0	+220	134	2.1
	-570	76.0	4.9	-220	134	5.3
IV.....	+220	24.0	8.0	+305	57	28.1
	-350	56.1	24.0	-120	57	56.4
V.....	+490	10.7	4.0	+410	57	11.7
	-590	10.7	2.2	-470	57	14.9
VI.....	+580	0	0	+580	134	0
	-710	0	0	-710	134	0
VII.....	+770	0	0	+770	134	0
	-690	0	0	-690	134	0
VIII.....	+430	0	0	+430	134	0
	-570	0	0	-570	134	0
IX.....	+430	56.0	13.3	+150	57	74.8
	-515	116.0	12.0	-160	57	179.0
X.....	+460	4.4	4.4	394	136	0
	-500	5.3	5.3	420	136	0
XI.....	+310	3.3	3.3	260	136	0
	-310	3.3	3.3	260	136	0
XII.....	+380	3.0	3.0	335	136	0
	-470	4.0	4.0	410	136	0
XIII.....	+350	2.7	2.7	310	136	0
	-325	1.0	1.0	315	136	0

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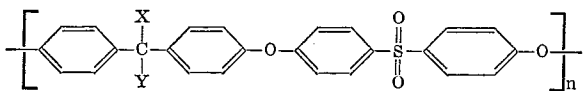
In the above table, sensitivity represents the initial discharge rate upon illumination in volts/100 foot candle seconds corrected for the rate of dark discharge. As shown by Examples I-IV, a mixture of a polysulfone resin and a Lewis acid is photoconductive. Examples V-VII show that a polysulfone resin used alone, with no Lewis acid, is not photoconductive. Example VIII indicates that a polysulfone resin-Lewis acid complex can be dye sensitized. As shown by Example IX, Lucite 2042, is not photoconductive. Examples X-XII show that the Lewis acids and sensitizing dyes used in Examples I-IV and VIII 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 Ser. Nos. 384,737, now U.S. Patent 3,384,565; 384,680; and 384,681; both now abandoned, 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 polysulfone resin 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 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 comprising from about 1 to about 100 parts of said resin for every one part of said Lewis acid.

3. The photoconductive charge transfer complex material of claim 1 wherein said resin comprises the reaction product of p,p'-dichlorodiphenylsulfone and 2,2-bis-(4-hydroxy-phenyl) propane.

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

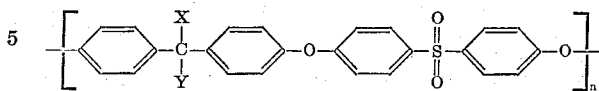
5. The photoconductive charge transfer complex material of claim 1 wherein said Lewis acid is selected from the group consisting of 2,4,7-trinitro-9-fluorenone, 9-(dicyanomethylene)-2,4,7-trinitro-fluorene, 2,3-dichloro-1,4-naphthaquinone, and mixtures thereof.

6. The charge transfer complex material of claim 1 wherein said Lewis acid comprises 2,4,7-trinitro-9-fluorenone.

7. A process for the preparation of a photoconductive charge transfer complex material which comprises mixing

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a Lewis acid and a polysulfone resin 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 charge transfer complex having at least one new absorption band within a range of from about 3200 to about 7500 Angstrom units.

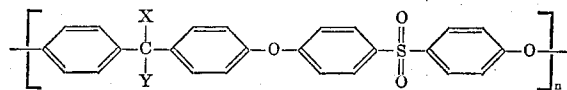
8. The process of claim 7 wherein from about 1 to about 100 parts of resin are mixed for every one part of Lewis acid.

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

10. The process of claim 7 wherein said Lewis acid is selected from the group consisting of 2,4,7-trinitro-9-fluorenone, 9-(dicyanomethylene)-2,4,7-trinitro-fluorene, 2,3-dichloro-1,4-naphthaquinone, and mixtures thereof.

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

12. 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 polysulfone resin comprising recurring units having the 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 having at least one new absorption band within the range of from about 3200 to about 7500 Angstrom units.

13. The electrophotographic plate of claim 12 wherein said Lewis acid is selected from the group consisting of 2,4,7-trinitro-9-fluorenone, 9-(dicyanomethylene)-2,4,7-trinitro-fluorene, 2,3-dichloro-1,4-naphthaquinone, and mixtures thereof.

14. The electrophotographic plate of claim 12 wherein said Lewis acid comprises 2,4,7-trinitro-9-fluorenone.

15. The electrophotographic plate of claim 12 comprising from about 1 to about 100 parts of said resin for every one part of said Lewis acid.

16. A method of forming a latent electrostatic charge pattern comprising charging the electrophotographic plate of claim 12 and exposing said plate to a pattern of activating electromagnetic radiation.

17. A method of forming a latent electrostatic pattern wherein the plate of claim 12 is electrostatically charged in an image pattern.

18. An electrophotographic process wherein the plate of claim 12 is electrically charged, exposed to an image pattern to be reproduced and developed with electrically attractable marking particles.

19. An electrophotographic process wherein the plate of claim 12 is electrostatically charged in an image pattern and developed with electrically attractable marking particles.

20. The process of claim 18 further including the steps of transferring said marking particles to the surface of a

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receiving sheet, and recharging, exposing and developing said plate to produce at least more than one copy of the original.

21. The process of claim 19 further including the steps of transferring said marking particles to the surface of a receiving sheet, and recharging, exposing and developing said plate to produce at least more than one copy of the original.

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**References Cited**

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