

1

3,408,186

ELECTROPHOTOGRAPHIC MATERIALS AND METHODS EMPLOYING PHOTO- CONDUCTIVE RESINOUS CHARGE TRANSFER 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. 426,431
24 Claims. (Cl. 96—1.5)

ABSTRACT OF THE DISCLOSURE

Photoconductive materials are prepared from polycarbonate 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. 2,297,691 involves uniformly charging the photoconductive insulating layer, and then dissipating this charge on that portion of the layer which is exposed to light.

The latent image formed thereon will correspond to the configuration of the light image passing through the original to be reproduced. This image is rendered visible by depositing on the insulating 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 that portion of the layer retaining a charge thereby distributing itself over the layer in a manner corresponding to the electrostatic image. The powder image may then be transferred to paper or other recording surfaces. The paper, upon being separated from the insulating layer, will bear the powdered image which may subsequently be made permanent by heating or other suitable fixing means. This above general process is also described in U.S. Patent 2,357,809, 2,891,011, and 3,079,342.

It is known that various photoconductive insulating materials may be used in making electrophotographic plates. 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 a 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 the serious limitations of, first, its spectral response is somewhat limited to the near ultraviolet blue and green region of the spectrum, and secondly, the preparation of vitreous selenium plates requires complicated, costly and complex procedures such as vacuum evaporation.

Further, selenium plates require the use of a separate conductive substrate layer, preferably with a further barrier layer thereon before deposition of the selenium photoconductor. Because of these economic and commercial considerations, there have been many recent efforts to develop photoconductive insulating materials other than selenium for use in electrophotographic plates.

It has been proposed that various two-phase materials may be used to prepare a photoconductive insulating layer for use in the manufacture of electrophoto-

2

graphic plates. It is known, for example, to use inorganic photoconductive pigments such as zinc oxide dispersed in suitable binder material to form this photoconductive insulating layer. 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 initial component used to prepare the photoconductive insulating layer be, of itself, a photoconductive insulating material. In a third type of plate, inherently photoconductive insulating polymers are used frequently in combination with sensitizing dyes or Lewis acids to form the photoconductive insulating layer. Again, in this type of plate at least one photoconductive insulating component is required in the manufacture of the layer. While the process of increasing sensitivity is by itself desirable commercially speaking, it does have the drawback of limitation to only those materials already having substantial photoconductivity.

These three known plates are similar to those defined 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 substantially low temperature distortion properties which make them undesirable in an automatic electrophotographic apparatus which often includes powerful lamps and thermal fusing devices and tends to heat up the xerographic plate. Also, the limitation in choice of physical properties has been dictated by the restriction to using only inherently photoconductive materials.

Inorganic pigment binder-type plates are limited in usefulness because they are often opaque in color and are thus limited in use to a system where light transmission is not required. These inorganic pigment binder plates have the further disadvantage of not being reusable due to fatigue and not readily cleaned because of their rough surfaces. Still another disadvantage of these known photoconductive insulating materials is that in their manufacture, the materials used have been restricted to those having photoconductive insulating properties. Therefore, the optical properties such as transparency, color and sensitivity range are limited to those materials of known photoconductors.

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 heretofore unobtainable.

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.

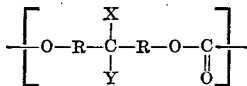
Another object is to provide a transparent self-supporting photoconductive film adapted for xerographic imaging without requiring a conductive backing.

A still further object of this invention is to provide a photoconductive insulating material which may be made substantially transparent and particularly adapted for use in systems where light transmission is generally 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 polycarbonate comprising recurring units having the formula:



wherein each —R— is selected from the group consisting of phenylene, halo substituted phenylene, and alkyl substituted phenylene;

X and Y are each selected from the group consisting of hydrogen, hydrocarbon radicals free from aliphatic unsaturation and of radicals which together and with the adjoining



atom form a cycloalkane radical, the total number of carbon atoms in X and Y being up to 12.

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 nonphotoconductive. After the above substantially nonphotoconductive Lewis acid is mixed or otherwise complexed with said substantially nonphotoconductive resinous material, a 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 using the resulting photoconductive material may be used.

It has been found by the present process that electron acceptor complexing may be used to render inherently nonphotoconductive electron donor-type insulators photoconductive and thus to greatly increase the range and selection of useful materials of electrophotography.

A Lewis acid, therefore, is any electron acceptor relative to other reagents present in this system; for example, 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 with 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 between 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 are appreciably perturbed by each other in the absence of photoexcitation.

(b) Donor-acceptor interaction is relatively strong in the photoexcited state, i.e., the components are at least partially ionized by photoexcitation.

(c) When the complex is formed, one or more new absorption bands appear in the near ultraviolet or visible region (wave lengths between 3200–7500 A.U.) 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 to xerographic imaging. It is generally considered that any insulator may be rendered "photoconductive" by excitation and/or radiation of sufficiently short wave lengths of adequate intensity. This statement applies generally to inorganic as well as to organic materials, including the inert binder resins used in binder plates, the electron acceptor type activators presently used, and the aromatic resins used in the present invention. However, the short wave length radiation sensitivity is not useful in practical imaging systems because adequately intense sources of wave lengths 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, we define the use of the term "photoconductive insulators" to those which are characterized as follows:

(1) They may be formed into continuous films which are capable of retaining electrostatic charge in the absence of actinic radiation.

(2) These films are sufficiently sensitive to illumination of wave lengths longer than 3200 A.U. to be discharged by at least one-half by a total flux of at most 10^{14} quanta per centimeter² of absorbed radiation.

This definition excludes the resins and Lewis acids of our disclosure, when these are used separately, from the class of "photoconductive insulators."

The preferred resins or thermoplastic material used are generally referred to as polycarbonates prepared from di-(monohydroxyaryl) alkanes and having a molecular weight of at least 20,000. The polycarbonates are prepared by either of two conventional methods. The first involves reacting the di-(monohydroxyaryl) alkanes with derivatives of carbonic acid such as for example carbonic acid diesters, phosgene, and bis-chlorocarbonic acid esters of di-(monohydroxyaryl)-alkanes. The second process involves the inter-esterification of the above hydroxyl compounds with a dicarbonate.

Any suitable di - (monohydroxyaryl)-alkane may be used to prepare the polycarbonate resin. 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 di-phenyl) 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)-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)-propane
 2,2-(3,5-3',5'-tetrabromo-4,4'-dihydroxy-diphenyl)-propane
 (3,3'-dichloro-4,4'-dihydroxy-diphenyl)-methane and
 2,2'-(dihydroxy-5,5'-difluoro-diphenyl)-methane
 (4,4' dihydroxy-diphenyl)-phenyl-methane and
 1,1-(4,4'-dihydroxy-diphenyl)-1-phenyl-ethane

and mixtures thereof.

Any other suitable hydroxy compound may be used, such as dihydroxy alkanes or tri - (monohydroxyaryl)-alkanes. Typical of these alkanes are resorcinol, phenolphthalein, o-cresolphthalein, fluorescein, phenolphthalimide and phenolisatin.

The polycarbonates may be obtained by reacting any of the above suitable alkanes with any of the derivatives of carbonic acid above noted. Any other suitable aromatic and/or aliphatic dihydroxy compound may be used in place of or in addition to the dihydroxy alkanes above listed. Any other additional material may be used with the dihydroxy compound, composition, or mixture to modify the properties of the final polycarbonate produced if desired.

In a second known method of preparing polycarbonates organic dihydroxy compounds are interesterified with dicarbonates. Any suitable aliphatic, cycloaliphatic, aromatic, dihydroxy compounds or mixtures thereof may be interesterified or transesterified with any suitable bis-alkyl, bis-cycloalkyl, bis-aryl-carbonate or mixtures thereof.

The polycarbonate prepared by either or both of the above methods 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 polycarbonate resins to form the desired photoconductive 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 separately. The addition to and mixture with one non-photoconductive component and the other seems to have a synergistic effect, that is much greater than additive.

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

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-methylantraquinone,
 1,4-dimethyl-antraquinone,
 1-chloroantraquinone,
 anthraquinone-2-carboxylic acid,

1,5-dichloroantraquinone,
 1-chloro-4-nitroantraquinone,
 phenanthrenequinone,
 acenaphthenequinone,
 5 pyranthrenequinone,
 chrysenequinone,
 thio-naphthene-quinone,
 anthraquinone-1,8 disulfonic acid and
 anthraquinone-2-aldehyde,
 10 triphthaloyl-benzene-aldehydes such as bromal,
 4-nitrobenzaldehyde,
 2,6-dichlorobenzaldehyde-2, ethoxy-1-naphthaldehyde,
 15 anthracene-9-aldehyde,
 pyrene-3-aldehyde,
 oxindole-3-aldehyde,
 pyridine-2,6-dialdehyde,
 biphenyl-4-aldehyde;
 20 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, tetrachloro-phthalic anhydride, perylene 3,4,9,
 25 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;
 30 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, 9 - benzoyl - anthracene, 4-(4-dimethylamino-cinnamoyl) - 1-acetylbenzene, acetoacetic acid anilide, indandione - (1,3),-(1,3 diketohydrindene), acenaphthene quinone-dichloride, anisil, 2,2-pyridyl and furil.
 Additional Lewis acids are mineral acids such as the
 45 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-coumarinylacetic acid (4); maleic acid
 50 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-bromo-benzoic acid, gallic acid, 3-nitro-2-hydroxyl-1-benzoic acid,
 55 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), malic acid, succinic acid, alpha-bromo-stearic acid, citroconic 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 photoconductivity as indicated in Table I

The substance to be evaluated is coated by suitable means onto a conductive substrate and dried. The coated substrate 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 Hivolt Power Supply Company, Condenser Products Division, Model PS-10-1 M operating at 7 kv. while maintaining the grid potential at 0.9 kv. using a Kepso, Incorporated regulated D.C. supply (0.1500 v.). Charging time is 15 seconds.

The 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 describes 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 containing 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 imaging test is also made on each material under study which shows photoconductivity. An electrophotographic image is produced by charging the material by corona discharge and exposing the material by projection to a light and shadow image and developing the latent charge image by cascade using a commercial developer, depending on the polarity of the initial corona charge given to the photoconductive material. Details of this procedure are cited in Example I.

EXAMPLE I

About 0.8 gram of a polyester of carbonic acid and bis (4-hydroxyphenyl) 2,2-propane (manufactured by the General Electric Company under the tradename of Lexan polycarbonate resin, grade 125, color 111 powder) is put into a 50 ml. beaker containing about 7.5 grams of dichloromethane and 1 gram of cyclohexanone solvent mixture. The mixture is agitated by means of a stirrer until the resin is fully dissolved. About 0.2 gram of 2,4,7-trinitrofluorenone is added to the polycarbonate resin solution prepared above. The mixture is stirred as before until solution of the 2,4,7-trinitrofluorenone is achieved.

The above solution is applied onto an aluminum sheet (0.005" x 5½" x 6" flat sheet of bright finished 1145-H19 aluminum foil made by the Aluminum Company of America) by means of a wire wound bar. (Other suitable means such as a dip coater, flow coater, whirler coater,

etc., may be used instead.) The coated sheet is dried. The thickness of the dried layer amounted to about 5 microns.

The above prepared plate is charged negative to about 540 volts by means of a corona discharge device maintained at about 7500 volts, exposed for about 15 seconds by projection using a Simmon Omega D3 enlarger equipped with an f/4.5 lens and a 75 watt opal bulb operating at a color temperature of 2950° K. 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 1824 developer over the plate. The developed image on the plate corresponds to the projected light and shadow pattern, i.e. a positive image is formed. The image developed on the plate is then electrostatically transferred to a receiving sheet and fused. The plate is subsequently cleaned of residual toner and reused in the above described process.

Another plate may be prepared as described above and positively charged, exposed and developed as previously described. Also, in an alternative case the image developed on the plate may be fused directly on the photoconductive layer. The results are tabulated in Table I.

EXAMPLE II

About one gram of a polyester of carbonic acid and bis(4 - hydroxyphenyl) - 2,2 - propane (manufactured by Mobay Chemical Company under the trade name of Merlon polycarbonate resin, type K-90) is put into a 50 ml. beaker containing about 19 grams of a one-to-one solvent blend of dichloromethane and dioxane. The mixture is agitated by means of a stirrer until the resin is fully dissolved.

About 0.3 gram of 2,4,7 - trinitrofluorenone is dissolved in 10 g. of cyclohexanone; the resultant mixture is added to the polycarbonate resin solution, and stirred to dissolve all of the materials.

The solution is coated onto an aluminum sheet and dried. The coated sheet is charged negatively by corona discharge, exposed, and developed as described in Example I above. The image developed on the plate corresponds to the original projected image.

A second plate is prepared as described above, and positively charged, exposed and electrometered as previously described. See Table I.

EXAMPLE III

About 5 mg. of Martius yellow dye is added to a coating solution prepared as described in Example II above. The latter is coated onto two aluminum sheets and dried. The coated sheets are charged, exposed, and electrometered as previously described. The data appear in Table I. These illustrate that increased visible light sensitivity may be obtained by the addition of a sensitizing dye to the composition.

EXAMPLE IV

About one gram of a polycarbonate resin obtained by reacting tetrachlorobisphenol A with phosgene and prepared according to U.S. Patent 3,119,787, is put into a 50 ml. beaker containing 19 g. of a one-to-one solvent blend of dichloromethane and cyclohexanone and agitated until the resin is fully dissolved. About 0.4 gram of 2,4,7-trinitrofluorenone dissolved in 5 g. of cyclohexanone is added to the resin solution, and stirred until all of the materials are well dispersed.

The solution is coated onto an aluminum sheet and dried. The coated sheet is charged negatively by corona discharge, exposed and developed as described in Example I, above. The image developed on the plate corresponds to the original projected light and shadow pattern.

Another plate is prepared as described above and positively charged, exposed and electrometered as previously described. The data appear in Table I.

EXAMPLE V

About 5 mg. of Fluorol 7GA dye is added to a coating solution prepared as described in Example IV above. The solution is coated onto two aluminum and dried. The coated sheets are then electrometered as previously described and the data tabulated in Table I.

These data illustrate once again that increased visible light sensitivity may be obtained by the addition of a sensitizing dye to the composition.

EXAMPLE VI

About 1 g. of a polycarbonate resin described in Example IV is put into a 50 ml. beaker containing 19 g. of a one-to-one solvent blend of dichloromethane and cyclohexanone. The mixture is agitated until the resin is fully dissolved.

About 0.3 g. of benzophenone-tetracarboxylic acid dianhydride dissolved in 5 ml. of cyclohexanone is added, and the mixture is stirred until all of the materials are dissolved. About 5 mg. of Rhodamine B base dye is stirred in. The solution is coated onto an aluminum sheet and dried. The coated sheet is then charged, exposed and developed as described in Example I. The image developed on the plate corresponds to the light and shadow pattern of the original.

A similar plate is charged, positively, exposed and electrometered as previously described; the data recorded in Table I.

EXAMPLE VII

A coating solution is prepared as described in Example I above except that (in place of the 2,4,7 - trinitrofluorenone) about 0.2 g. of 2,3-dichloro 1,4-naphthaquinone is added to the solution of the polyester of carbonic acid and bis(4-hydroxyphenyl)-2,2 - propane. This coating solution is applied to two aluminum sheets as before and dried. The plates are charged, exposed, and electrometered and the results are listed in Table I.

EXAMPLE VIII

A coating solution is prepared as described in Example I above except that no Lewis acid is added to the resin solution. This is coated onto two aluminum sheets, as described, and dried. The plates are charged, exposed and electrometered; the results are listed in Table I. This example may be considered to be a reference or "control" indicating that the polycarbonate is not light sensitive unless a Lewis acid is added as sensitizer.

EXAMPLE IX

A coating solution is prepared as described in Example II above except that no Lewis acid is added to the polyester of carbonic acid and bis(4-hydroxyphenyl)-2,2-propane resin solution. This solution is coated onto two aluminum sheets and dried. The plates are charged, exposed, and electrometered, and the results are tabulated (see Table I). This is a second "control" experiment indicating that another polycarbonate resin is not photoconductive in the absence of a Lewis acid activator.

EXAMPLE X

A coating solution is prepared as described in Example IV above except that the Lewis acid is omitted. This solution is coated onto two aluminum sheets and dried. The plates are charged, exposed, and electrometered and the results are tabulated (see Table I). This is a third "control" on a noncomplexed resin.

The electrometer data in Examples VIII-X show that polycarbonate resins by themselves are nonphotoconductive.

EXAMPLE XI

About one gram of Lucite 2042, an ethyl methacrylate resin manufactured by E. I. duPont de Nemours and Company, is dissolved by stirring in a solvent blend consisting

of 8.8 g. of benzene and 15 ml. of toluene. The solution is dip coated onto two aluminum sheets and dried. These plates are charged, exposed, and electrometered and the results are tabulated (see Table I). The Lucite resin is used as inert matrix in control experiments to determine the photoconductivity of the Lewis acids in the absence of polycarbonate resins.

EXAMPLE XII

About 0.4 g. of 2,4,7-trinitrofluorenone is added to the Lucite solution as described in Example XI. The solution is coated onto aluminum sheets and dried. The plates are charged, exposed, and electrometered, and the data is tabulated in Table I.

EXAMPLE XIII

The experiment of Example XII was repeated, with the addition of about 5 mg. of Fluorol 7GA sensitizing dye to the Lucite-trinitrofluorenone solution. The solution is coated onto two aluminum sheets and dried. The plates are charged, exposed and electrometered and the results are listed in Table I.

EXAMPLE XIV

About 0.3 gram of benzophenonetetracarboxylic acid dianhydride dissolved in a solvent blend of 15 ml. of cyclohexanone and 5 ml. of ethyl Cellosolve is stirred into the ethyl methacrylate resin solution described in Example XI above. About 5 mg. of Rhodamine B base dye is added, and the mixture stirred until the dye is fully dissolved and evenly dispersed throughout. The above solution is coated onto two aluminum substrates and dried. The plate is charged, exposed, and electrometered, and the results are tabulated (see Table I).

EXAMPLE XV

About 0.2 g. of 2,3-dichloro-1,4-naphthaquinone is added to an acrylic resin solution, prepared as described in Example XI. The solution is coated onto two conductive sheets and the plates are charged, exposed, and electrometered. The data are recorded in Table I.

The data from the experiments of Examples XI-XV show that the Lewis acids tested are nonphotoconductive in an inert binder resin; even in the presence of typical sensitizing dyes.

EXAMPLE XVI

About 5 mg. of zinc stearate is put into a coating solution prepared as described in Example III above and stirred to dissolve all of the materials. The solution is coated onto a smooth surfaced aluminum sheet and dried. The solution is applied until the dry film thickness is about 0.0005 inch. The dried polycarbonate layer is stripped-off the aluminum plate to yield a self-supporting photoconductive film.

EXAMPLE XVII

A self-supporting photoconductive film is prepared as described in Example XVI above and placed on a conductive support to facilitate handling. The film is charged, exposed and developed as described in Example VII. The image developed on the film corresponds to the original projected subject. The film is removed from the support to yield a transparency suitable for use in projection display devices.

EXAMPLE XVIII

A self-supporting photoconductive film is prepared as described in Example XVI above. The film is placed in a modified corona charging unit which charges the front surface negative and the back surface positive. The film thus corona charged is exposed and developed and the image formed directly on the film. The image developed on the film corresponds to the original projected subject.

TABLE I.—ELECTROMETER DATA ON PHOTOCONDUCTIVE POLYCARBONATE RESINS

Material Tested	Initial Potential (Volts)	Light Discharge (Volts/sec.)	Dark Discharge (Volts/sec.)	Residual Potential After 15 secs. (volts)	Illumination Level at 2,800° K. (Foot Candles)	Sensitivity, ¹ Volts/Foot Candle Second
Ex. 1. Lexan-125 Resin and 2,4,7-trinitrofluorenone.	-540	16.7	3.6	330	35	0.516
Ex. 2. Merlon-K-9 Resin and 2,4,7-trinitrofluorenone.	+270 -350	8.9 22.2	3.6 1.7	180 175	35 35	0.151 0.586
Ex. 3. Merlon-K-90 Resin and 2,4,7-trinitrofluorenone and Martius Yellow dye.	+350 -410	11.4 26.7	5.9 Trace	210 210	35 35	0.157 0.763
Ex. 4. Tetrachloro Bisphenol A Polycarbonate and 2,4,7-trinitrofluorenone.	+310 -380	12.5 26.7	7.6 Trace	170 210	195 195	0.025 0.136
Ex. 5. Tetrachloro Bisphenol A Polycarbonate and 2,4,7-trinitrofluorenone and Fluorol 7GA Dye.	+240 -385	26.7 14.7	5.9 1.7	60 50	195 195	0.107 0.74
Ex. 6. Tetrachloro Bisphenol A Polycarbonate and Benzophenone Tetracarboxylic Acid Dianhydride and Rhodamine B Base Dye.	+200 -295	35.6 120.0	0 0	120 120	195 195	0.182 0.616
Ex. 7. Lexan-125 Resin and 2,3-dichloro-1,4-naphthoquinone.	+420 -485	8.9 22.2	0 0	360 390	195 195	0.046 0.114
Ex. 8. Lexan-125 Resin 100%.	+610 -575	0 0	0 0	610 575	195 195	0 0
Ex. 9. Merlon-K-90 Resin 100%.	+470 -490	0 1.5	0 1.5	470 467	195 195	0 0
Ex. 10. Tetrachloro Bisphenol A Polycarbonate 100%.	+580 -590	0 0	0 0	580 590	195 195	0 0
Ex. 11. Lucite-2042 (100%) without Lewis Acid.	+460 -500	4.4 5.3	4.4 5.3	394 420	94 94	0 0
Ex. 12. Lucite-2042 and 2,4,7-trinitrofluorenone.	+430 -410	0 0	0 0	430 410	195 195	0 0
Ex. 13. Lucite-2042 and 2,4,7-trinitrofluorenone and Fluorol 7GA Dye.	+560 -485	1.5 0	1.5 0	438 485	195 195	0 0
Ex. 14. Lucite-2042 and Benzophenone-tetracarboxylic Acid Dianhydride and Rhodamine B Base Dye.	+510 -450	4.8 3.6	4.8 3.6	440 400	195 195	0 0
Ex. 15. Lucite-2042 and 2,3-dichloro-1,4-dinaphthaquinone.	+380 -470	3.0 4.0	3.0 4.0	335 410	94 94	0 0

¹ Sensitivity=Figure of merit is initial discharge rate upon illumination in volts/ft. candle second, corrected for rate of dark discharge.

In the above table, Examples I, II, IV, VII show that a charge transfer complex comprising a polycarbonate resin and a Lewis acid is photoconductive. Examples III, V, and VI indicate that the sensitivity of such complexes can be increased by the addition of sensitizing dyes. As shown by Examples VIII-X polycarbonate resins are not photoconductive when used alone. Example XI shows that Lucite 2042 is a nonphotoconductor. Examples XII-XV show that Lewis acids and sensitizing dyes are nonphotoconductive in an inert binder resin. That the polycarbonate resin-Lewis acid photoconductor may be made in the form of a self-supporting film is indicated by Examples XVI-XVIII.

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

Although specific materials and conditions were set forth in the above examples, these were merely illustrative of the present invention. Various other compositions, such as the typical materials listed above and various conditions where suitable, may be substituted for those given in the examples with similar results. 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 filed July 23, 1964, now abandoned and 384,681, filed July 23, 1964 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.

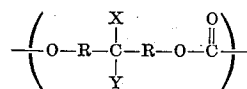
What is claimed is:

1. A photoconductive charge transfer complex material comprising a mixture of a polycarbonate resin and a Lewis acid, 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 mate-

rial of claim 1 comprising from about 1 to about 100 parts of said resin for every one part of said Lewis acid.

3. A photoconductive charge transfer complex material which comprises a mixture of a Lewis acid and a polycarbonate resin comprising recurring units having the formula:



wherein each R is selected from the group consisting of phenylene, halo-substituted phenylene and alkyl substituted phenylene,

X and Y are each selected from the group consisting of hydrogen, hydrocarbon radicals free from aliphatic unsaturation and of radicals which together and with the adjoining



atom form a cycloalkane radical, the total number of carbon atoms in X and Y being up to 12, said photoconductive charge transfer complex having at least one new absorption band within a range of from about 3200 to about 7500 angstrom units.

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

5. The charge transfer complex as disclosed in claim 4 wherein said Lewis acid comprises 2,4,7-trinitro-9-fluoronone.

6. The photoconductive charge transfer complex material of claim 3 wherein said resin comprises the reaction product of a dihydroxy diphenyl alkane and phosgene.

7. The photoconductive charge transfer complex material of claim 3 wherein said resin comprises the reaction product of 2,2-bis(4-hydroxyphenyl)propane and phosgene.

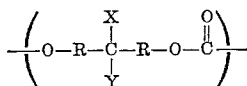
8. A process for the production of a photoconductive charge transfer complex material which comprises mixing a polycarbonate resin and a Lewis acid, said charge trans-

13

fer complex having at least one new absorption band within a range of from about 3200 to about 7500 angstrom units.

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

10. A process for the production of a photoconductive charge transfer complex material which comprises mixing a Lewis acid and a polycarbonate resin comprising recurring units having the formula:



wherein each R is selected from the group consisting of phenylene, halo-substituted phenylene and alkyl substituted phenylene,

X and Y are each selected from the group consisting of hydrogen, hydrocarbon radicals free from aliphatic unsaturation and of radicals which together and with the adjoining



atom form a cycloalkane radical, the total number of carbon atoms in X and Y being up to 12, said charge transfer complex having at least one new absorption band within the range of from about 3200 to about 7500 angstrom units.

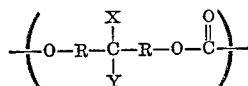
11. The process as disclosed in claim 10 wherein said Lewis acid comprises at least one member of the group consisting of 2,4,7-trinitro-9-fluoronone, benzophenone, tetracarboxylic acid dianhydride, tetrachlorophthalic anhydride, chloranil, picric acid, benz(a) anthracene-7,12-dione, 1,3,5-trinitrobenzene and 2,3-dichloro-1,4-naphthoquinone.

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

13. The process of claim 10 wherein said resin comprises the reaction product of a dihydroxy diphenyl alkane and phosgene.

14. The process of claim 10 wherein said resin comprises the reaction product of 2,2-bis(4-hydroxy-phenyl)-propane and phosgene.

15. 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 polycarbonate resin comprising recurring units having the formula:



wherein each R is selected from the group consisting of phenylene, halo-substituted phenylene, and alkyl substituted phenylene;

X and Y are each selected from the group consisting of

14

hydrogen, hydrocarbon radicals free from aliphatic unsaturation and of radicals which together and with the adjoining



atom form a cycloalkane radical, the total number of carbon atoms in X and Y being up to 12, said photoconductive charge transfer complex having at least one new absorption band within the range of from about 3200 to about 7500 angstrom units.

16. The electrophotographic plate of claim 15 wherein said Lewis acid comprises at least one member of the group consisting of 2,4,7-trinitro-9-fluoronone, benzophenone, tetracarboxylic acid dianhydride, tetrachlorophthalic anhydride, chloranil, picric acid, benz(a) anthracene-7,12-dione, 1,3,5-trinitrobenzene and 2,3-dichloro-1,4-naphthoquinone.

17. The electrophotographic plate of claim 16 wherein said Lewis acid comprises 2,4,7-trinitro-9-fluoronone.

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

19. A method of forming a latent electrostatic charge pattern comprising charging the electrophotographic plate of claim 15 and exposing said plate to a pattern of activating electromagnetic radiation.

20. An electrophotographic process wherein the plate of claim 15 is electrically charged, exposed to an image pattern to be reproduced and developed with electrically attractable marking particles.

21. A method of forming an electrostatic charge pattern by the process wherein the plate of claim 15 is electrostatically charged in an image pattern.

22. An electrophotographic process wherein the plate of claim 15 is electrostatically charged in an image pattern and developed with electrically attractable marking particles.

23. The process as disclosed in claim 20 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.

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

References Cited

UNITED STATES PATENTS

3,037,861	6/1962	Hoegl et al.	96—1
3,277,029	10/1966	Chadwick et al.	260—2.5

NORMAN G. TORCHIN, *Primary Examiner*.

J. C. COOPER, *Assistant Examiner*.