

[54] **POLYESTER COATED PAPER AS A CONDUCTIVE SHEET MATERIAL**
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3,118,785	1/1964	Anderson et al.	117/218 X
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[73] Assignee: **ICI America Inc.**, Wilmington, Del.
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FOREIGN PATENTS OR APPLICATIONS
42/27193 12/1967 Japan..... 96/1.8

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[63] Continuation of Ser. No. 97,391, Dec. 11, 1970, abandoned.

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[51] **Int. Cl.**..... **G03g 5/00, D21f 13/00**
[58] **Field of Search**..... 117/201, 218, 155 R; 162/138; 96/1.5, 1.8

[57] **ABSTRACT**

An electrically conductive sheet material prepared from paper and a particular class of polyester resins is disclosed. The use of this conductive paper as the substrate in preparing a photoconductive recording sheet material is also disclosed.

[56] **References Cited**
UNITED STATES PATENTS
3,248,279 4/1966 Geyer 96/1.5 X

12 Claims, No Drawings

POLYESTER COATED PAPER AS A CONDUCTIVE SHEET MATERIAL

This is a continuation, of application Ser. No. 97,391, filed Dec. 11, 1970, now abandoned.

This invention relates to an electrically conductive sheet material. More particularly this invention relates to a conductive paper prepared from a polyester and paper which is useful as a conductive substrate in the preparation of photoconductive recording sheet material.

In the art of preparing photographic reproductions of originals by electrostatic printing techniques there are two distinct methods, a direct and an indirect process. The indirect process, commonly called xerography, employs a reusable drum which records, by electrostatic forces, the image which is to be printed and then transfers this image to a sheet of paper which is devel-

oped by depositing and fusing thereon a xerographic ink. This results in a clear reproduction of the original. In the direct process a sheet material which has the capability of accepting an electrostatic image directly from the original is used and an electrostatic ink, which can be identical to a xerographic ink, is then placed on the sheet material and the final copy prepared.

The sheet material used in the direct electrostatic printing method is usually a multi-layer material. The most common type of sheet material uses as its base a light weight paper, such as a paper that weighs less than 50 pounds per ream, upon which a coating containing a photoconductive pigment such as zinc oxide is deposited. This sheet material can then receive an electrostatic image and be developed to produce a good copy of the original. It has been found in the practice of the direct process that paper by itself does not form a good conductive substrate for the photoconductive layer of a photoconductive recording material, i.e. photoconductive paper. One reason that paper does not form a good conductive substrate is that paper has a varying resistivity with humidity, and this resistivity may become too great or possibly too small to produce the proper electrical effect necessary for preparing a good electrostatic copy. It has become prevalent in the art to impregnate paper with conductive materials, such as salts, acids, quaternary ammonium salts, and conductive polymers, which enhance the conductive property of the paper as a conductive substrate. The primary types of materials used in commercial photoconductive paper are conductive polymers which contain quaternary ammonium substituents. The exact mechanism by which the conductive polymer functions is not material to its effectiveness when used for photoconductive paper. Thus, although those polymers now commercially available use an ion transfer technique due to the quaternary ammonium salt substituents, any resin which would enhance the electrical conductivity of paper is a candidate for use in a conductive substrate. Not only must a resin or another material enhance the conductivity of the paper, it must also maintain a relatively

constant conductivity in varying environments, especially with changing relative humidity. A suitable resin must also be relatively insoluble in organic solvents used in the preparation of the photoconductive layer.

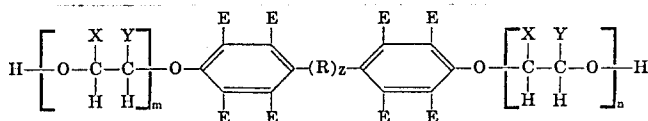
These solvents are toluene and similar aromatic hydrocarbon materials.

It is an object of this invention to provide a conductive paper suitable for use in a photoconductive paper.

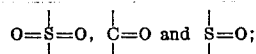
It is another object of this invention to provide a photoconductive paper.

These and still other objects of this invention will become apparent to those skilled in the art from the following detailed description of the invention.

In accordance with this invention excellent conductive sheet material is provided which comprises paper coated with a conductive polyester resin of a dicarboxylic acid and an etherified diphenol which can be represented by the formula



In this formula z is 0 or 1; R is a radical selected from the group consisting of alkylene radicals containing from 1 to 5 carbon atoms, oxygen, sulfur,



each E is individually either a halogen atom or a hydrogen atom; m and n are integers from 0 through about 15 with the proviso that the sum of m and n is at least 7 and usually no more than about 30; X and Y are individually selected from the group consisting of methyl radicals and hydrogen atoms with the proviso that in any X and Y pair on adjacent carbon atoms either X or Y is hydrogen.

In a preferred conductive polyester resin the sum of the integers represented by m and n in said etherified diphenol will be at most 20 and at least 9.

The etherified diphenols used are prepared from a diphenol. Exemplary of these diphenols are 2,2-bis(4-hydroxyphenyl) propane; 2,3-bis(4-hydroxyphenyl) butane; 4,4'-dihydroxydiphenyl ether; bis(dichloro, difluoro-4-hydroxyphenyl) methane; 2,2-bis(2,6-dichloro-4-hydroxyphenyl) propane; bis(2,3,5,6-tetrafluoro-4-hydroxyphenyl) sulfoxide; 3,3-bis(2,3,5,6-tetrabromophenyl) pentane; and 4-hydroxyphenyl-2'-chloro-4'-hydroxyphenyl ketone. The diphenols are etherified for use in accordance with the present invention. Etherification may be accomplished by the addition to the diphenol of ethylene oxide, propylene oxide or a mixture of same. The ether may also be prepared by reacting an olefin halohydrin with a diphenol as disclosed in U. S. Pat. No. 2,331,265. Methods of performing the reactions are well known in the art. It should be noted, however, that where mixtures of alcoholic and phenolic hydroxyl groups are present, the oxide compound reacts preferentially with phenolic hydroxyl groups. Thus, when an excess of an oxide compound is reacted with a diphe-

nol, both phenolic hydroxyls are etherified prior to any extensive ether chains being formed.

The preferred etherified diphenols within the class characterized by the above formula are the following etherified bisphenols: polyoxypropylene 2,2-bis(4-hydroxyphenyl) propane; polyoxyethylene 2,2-bis(4-hydroxyphenyl) propane; polyoxyethylene 2,2-bis(4-hydroxy-2,6-dichloro-phenyl) propane; and polyoxypropylene 2,2-bis(4-hydroxy-2,6-dichlorophenyl) propane; wherein the number of polyoxyalkylene units per mol of diphenol is from 9 to 20.

In general, the dicarboxylic acid used in preparing the conductive polyester resins of this application may be saturated or unsaturated and may contain substituents such as halogen or sulfur. Among these dicarboxylic acids are the following: phthalic acid, fumaric acid, maleic acid, succinic acid, isophthalic acid, cyclohexane dicarboxylic acid, malonic acid, glutaric acid, and the anhydrides of these acids. A preferred group of acids include fumaric, maleic, and their anhydrides. Mixtures of dicarboxylic acids may also be used in which case it is preferred that at least 50 weight percent of the acids be unsaturated.

The conductive polyesters used to make the products of this invention are prepared by the reaction of the etherified diphenol and the dicarboxylic acid, preferably in approximately stoichiometric amounts. The reaction may be performed in an inert atmosphere employing moderate temperatures and substantially atmospheric pressure during an early stage, to minimize the loss of dicarboxylic acid by volatilization. As the reaction proceeds the temperature may be increased and the pressure reduced. Esterification catalyst may be used although it is generally preferred to carry out the reaction in the absence of excessive amounts of catalyst to avoid contamination of the final resinous product. It is usually desirable to include a small amount of polymerization inhibitor such as hydroquinone, pyrogallol, or the like when an unsaturated dicarboxylic acid is used. The reaction temperature for preparing the final polyesters of this invention will usually include heating to about 200°C. for a portion of the reaction. The resultant conductive polyesters usually have acid numbers less than about 30.

The conductive polyesters preferably are applied to the paper substrate by dispersing them in a liquid vehicle. Solvents such as aromatic hydrocarbons are usually suitable vehicles. Other examples are polyvinyl alcohol, isopropanol, water, and ethylene glycol monoethyl ether acetate.

Preferred modifications of these conductive polyester resins, which are not prone to becoming sticky when contacted with organic solvents, such as toluene and styrene, which are used as carriers for the photoconductive coatings applied to the conductive substrate, are those conductive polyester resins which have been modified with a modifying agent such as either an ethylenically unsaturated monomer, a polyfunctional hydroxy compound, a polyisocyanate, a di- or triamine or an alkaline earth or alkali metal hydroxide. Usually from 1 to 50 parts by weight of said modifying agent per 100 parts of the polyester resin and modifying agent combination are effective. Preferably 5 to 30 parts are employed.

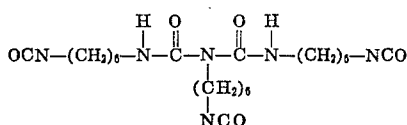
The ethylenically unsaturated monomers may be used to modify only those conductive polyester resins

of this invention which contain ethylenic unsaturation contributed by presence of unsaturated dicarboxylic acid residues. In general only homopolymerizable ethylenically unsaturated monomers are used. Among the numerous ethylenically unsaturated monomers which may be used are styrene, vinyl toluene, chlorostyrene, divinyl benzene, diallyl phthalate, acrylonitrile, methyl methacrylate, vinyl acetate, ethyl acrylate, alpha-methylstyrene, vinyl pyridine, and 2-ethylhexyl acrylate.

In preparing modifications of conductive polyester resins with ethylenically unsaturated monomers a conductive polyester resin is dissolved in the ethylenically unsaturated monomer which acts as both a vehicle for the conductive polyester and as a modifier. When applying the conductive polyester-ethylenically unsaturated monomer solution to paper to prepare a conductive substrate, accelerators, or catalysts are usually added to the solution so that the polyester may be modified by copolymerizing with the ethylenically unsaturated monomer. These catalysts include the kind frequently referred to as "free radical catalysts", such as methyl ethyl ketone peroxide, benzoyl peroxide, tertiary butyl perbenzoate, cumene hydroperoxide, and succinic peroxide. Exemplary of accelerators are dimethyl aniline and cobalt naphthenate.

Among the polyhydroxy compounds which are contemplated as modifying agents for the conductive polyester resins are hexamethylol melamine [commercially available as CYMEL 301], methylol urea formaldehyde resins, and methylolated phenol formaldehyde condensation products. In all cases these modifying agents should be dispersible in any vehicle used for dissolving the conductive polyester resins. Water or toluene, benzene, and similar aromatic hydrocarbons are suitable vehicles. The polyhydroxy compound when dispersed along with the conductive polyester resins within the class disclosed above is usually accompanied with an acidic catalyst to promote the cross-linking of the modifier's hydroxyl groups with residual hydroxyl and carboxyl groups of the conductive polyester resin. These catalysts include sulfonic acid, borontrifluoride etherate, sulfuric acid, hydrochloric acid, paratoluene sulfonic acid, and similar acid catalysts.

The polyisocyanate modifications of the conductive polyester resins disclosed above are prepared by reacting the resins with sufficient isocyanate groups to react with residual hydroxyl groups of the conductive polyester resin. Thus to obtain complete modification with polyisocyanate the minimum isocyanate group to residual hydroxyl group ratio is 1 but ratios as high as 3 yield acceptable modified conductive polyester resins. Among the polyisocyanates which can be used in preparing the modified conductive polyester resins are toluene diisocyanate, diphenyl diisocyanate, chlorophenyl-2,4-diisocyanate, 1,4-tetramethylene diisocyanate, para-phenylene-diisocyanate, 3,3'-dimethyl-4,4'-phenylene diisocyanate, 3,3'-dimethoxy-4,4'-diphenyl diisocyanate, polymethylene polyphenyl polyisocyanate (PAPI), methylene-bis(4,4'-polyphenyl polyisocyanate) (MONDUP MR), condensation product of a polyol and isocyanate for example, the condensation product of 3 mols of toluene diisocyanate and 1 mol of trimethylol propane, urea condensed isocyanates such as the one sold under the tradename DESMODUR N and having the formula



and other polymethylene polyphenyl isocyanates containing an average of from 2 through about 3.3 isocyanate groups per molecule. These isocyanates can be used to cross-link the unsaturated or the saturated conductive polyester resins. Preferably said polyisocyanates contain an average of more than 2.5 isocyanate groups per molecule. The crosslinking may be aided by the addition of standard catalysts used in promoting urethane reactions. Exemplary of these catalysts are dibutyl tin dilaurate, trimethyl amine, N-methyl piperazine and N-methyl morpholine. The isocyanate and polyester are usually applied to the paper from an aromatic organic solvent such as benzene or toluene. However, where a catalyst is used the catalyst is usually added just prior to application to minimize crosslinking before application of the coating.

The di- and triamine and alkaline earth or alkali metal hydroxide modifications of the conductive polyester resins of this invention are prepared by mixing a conductive polyester resin with an amine or hydroxide at about room temperature and mixing for 5 to 30 minutes. The conductive polyesters are usually liquid, but the conductive polyester-amine or inorganic salt mixture usually takes on a gel like consistency. The products are water soluble and relatively insoluble in aromatic hydrocarbons, and thus they may be applied from water solution. The amines are generally saturated acyclic, alicyclic, or aromatic. Exemplary of amines contemplated are triethylene diamine, cyclohexyldiamine, piperidine, hexamethylene triamine, tetraethylene triamine, and benzoguanamine. Exemplary of the hydroxides are calcium, barium, lithium, sodium, and potassium hydroxide.

In order for those skilled in the art to better understand the concepts of and the practice of this invention the following non-limiting examples for the preparation of the conductive polyester resins disclosed above are given:

EXAMPLE 1

5,940 grams of polyoxypropylene(16)-2,2-bis(4-hydroxyphenyl) propane; 575 grams of fumaric acid; and 2 grams of hydroquinone are added to a four-necked, four-liter reaction vessel. This reaction mixture is purged with nitrogen and heated to 210°C. The water of esterification is removed through a condenser as it is formed. The acid value of the reaction mixture is determined by the taking of hourly samples. When the acid value falls below 25, the reaction is stopped by removing the mixture from the heat source and pouring the reaction mixture into an open pan. The resulting polyester resin is a viscous liquid.

EXAMPLE 2

3,460 grams of polyoxyethylene(12)-2,2-bis(4-hydroxyphenyl) propane; 540 grams of fumaric acid; and 2.0 grams of hydroquinone are placed in a 4-necked, 4-liter reaction vessel. The reaction mixture is heated with stirring to a temperature of 210°C. ± 5°, and the reaction vessel is purged with nitrogen during

the heat up period. Maintaining the 210°C. and the inert nitrogen atmosphere, hourly samples of the reaction mixture are taken and when the acid value of the polyester reaches less than 25, the reaction mixture is removed from the heat and poured into an open pan for cooling. During the course of the reaction the water of esterification is continually removed. The resultant cooled resin is a viscous liquid polyester with an acid value of 19.2.

EXAMPLE 3

According to the procedure of Example 1, 1,436 grams of polyoxypropylene(9)-2,2-bis(4-hydroxyphenyl) propane, 232 grams of fumaric acid, and 1.1 gram of hydroquinone are added to a 4-necked 4-liter reaction vessel. The reaction mixture is heated to 205°C. and samples taken every hour and the acid value determined. When the acid value is determined to be less than about 20 the reaction vessel is removed from the heat source and the resin poured into an open pan for cooling. The resulting resin is a viscous liquid polyester.

EXAMPLE 4

3,782 grams of polyoxypropylene(16)-2,2-bis(2,6-difluoro-4-hydroxyphenyl) propane and 434 grams of phthalic anhydride are added to a 4-liter, 4-necked reaction vessel and reacted according to the procedure of Example 2, at 205°C. Hourly samples are removed from the reaction mixture and when the acid value is less than about 30 the resin is removed from the heat source and cooled in an open pan. The resulting polyester resin is a viscous liquid.

EXAMPLE 5

According to the procedure of Example 1, 1,952 grams of polyoxyethylene(20)-4,4'-diphenyl ketone, 396 grams of glutaric acid, and 1.1 grams of hydroquinone are added to a 4-necked, 4-liter reaction vessel. The reaction is maintained at 200°C. and hourly samples taken and the acid value of these samples determined. When the acid value is less than 20, the reaction mixture is removed from the heat source and cooled in an open pan. The resultant resin is a viscous liquid polyester resin.

EXAMPLE 6

According to the procedure of Example 1, 583 grams of polyoxyethylene(9)-2,2-bis(4-hydroxyphenyl) propane, 540 grams of fumaric acid and 2 grams of hydroquinone are reacted at 210°C. When the acid value of the reaction mixture reaches less than about 25 the reaction is stopped. The product is a viscous liquid resin with an acid value of 15.1.

The conductive sheet material of this invention may be prepared by coating a paper, suitably a bond paper, similar to that described in U. S. Pat. No. 3,501,295, Column 5, line 53 through Column 6, line 43, with, for example, from 0.5 to 5.0 pounds of said conductive polyester resins per ream of paper; in which case the conductive polyester resin portion of the conductive substrate will be from about 1 to about 15 percent of the base paper. Papers used for preparing photoconductive paper include, for example glassine paper and paper sold by Riegel Paper Company under the Trade No. EC-38-XA and No. EC-35-XE.

In general the conductive substrate of this invention is prepared by coating a sheet of paper with a conductive polyester composition, which may include a modifier, in a vehicle. The conductive polyester resin concentration will normally be from about 1 through 95 weight percent of said coating composition. The coating compositions applied by any standard paper coating method such as roller coating, size press, etc. depending upon the base paper stock used. The vehicle may be, for example, water or an organic aromatic compound such as benzene, toluene, or ethyl benzene. After application the coated paper is dried driving off the vehicle.

To increase the film forming tendencies of the conductive polyester and to allow easier manipulation of the viscosity of the polymer solution film-extending materials are preferably incorporated in the solution. These materials may be added in a weight ratio of from 3 to 0.5 parts of film extender per part of conductive polyester resin. The viscosity of the final formulation; that is, the polymer, the film extender, and the solvent, is adjusted so that the total viscosity is below 20,000 centipoises. When a film extender is used it is sometimes desirable to employ an emulsifier to aid in dispersing the film extender in the vehicle. Exemplary of the emulsifiers are polyoxyethylene hexitol fatty acid esters, and polyoxyethylene hexitan fatty acid esters. Exemplary of film extenders are pigments, starches and rubber-like polymers; specific examples are TiO_2 , kaolin clay, butadiene-styrene copolymers, and low molecular weight polyethylene or polypropylene.

A laboratory method of coating paper employs wire wound rods. A conductive polyester resin solution is poured onto the paper to be coated in one corner or at one edge of the paper. A wire wound rod is then passed across the paper starting at the solution containing edge. The thickness of the coating depends upon the wire thickness of the wire wound rod. The coated paper is then dried at between 50° and 120°C . to remove all residual solvent. The resulting dry paper is relatively impermeable to organic solvents used for depositing the photoconductive zinc oxide compositions of the final photoconductive paper.

Conductive substrates of this invention are prepared by using the above wire wound rod technique of spreading the resin on paper. The conductive resin may be applied as a conductive coating composition in a liquid vehicle as a solution or dispersion. The resins are dispersed or dissolved in the liquid vehicle by blending, mixing, stirring, or by other mechanical methods. Where a modifying agent, a catalyst, a film extender, or other additional ingredients which will make up part of the final coating are to be applied they are dissolved or dispersed with the conductive resin in the liquid vehicle. The conductive coating compositions Examples 7-20, which are tabulated Table I, are prepared by mixing all the ingredients into a vehicle, which is listed as the solvent in Table I.

Table I lists various conductive coating compositions which are applied to either aluminum foil or paper. Examples 7 to 15 which use aluminum foil are not representative of the conductive substrates of this invention but are used to illustrate the good conductive properties of the coatings used in accordance with this inven-

tion. Thus when a conductive coating is applied on a conductive substrate, such as aluminum foil as in Examples 7 to 15, the conductive properties of the coating can be determined independently of the substrate by subjecting the coated aluminum foil to a voltage discharge of, for example, 9000 volts for about 5 seconds in a corona discharge unit capable of maintaining an 8500 to 9500 volt field. It will be found that no charge is accepted by the coated foil of Example 7-15. This result indicates that the resin coating is indeed very conductive.

Examples 16-20 in Table I illustrate conductive substrates of particular conductive coating compositions on paper. These conductive substrates are prepared in accordance with the aforementioned coating procedure, and are electrically conductive sheet materials of this invention. When these conductive substrates are subjected to a corona discharge, in accordance with the procedure discussed above for coated aluminum foil, the charge acceptance is also zero.

The preferred system of drying the coating after coating the paper to result in the final conductive substrate varies depending upon the conductive polyester resin composition. These procedures are shown as (A) through (D) in Table I and correspond to the following procedures:

30 Procedure A. A conductive polyester resin is dissolved in a solvent and coated on paper or aluminum foil using a wire wound rod supplied by R. D. Specialties of Webster, N.Y. The paper is then dried at 75°C . to 100°C . for 2 to 20 minutes resulting in a dry, flexible conductive paper or substrate.

40 Procedure B. A conductive polyester resin containing ethylenic unsaturation within the class of conductive polyester resins disclosed above is dissolved in ethylenically unsaturated monomer along with a free radical catalyst and the resulting solution is coated as in Procedure A on aluminum foil or paper sheets and cured at 100°C . for 20 minutes.

45 Procedure C. A conductive polyester resin within the class of conductive polyester resins disclosed above is dispersed in water with an acid catalyst and polyhydroxy compound within the class disclosed above. This dispersion is coated as in Procedure A on aluminum foil or paper and cured for 30 minutes at 100°C .

55 Procedure D. A conductive polyester resin within the class disclosed above is mixed with a polyisocyanate in an aromatic hydrocarbon. This mixture is coated as in Procedure A on aluminum foil or paper and cured at room temperature for an hour.

In Table I the catalyst is listed as W, X, Y, or Z. W is a mixture of 1 part benzoyl peroxide and 0.4 parts of dimethyl aniline by weight, X is paratoluene sulfonic acid, Y is triethylene diamine and Z is dibutyl tin dilaurate. The following additional abbreviations are used in Table I: TDI - toluene diisocyanate; HMM - Hexamethylolmelamine; EG MEA-Ethylene glycol monoethyl ether acetate; PTDI - condensation product of 3 mols of toluenediisocyanate and 1 mol of trimethylol propane; and EC-35-XE - A bond paper produced by the

Reigel Paper Company. All quantities in Table I are parts by weight.

The short chain etherified diphenols used in the insulating polyester resin of the photoconductive composi-

TABLE I.—CONDUCTIVE SUBSTRATE

Conductive coating compositions												Drying procedure	Lbs. coating/ream
Conductive polyester of	Parts	Modifier	Parts	Solvent	Parts	Film extender	Parts	Catalyst	Parts	Substrate			
Example:													
7.....	Example 1..	50	-----		Toluene.....	50	-----				Aluminum foil.	A	4
8.....	do.....	90	Styrene.....	10	-----			W	1.4	do.....	B	5	
9.....	do.....	60	do.....	40	-----			W	1.4	do.....	B	5	
10.....	do.....	90	HMM.....	10	Toluene.....	25	-----	X	2	do.....	C	5	
11.....	do.....	70	do.....	30	Isopropyl alcohol.....	25	-----	X	2	do.....	C	3	
12.....	do.....	45.2	TDI.....	4.8	Xylene.....	25	-----	Y	0.3	do.....	D	2	
13.....	do.....	38.6	PTDI.....	15.2	EGMEA.....	25	-----	Y	0.3	do.....	D	4	
14.....	do.....	41.9	DESMODUR-N.....	8.1	do.....	25	-----	Z	0.3	do.....	D	3	
15.....	Example 6..	30	-----		Toluene.....	70	-----			EC-35-XE.....	A	4	
16.....	Example 2..	30	-----		do.....	70	-----			EC-35-XE.....	A	4	
17.....	Example 1..	2	-----		do.....	98	-----			EC-35-XE.....	A	4	
18.....	do.....	70	HMM.....	30	Toluene.....	25	-----	X	2	EC-35-XE.....	C	4	
19 ¹	do.....	20.2	-----		Isopropanol.....	20	Kaolin Clay.....	70	-----	EC-35-XE.....	A	4	
					Water.....	312	Kaolin clay.....	70	-----				
20.....	do.....	30	Triethylene amine.....	1	Water.....	300	TiO ₂	5	-----	EC-35-XE.....	A	4	
							Dow Latex 636. ²	70	-----				

¹ Conductive coating contains 0.5 part of polyoxyethylene (20) sorbitan monooleate as an emulsifier.

² A 50% water solution of a butadiene-styrene copolymer of Dow Chemical Co.

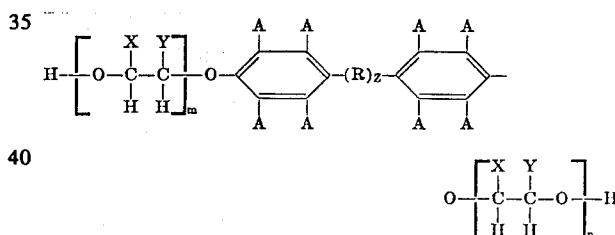
The conductive substrate of this invention may be coated with a photoconductive composition consisting of a photoconductive pigment such as zinc oxide imbedded in an electrically insulating binder resin. The coated conductive substrate is a photoconductive paper. Photoconductive pigments which may be used include zinc oxide, cadmium sulfide, sulfur, anthracene, anthraquinone, lead iodide, cadmium selenide, and oxides of antimony, bismuth, aluminum, cadmium, and molybdenum.

A number of resins are available which may be used as binder resins in the photoconductive composition which comprises the top layer of a photoconductive paper. Among these binder resins are silicone resins, cellulose esters (such as cellulose acetate, cellulose acetate butyrate, and cellulose nitrate), cellulose ethers (such as ethyl cellulose and methyl cellulose), polyvinyl acetate, polystyrene, acrylics, and polyesters.

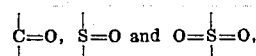
The photoconductive composition may in general be comprised of from about 15 parts to 2.5 parts of a photoconductive pigment per part by weight of binder resin. In preferred photoconductive compositions the ratio of photoconductive pigment to binder resin is from 9 to 5.

Polyester resins, which may be advantageously used as binder resins in a photoconductive composition, are those electrically insulating polyester resins prepared from a dicarboxylic acid and a polyol composition which comprises a short chain etherified diphenol, or a mixture of a dihydroxy alkane and a short chain etherified diphenol.

tion may be represented by the following formula:



wherein z represents an integer of 0 or 1; R is a radical selected from the group consisting of alkylene radicals of 1 to 5 carbon atoms, oxygen, sulfur,



A is individually selected from a halogen atom or hydrogen atom, the letters m and n are integers from 0 through 6 with the proviso that the sum of m and n is at least about 2 and less than 7; X and Y are radicals which are individually selected from the following group: alkyl radicals of 1 to 3 carbon atoms, a phenyl radical, or a hydrogen atom; provided that in any and Y pair an adjacent carbon atom either X or Y is a hydrogen atom.

A preferred group of short chain etherified diphenols within the above formula include those where A is a chlorine atom or a hydrogen atom and/or R is an alkylene radical containing 1 to 3 carbon atoms and X and Y are either hydrogen or a methyl radical. In this preferred group the average sum of n and m is at most about 3.

Examples of short chain etherified diphenols within

the above formula include the following:

polyoxyethylene-(3)-2,2-bis(4-hydroxyphenyl) propane;
 polyoxystyrene(6)-bis(2,6-dibromo-4-hydroxyphenyl) methane;
 polyoxybutylene(2.5)-bis(4-hydroxyphenyl) ketone;
 polyoxyethylene(3)-bis(4-hydroxyphenyl) ether;
 polyoxystyrene(2.8)-bis(2,6-dibromo-4-hydroxyphenyl) thioether;
 polyoxypropylene(3)-bis(4-hydroxyphenyl) sulfone;
 polyoxystyrene(2)-bis(2,6-dichloro-4-hydroxyphenyl) ethane;
 polyoxyethylene(3)-bis(4-hydroxyphenyl) thioether;
 polyoxypropylene(4)-4,4'-bisphenol; polyoxyethylene(65)-bis(2,3,6-fluorodichloro-4-hydroxyphenyl) ether; polyoxyethylene(3.5)-4,4-bis(4-hydroxyphenyl) pentane; polyoxystyrene(4)-2-fluoro-4-hydroxy-phenyl 4-hydroxyphenyl sulfide; and polyoxybutylene(2)-3,2-bis(2,3,6-tribromo-4-hydroxyphenyl) butane.

A preferred class of polyester resins within the above class are those containing 2,2-bis(4-hydroxyphenyl) propane or the corresponding 2,6,2',6'-tetrachloro, tetrabromo, or tetrafluoro bisphenol alkoxylated with from two to four mols of propylene or ethylene oxide per mol of bisphenol.

The dihydroxy alkanes which can be present at a level up to 60% by weight of the polyol composition used in preparing the non-conductive polyester resins of the photoconductive composition used to prepare electrofax paper in accordance with this invention are dihydroxy alkanes containing from 2 to 8 carbon atoms. A preferred group of dihydroxy alkanes include propylene glycol, ethylene glycol, and neopentyl glycol. Examples of other dihydroxy alkanes which can be used include 1,3-dihydroxybutane, 1,4-dihydroxypentane, 1,2-dihydroxyhexane, 2,3-dihydroxybutane, and 1,2-dihydroxyoctane.

In addition to said dihydroxy alkanes or in lieu of same up to about 3 weight percent of said polyol composition can be comprised of a polyhydroxy alkane containing 3 to 6 carbon atoms and 3 to 6 hydroxyl groups or etherified derivatives of said polyhydroxy alkanes wherein the etherifying compounds are preferably ethylene or propylene oxide and there is up to 10 mols of oxide per hydroxyl group of said polyhydroxy alkane and preferably at least 1 mol of oxide per hydroxyl group. Exemplary of these polyhydroxy alkanes and the etherified polyhydroxy alkanes are sorbitol; erythritol, xylitol; pentaerythritol; 1,2,3-butane-triol; 1,2,5,6-hexanetetrol; polyoxyethylene(3) glycerol; polyoxypropylene(25) sorbitol; polyoxyethylene(6) 1,2,4,-butane-triol and polyoxypropylene(50) mannitol.

In general the dicarboxylic acid used in preparing the non-conductive polyester resin may be saturated or unsaturated and may contain substituents such as halogen. Among these dicarboxylic acids are the following; phthalic acid, fumaric acid, maleic acid, isophthalic acid, malonic acid, glutaric acid, adipic acid, and the anhydrides of these acids. A preferred group of acids and anhydrides include fumaric, maleic, and succinic acids.

The electrically insulating polyester resins are usually prepared by the reaction of a dicarboxylic acid with a polyol composition selected from those disclosed above. The reaction may be performed in an inert at-

mosphere employing moderate temperatures and substantially atmospheric pressures during the early stage, thus minimizing the loss of dicarboxylic acid by volatilization. As the reaction proceeds the temperature may be increased and the pressure reduced. Esterification catalyst may be used although it is generally preferred to carry out the reaction in the absence of excessive amounts of catalyst to avoid contamination of the final resinous product. When an unsaturated dicarboxylic acid is used it is usually desirable to include a small amount of polymerization inhibitor such as hydroquinone, or pyrogallol. The reaction temperature required for preparing the final polyesters will usually include heating to about 200°C. for a portion of the reaction. The resultant polyesters have low acid numbers; that is acid numbers less than about 30. Usually the ratio of carboxyl groups and hydroxyl groups in the reaction mixture used for preparing the polyester resins of this invention is about 1. However, ratios as low as about 0.8 and as high as about 1.2 can readily be used.

In order for those skilled in the art to better understand the preparation of these insulating polyester resins the following examples are given.

EXAMPLE 21

1,865 grams of polyoxypropylene(2.2)-2,2-bis(4-hydroxyphenyl) propane and 2.9 grams of polyoxypropylene(6)sorbitol are charged to a 3 liter, 4 necked, round-bottom reaction flask which is fitted with a thermometer, a stainless steel stirrer, a gas inlet tube, and a downward condenser. The flask is supported in a GLAS-COL electric heating mantle. Through the gas inlet tube nitrogen gas is allowed to flow sparging the polyol blend and resulting in an inert atmosphere in the reaction vessel. The agitator and heating mantle are then activated and the polyol composition is heated to 50°C. at which time 628 grams of fumaric acid and 1.25 grams of hydroquinone are added to the reaction vessel. The nitrogen gas flow was then regulated at a setting of 2.5 on a SHO-RATE meter of the Brooks Rotometer Company. The reaction mass is heated to a temperature of 210°C. over a period of 5 hours. Water of the esterification reaction is removed as it is formed and the mass is maintained at 210°C. for an additional 6 ½ hours. The course of the reaction is followed by acid value determinations at hourly intervals. At the end of the reaction, when an acid value of about 20 is achieved, the resin is cooled to room temperature. The resin has an acid value of 18.6, a ball and ring softening point of 104°C., a tack point of 75°C., and a liquid point of 100°C. The ratio of hydroxyl groups and carboxyl groups in the preparation of this resin is 1 to 1.

EXAMPLE 22

In accordance with the procedure of Example 1, 985 grams of polyoxyethylene(3) bis(4-hydroxyphenyl) ketone and 44.3 grams of polyoxyethylene(30) pentaerythritol are placed in a 3 liter, round-bottom flask. This mixture is heated and when the reaction temperature reaches 50°C. 348 grams of succinic acid are added. The reaction mixture is then heated to a temperature of 215°C. and the water of reaction is continually removed. The course of the reaction is followed by taking hourly samples in determining the acid value. After an acid value of 30 is reached the heat is removed and the reaction mixture is slowly cooled to room tem-

perature. The resulting polyester is hard, tough and solid.

EXAMPLE 23

According to the procedure of Example 1, 2190 grams of polyoxyethylene(2.5)-2,2-bis(4-hydroxy-2,6-chlorophenyl) propane and 21 grams of polyoxyethylene(12) xylitol are placed in a 4 liter flask. This mixture is heated and when a temperature of 50°C. is obtained, 465 grams of maleic acid is added. The heating is continued until a temperature of 210°C. is achieved at which point the temperature is maintained at 210°C. The water of esterification is removed as it is formed through a condenser. The acid value of the reaction mixture is tested at hourly intervals and when the acid number is less than 30, the reaction mixture is cooled to room temperature. The resultant polyester is a tough solid resin.

EXAMPLE 24

1,882 grams of polyoxypropylene(2)-2,2-bis(4-hydroxyphenyl) propane is charged to a reaction kettle, fitted with a gas inlet tube, a condenser, an agitator, and a thermometer. The reactant is then heated with stirring and inert gas purging. When the temperature reaches 80°C., 618 grams of fumaric acid and 1.25 grams of hydroquinone are added to the reaction vessel. The heating is continued until 210°C. is reached and then the temperature is maintained at this level. Periodic samples of the reaction mixture are taken and

pigment in a mechanical mixing device such as a rubber mill, ball mill or knife mill in the presence or absence of a solvent for the binder resin. Any other additives such as a sensitizer is added simultaneously.

The photoconductive compositions may then be coated on conductive sheet material of this invention by standard paper coating techniques such as roller coating, size press, air knife or trailing blade coating. In the laboratory the aforementioned wire wound rod technique is desirably used.

Examples 25 to 36 tabulated in Table II illustrate photoconductive paper of the invention. The photoconductive composition listed in Table II are prepared by dissolving the electrically insulating polyester in one third of the solvent, i.e. toluene, and mixing the so formed solution with a slurry of the photoconductive pigment in the remaining two thirds of the solvent. This mixture is then charged to an 8580 Eberbach stainless steel container fitted for a WARING Blendor and ground to a finess of 5 to 6.5 of the N. S. Hegman scale. The parts listed in Table II are parts by weight.

The products of Examples 25-36 are exceptionally good photoconductive papers for the direct electrostatic process. When prints were prepared from the photoconductive paper illustrated in Table II, excellent clarity and black and white contrast are observed. This photoconductive paper can be used in any electrostatic direct process machine whether it is a dry or a wet developing machine.

TABLE II.—ELECTROFAX PHOTOCONDUCTIVE PAPER

Photoconductive composition											
Resin		Solvent		Photoconductive pigment		Sensitizer		Pounds/ream	Conductive paper of		
Type	Parts	Type	Parts	Type	Parts	Type	Parts				
Example:											
25.....	Example 21.....	16.75	Toluene.....	100	ZnO.....	133.3	A.....	.00133	14	Example 15.	
26.....	do.....	16.75	do.....	100	ZnO.....	133.3	A.....	.00133	14	Example 16.	
27.....	do.....	16.75	do.....	100	ZnO.....	133.3	A.....	.00133	14	Example 17.	
28.....	do.....	16.75	do.....	100	ZnO.....	133.3	A.....	.00133	14	Example 18.	
29.....	do.....	16.75	do.....	100	ZnO.....	133.3	A.....	.00133	14	Example 19.	
30.....	do.....	16.75	do.....	100	ZnO.....	133.3	A.....	.00133	12	Example 20.	
31.....	Example 22.....	20.50	do.....	120	ZnO.....	166	B.....	0.0015	20	Example 18.	
32.....	Example 23.....	20.50	do.....	120	ZnO.....	166	B.....	0.002	21	Example 16.	
33.....	Example 24.....	20.50	do.....	120	ZnO.....	166	B.....	0.001	21	Example 16.	
34.....	De Soto EO41.....	14.00	do.....	80	ZnO.....	106.6	A.....	0.00106	15	Example 15.	
35.....	Aratap 3201.....	14.00	do.....	80	ZnO.....	106.6	A.....	0.00106	15	Do.	
36.....	Gelva 269.....	13.00	do.....	80	ZnO.....	106.6	A.....	0.00106	15	Do.	

acid value is determined. When the acid value is less than 25 but more than 15, the reaction mixture is removed from the heat source and allowed to cool to room temperature on a tray cooler. The final acid value for this resin is 16.4 and the resin exhibits a ball and ring softening point of 103°C.

In preparing the photoconductive composition used in coating the conductive substrate of this invention it is frequently desirable to include sensitizers such as bromophenol blue, dibromofluorescein, acrydin yellow, rose bengal, disodium fluorescein, alizarin cyanine green GWA, and other sensitizers as illustrated in U. S. Pat. No. 3,245,735 at line 54, column 15. The sensitizer concentration will vary from about 0.01 to about 5.0 weight percent based upon the photoconductive material, with a preferred concentration of 0.01 to 0.1.

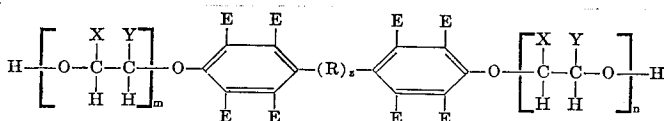
The photoconductive compositions may be prepared by mixing the binder resin and the photoconductive

The zinc oxide listed in Table II is photoconductive quality and sold under the trademark of PHOTOX 80 zinc oxide. The sensitizer listed as part of the photoconductive composition in Table II is a mixture of bromophenol blue, disodium fluorescein, alizarin cyanine green GWA, and auramin O in a 1/1.4/1/0.1 weight ratio respectively and labeled sensitizer A or a 10 to 1 blend of rose bengal and bromophenol blue labeled sensitizer B. Three commercial resins are listed in Table II; namely, DE SOTO EO41, a styrene-acrylic copolymer of DE SOTO Chemical Co.; ARATAP 3201, an alkyd resin produced by Ashland Oil Co.; and GELVA 269, a vinyl polymer of the Monsanto Chemical Co.

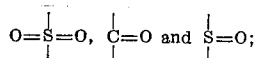
Having thus described the invention the following is claimed:

1. An electrically conductive sheet material which comprises paper coated with a conductive polyester

resin of a dicarboxylic acid and an etherified diphenol which can be represented by the formula



wherein z is 0 or 1; R is a radical selected from the group consisting of alkylene radicals containing from 1 to 5 carbon atoms, oxygen, sulfur,



each E is individually selected from a halogen atom or a hydrogen atom; m and n are integers from 0 through about 15 with the proviso that the sum of m and n is at least 7.0 through about 30; and X and Y are individually selected from the group consisting of a methyl radical and a hydrogen atom with the proviso that in any X and Y pair on adjacent carbon atoms either X or Y is hydrogen.

2. An electrically conductive sheet material according to claim 1 wherein said dicarboxylic acid is selected from unsaturated dicarboxylic acids and mixtures of unsaturated dicarboxylic acids containing at least about 50% unsaturated dicarboxylic acid and wherein in said etherified diphenol the sum of m and n is at most 20 and at least 9.

3. An electrically conductive sheet material according to claim 1 wherein the said etherified diphenol is selected from the group consisting of polyoxypropylene 2,2-bis(4-hydroxyphenyl) propane; polyoxyethylene 2,2-bis(4-hydroxyphenyl) propane; polyoxyethylene 2,2-bis(4-hydroxy-2,6-dichloro-phenyl) propane; and polyoxypropylene 2,2-bis(4-hydroxy-2,6-dichlorophenyl) propane; and wherein the number of polyoxypropylene or polyoxyethylene units per mol of etherified diphenol is from 9 to 20.

4. An electrically conductive sheet material according to claim 1 wherein said conductive polyester resin has been modified with a modifying agent selected from the group consisting of an ethylenically unsaturated monomer, a polyfunctional hydroxy compound dispersible in aromatic hydrocarbons, a polyisocyanate, a di- or triamine, and an alkaline earth or alkali metal hydroxide and wherein from 1 to 50 parts of modifying agent are present per 100 parts of the combination of polyester resin and modifying agent.

5. An electrically conductive sheet material according to claim 4 wherein said ethylenically unsaturated monomer is homopolymerizable, said polyisocyanate contains an average of more than 2.5 isocyanate groups per molecule, and said di- and triamines are either saturated acyclic, alicyclic, or aromatic compounds.

6. An electrically conductive sheet material according to claim 1 wherein a film extending material is in admixture with said conductive polyester resin in a weight ratio of from 3 to 0.5 parts of film extender to polyester resin.

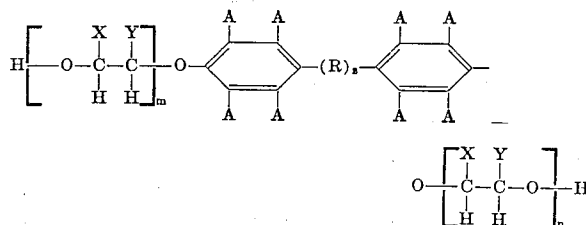
7. A photoconductive paper composition which comprises an electrically conductive sheet material of claim 1 coated with a photoconductive composition containing a photoconductive pigment and a binder resin wherein the weight ratio of said photoconductive mate-

rial to said binder resin is from 15 to 2.5.

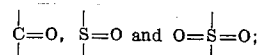
8. A photoconductive paper composition which com-

prises an electrically conductive sheet material of claim 4 and a photoconductive composition coated thereon which comprises a photoconductive pigment and a binder resin wherein the weight ratio of said photoconductive material to said binder resin is from 15 to 2.5.

9. A photoconductive paper composition which comprises an electrically conductive sheet material of claim 1 coated with a photoconductive composition comprising a photoconductive pigment and a binder resin wherein said binder resin is an electrically non-conductive polyester resin of a dicarboxylic acid and a polyol composition which contains a short chain etherified diphenol which may be represented by the formula:

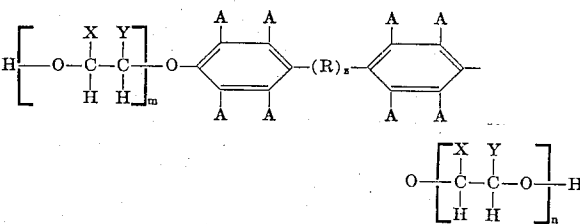


wherein z an integer of 0 or 1; R is a radical selected from the group consisting of alkylene radicals of 1 to 5 carbon atoms, oxygen, sulfur,



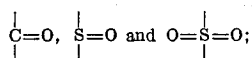
A is individually selected from a halogen atom or a hydrogen atom; the letters m and n are integers from 0 through 6 with the proviso that the sum of m and n is at least 2 and less than 7; and X and Y are radicals which are individually selected from the group consisting of alkyl radicals containing 1 to 3 carbon atoms, a phenyl radical, and a hydrogen atom, with the proviso that in any X and Y pair on adjacent carbon atoms either X or Y is a hydrogen atom.

10. A photoconductive paper composition which comprises the electrically conductive sheet material of claim 4 coated with a photoconductive composition consisting of a photoconductive pigment and binder resin wherein said binder resin is an electrically non-conductive polyester resin of a dicarboxylic acid and a polyol composition which contains a short chain etherified diphenol which may be represented by the formula:



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wherein z represents an integer of 0 or 1; R is a radical selected from the group consisting of alkylene radicals of 1 to 5 carbon atoms, oxygen, sulfur



A is individually selected from a halogen atom or a hydrogen atom; the letters m and n are integers from 0 through 6 with the proviso that the sum of m and n is at least 2 and less than 7; and X and Y are radicals which are individually selected from the group consisting of alkyl radicals containing 1 to 3 carbon atoms, a phenyl radical, or a hydrogen atom, with the proviso that in any X and Y pair on adjacent carbon atoms ei-

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ther X or Y is a hydrogen atom.

11. A photoconductive paper composition according to claim 9 wherein said polyol composition includes up to 60 weight percent of a dihydroxy alkane containing from 2 to 8 carbon atoms.

12. A photoconductive paper composition according to claim 9 wherein said polyol composition contains up to about 3 weight percent of a polyhydroxy alkane containing from 3 to 6 carbon atoms and from 3 to 6 groups or an ethylene or propylene oxide derivative of said polyhydroxy alkane, said derivative containing up to 10 mols of oxide per hydroxyl group of said polyhydroxy alkane.

* * * * *

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UNITED STATES PATENT OFFICE CERTIFICATE OF CORRECTION

Patent No. 3,754,909 Dated August 28, 1973

Inventor(s) Joseph Feltzin and Erich Kuehn

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 4, line 62, "(MONDUP MR)" should read -- (MONDUR MR) --.

Column 5, line 8, "averate" should read -- average --.

Column 7, line 15, "flim" should read -- film --.

Column 8, line 32, "Speciali-" should read -- Special- --.

Column 8, line 47, after the word "water" and before the word "with" insert the word -- along --.

Column 8, line 60, "sulfoncic" should read -- sulfonic --.

Column 9, line 55, after the word "to" and before the word "2.5" insert the word -- about --.

Column 9, line 65, "dephenol," should read -- diphenol, --.

Column 11, line 59, "furmaric" should read -- fumaric --.

Column 11, line 59, after the words "maleic acid," and before the word "isophthalic" insert the words -- succinic acid, --.

Column 13, line 52, "teh" should read -- the --.

Column 16, Claim 9, line 34, after the word "z" and before the word "an" insert the word -- represents --.

Column 16, Claim 10, line 53, after the word "and" and before the word "binder" insert the word -- a --.

Column 18, Claim 12, line 9, at the end of the line and after the words "and from 3 to 6" insert the word -- hydroxyl --.

Signed and sealed this 9th day of July 1974.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents