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[54] **ELECTROGRAPHIC PRINTING ELEMENT**
3 Claims, 2 Drawing Figs.

[52] **U.S. Cl.** **117/218,**
117/17.5, 117/76 P, 117/155 R, 252/501
[51] **Int. Cl.** **G03g 5/02**
[50] **Field of Search** 96/1, 1.3;
117/201, 215, 218, 17.5, 76 P, 155 R; 252/501

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ABSTRACT: A copy sheet for electrographic printing comprising a paper base sheet, a layer of photoconductive material extending over one side of the sheet, and a dielectric coating extending over the photoconductive layer adapted to receive an image-defining electrostatic charge. The photoconductive layer is sensitized by exposure to light to render it conductive, and after such sensitizing an image-defining electrostatic charge is deposited on the dielectric layer which is developed to form a visible image.

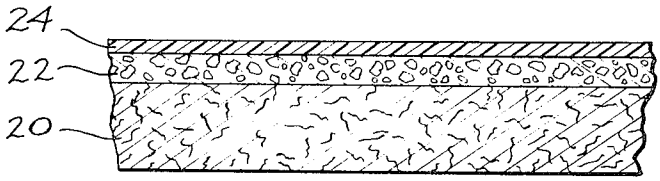


Fig. 1.

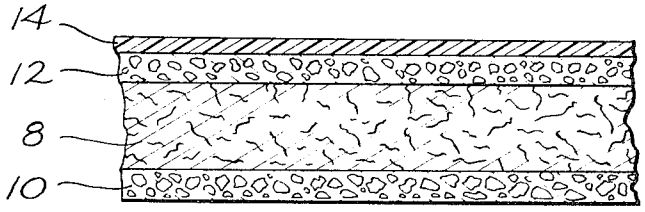


Fig. 2.

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ELECTROGRAPHIC PRINTING ELEMENT

This invention relates to electrographic printing, and more particularly to an improved coated product useful in making printed copies, as well as a unique electrographic printing process whereby prints are produceable from the coated product.

Electrographic printing, as the term is used herein, refers to an electrostatic printing process which differs from and is not to be confused with another form of electrostatic printing process often referred to as electrophotographic printing. In an electrographic printing process, an image-defining electrostatic charge is laid directly down upon an insulating or dielectric surface, using such electronic devices as a cathode ray tube, a pin matrix and pulsing corona discharge, or by means of a direct image transfer from one surface to another. In comparison, in the electrophotographic printing process a copy sheet including a photoconductive layer may first be given a uniform charge over its entire surface in the dark. Then, an image-defining charge pattern may be formed by exposure of the charged photoconductive layer to light through a positive image, much like a photographic process.

The two types of processes differing as they do in the manner in which an image is formed, have distinct requirements with respect to the type of copy sheet or product best used in the process for the reproduction of an image. Prior art patents which discuss electrographic printing and problems related to this type of printing comprise U.S. Pat. Nos. 3,075,859 and 3,110,621.

Speaking in general terms, a product used in making electrographic prints, such as a copy sheet, should include means for presenting a dielectric or insulating surface for the reception of the image-defining electrostatic charge, most usually in the form of a thin film or layer of dielectric material, and support for this film which is electrically conductive, whereby any stray electrical charges in the means supporting the film are dissipated to produce clearer prints. With a suitable dielectric material selected for the film, which is capable of accepting a charge transferred thereon and retaining this charge, best print resolution and density and minimum background result in a print produced from the copy sheet if the dielectric film is relatively thin, as this inhibits tendencies of the dielectric film to retain in the body thereof a diffused and scattered charge emanating from the sharply defined charge laid down on the surface of the film. With a conductive surface spaced relatively close to the charge receiving surface of the dielectric film, as is possible when the dielectric film is quite thin, any of such scattered charges are quickly dissipated through the conductive surface.

In general terms, an object of this invention is to provide a novel copy product, more specifically a copy sheet, for receiving an image defining electrostatic charge, that features a novel conductive backing for the dielectric or insulating film in the product.

More specifically, an object is to provide an improved copy product, ordinarily a copy sheet, including a dielectric or insulating film for receiving an image defining electrostatic charge, that further comprises a layer of material backing the dielectric film which possesses requisite electrical conductivity at the time that an image defining charge is deposited on the dielectric film, without depending upon the presence of humidity conditions within a limited range to obtain this conductivity. To further explain, with certain types of copy sheets including a dielectric film spread over a base paper sheet, conductivity in the base paper sheet is relied upon to provide the necessary conductive base for the dielectric film. This conductivity is largely the result of certain moisture conditions in the base paper sheet, and as a consequence, certain humidity conditions are necessary to obtain proper quality in copies produceable with the sheets. With the copy sheets of this invention, this dependence upon specific range of humidity conditions is largely eliminated.

Yet another object of the invention is to provide a novel method of producing a copy, in an electrographic printing process, wherein a copy sheet or product is excited by a pretreatment before depositing an image defining electrostatic charge on the dielectric film of the product, which excitement produces the desired conductivity in a layer of material backing up the dielectric film that receives the charge.

A related object is to provide such a process where the treatment to produce excitement comprises a light treatment of a photoconductive layer, which is easily and quickly done before depositing an image-defining electrostatic charge on the dielectric film.

In a specific embodiment of the invention, and also contemplated herein as an object, a paper base sheet is provided having over both faces thereof a layer of photoconductive material which is excited by light to become electrically conductive. Over the layer, on one side of the sheet only, there is provided a dielectric film which is translucent, i.e., light permeating and preferably nearly transparent, and which, therefore, enables the passage of light from a light source on said one side of the sheet through the film to excite and make conductive the photoconductive layer between the film and the paper base sheet. The photoconductive layer on the opposite side of the paper base sheet may also be excited by a light source on the opposite side of the sheet, and the two layers together form a backing for the dielectric film which will dissipate substantially completely any stray charges and produce with a relatively thin spread of dielectric material prints with high density, good resolution and a minimum of background.

As a feature related to the above, it is contemplated that in producing a copy from a copy sheet comprising a photoconductive layer over opposite faces of a paper base sheet, the photoconductive layers on opposite sides of the sheet will first be excited by exposing these to light sources disposed on either side of the sheet to prepare the copy sheet for the reception of an electrostatic image-defining charge.

These and other objects and advantages are attained by the invention and the same is described hereinbelow in conjunction with the accompanying drawings, wherein:

FIG. 1 is a cross-sectional view, somewhat enlarged, of portions of a copy sheet according to one form of the invention, and illustrating various layers making up the sheet; and

FIG. 2 is a similar cross-sectional view of a modified form of copy sheet as contemplated herein.

As indicated above, in an electrographic printing process an image-defining electrostatic charge is deposited on a dielectric or insulating film, and such charge is retained on the film whence it is utilized to develop a printed image as by dusting the surface of the film with a powder, toner or colored resinous substance in particle form, with such substance having an opposite electrostatic charge to the charge deposited on the dielectric film. To produce best line definition and image resolution, the dielectric film should extend over a conductive layer, and in most applications it has been noted that a conductivity level within the range of about 10^6 to 10^7 ohms/square surface resistivity is desirable. While a copy product comprising a metal sheet forming the backing for the dielectric film is possible, as a practical matter and to produce copy sheets of low-cost and in high-volume, a paper base sheet is employed.

With a paper base sheet, or other sheet or web of cellulosic material, the requisite conductivity in the sheet may exist if the sheet has a certain moisture content. However, such a product depends upon relative humidity conditions for good resolution and detail to be obtained in a reproduction. To eliminate this dependence upon relative humidity conditions, and to enable the uniform production of good copies, the copy sheet of this invention features a layer of material under the dielectric film which is excited before an electrostatic image is deposited on the copy sheet by a pretreatment which renders the layer suitably conductive regardless of specific humidity conditions. Thus, and according to this invention, a copy sheet is prepared by coating paper on at least one side with a coating of photoconductive material, which extends as a substantially continuous layer over this one side. A coating is then applied

to the paper over the side which has been coated with photoconductive material, which coating forms a dielectric film on the paper for the reception of an image-defining electrostatic charge. In producing a copy, a sheet of such paper is first excited by directing light against the side of the paper provided with the photoconductive layer. The dielectric film is transparent or at least light pervious, and light passing through the film excites the photoconductive layer to render the same electrically conductive. Paper pretreated in this manner may then have an electrostatic charge applied to the dielectric or insulating film, and if such a charge is then developed as by dusting a toner onto the paper and setting such toner (for instance, by exposing the same to heat and/or pressure), as set forth in Pat. No. 3,075,859, reproduction or copy is produced where the image printed corresponds to the electrostatic image first deposited on the dielectric film.

The following example illustrates the manufacture of a copy sheet, and the reproduction of an image on that sheet, where the copy sheet comprises a paper base sheet coated on opposite sides with a photoconductive material in the form of zinc oxide.

EXAMPLE I

A 37 pound/ream bleached sulfite tablet base paper was coated with a zinc oxide composition consisting of the following:

Zinc oxide (Green Seal-8, New Jersey Zinc. Co.)	100 parts
Pigment dispersent (tetra sodium pyrophosphate)	0.3 parts
Polyvinyl alcohol binder (Dupont Elvanol 72-60)	5 parts

Each side of the paper was coated with 5 pounds/ream (24×36×) of the composition, on an air knife coater, the composition for spreading purposes first being prepared into an aqueous mixture containing 25 percent solids. After the coating had dried, one side of the paper had a coating of styrene-butadiene polymer (about 80 percent styrene) applied thereover, using a spread of 4 pounds of polymer/ream. The polymer during its application was carried in a solution comprising 40 percent toluene and 40 percent methyethyl ketone. Copy sheets were thus produced, comprising a paper base sheet having a photoconductive layer over opposite faces, and a dielectric or insulating film superimposed over one of the photoconductive layers, as shown in FIG. **2** of the drawings, where the paper base sheet is shown at **8**, the photoconductive layers at **10** and **12**, and the dielectric film at **14**.

Copy sheets so produced were used in the reproduction of prints employing the steps of first exposing the copy sheets to light, and then running the sheets through an electrographic printing machine. In the printing machine an electrostatic image charge was deposited on the dielectric film forming one side of the copy sheet, and this image charge was then converted into a visible image by dusting the surface with a developer comprising a toner having an electrostatic charge opposite to that of the image charge on the sheet, and then permanently setting this toner on the surface of the copy sheet.

When exposing the copy sheets to light, the copy sheets were given a short exposure to ultraviolet light from sources of light located on both sides of the sheet. The ultraviolet light source was a 5 watt bulb, held 1 centimeter above the paper, and the paper was passed under the illuminating light at a travel speed of 20 inches per second, through an illuminated length of 6 inches, for an effective period of illumination of 0.3 second. The paper was then run directly through the electrographic printing machine at the same speed.

The product printed well at all humidities tested including oven dry, 10 percent relative humidity, 50 percent relative humidity and **relative humidity**.

Exemplary of copy sheets prepared according to this invention are the following sheets having a photoconductive layer applied over one side of a paper base sheet only.

EXAMPLE II

A 35 pound/ream bleached bond paper was coated with a zinc sulphide-cadmium sulfide composition consisting of:

Zinc sulfide-cadmium sulfide (U.S. Radium Corp. Helecon 1757)	100 parts
Polyvinyl acetate Binder (Dupont Elvacet 81-900)	14 parts

This composition, when mixed with water to yield a 32 percent solids mixture, was applied over the smooth side of the bond paper (its top side), using a spread of 7 pounds/ream. Over this photoconductive coating, and after drying of the paper, a dielectric coating was applied by spreading an aqueous solution of polyvinyl acetate-crotonic acid copolymer (about 86 percent water), over the paper and using a spread on a solids basis of 5 pounds/ream. Drying gave the final copy sheets where, as shown in FIG. **1**, a paper base sheet **20** had a photoconductive layer **22** over one side, and extending over the photoconductive layer a dielectric film **24**.

Such sheets were exposed to 70 foot candles of ordinary room light before printing. The print quality obtained with these sheets was good at all the relative humidity conditions set forth in example I.

The incorporation of water soluble conductive salts into the photoconductive composition was found helpful in lowering the coating weight required of the photoconductive composition for certain substrates. This was found especially helpful at relatively high humidity conditions, for papers with low zinc oxide coating weights, and using pigment binders which do not have adequate moisture resistance. The conductive salts that are usable are those that do not react with the photoconductive layer to form an insoluble insulating coating around the particles forming the layer. Illustrative of conductive salts which have been found effective as additives to the photoconductive layer are such materials as calcium chloride, sodium chloride, potassium chloride, lithium chloride, sodium nitrate and trimethyl sulfonium chloride. The following examples illustrate the inclusion of such conductive salts in the photoconductive coating applied to the paper base sheet.

EXAMPLE III

A photoconductive coating composition was prepared containing the following:

Zinc oxide (Kadox 515, New Jersey Zinc Co.)	100 parts
Pigment dispersant (tetra sodium pyrophosphate)	0.3 parts
Binder (Penford gum 280, Penick and Ford)	16 parts
Organic salt (trimethyl sulfonium chloride)	10 parts

An aqueous mixture was prepared from the above, containing 50 percent solids. Both sides of bleached tablet paper of the type set forth in example I were coated with such a composition using a blade coater. After drying and over the coating on one side (the smooth or felt side), there was then applied a dielectric material carried in a solvent base, consisting of a mixture of vinylchloride/vinylidene chloride copolymer and polyvinyl acetate, containing a 4:1 ratio of such polymers. A spread, on a solids basis, of 3 to 4 pounds/ream was used. When subjected to the ultraviolet light treatment set forth in example I the product printed well at all humidities indicated in example I.

EXAMPLE IV

A photoconductive composition was prepared from the following:

Zinc oxide (Red seal-9, New Jersey Zinc Co.)	100 parts
Pigment dispersent (tetra sodium pyrophosphate)	0.3 parts
Binder (Essex gum 1390, Penick and Ford)	15 parts
Calcium chloride	30 parts

This composition dispersed in water to give a mixture of 30 percent solids, was spread at the rate of 5 pounds/ream on a

solids basis, on the wire side of tablet paper of the type described in example I. A 3 to 4 pound/ream dielectric coating was then prepared over this photoconductive layer, using a mixture of vinyl chloride/vinylacetate polymer (Bakelite VYHH-4, Union Carbide) and polyvinyl acetate (Vinac V-7, Colton) with the mixture containing about a 4:1 ratio of the two resins carried in a solvent base. Such paper when exposed to ultraviolet light as in example I and subjected to printing produced good prints at all humidity conditions indicated in example I.

It will be noted that this invention contemplates a process for printing which comprises treating the copy sheet by exposure of the sheet to light prior to forming an image-defining electrostatic charge on the dielectric film. This enables the sheet to be printed at substantially any humidity condition, including an oven dry condition, with consistently good print resolution and density. The photoconductive coating on the paper base sheet does not make the base sheet conductive uniformly throughout, as does impregnation of the base sheet with a water soluble metallic salt. In fact, the base paper sheet which provides support for the photoconductive layer may approach a dielectric material under very dry conditions, yet the inclusion of the photoconductive layer under the dielectric film, even under such conditions, enables good prints to be obtained in the same manner as were the base sheet uniformly conductive throughout. The role that the photoconductive layer plays in the electrographic printing is not completely understood, as it has been generally believed that the sheet forming the base for the dielectric film should be uniformly conductive to enable the production of a good print.

Copy sheets having a photoconductive layer spread over both faces prove to be advantageous in that this apparently enables some reduction in the thickness of the photoconductive layer deposited over any particular face, the two layers on opposite faces complementing each other to a certain extent in producing a conductive base for the dielectric film. By the inclusion of the layer of photoconductive material over the face of the base paper sheet opposite the one carrying the dielectric film, the advantage has been noted that such tends to eliminate stray electrical charges on the paper base sheet by providing a conductive path to the support for the copy sheet during the printing process whereby undesirable background is better eliminated. Suffice it to say that a photoconductive layer over one side of the paper base sheet has proved to be effective in producing good prints under oven dry humidity conditions, and in certain instances by the inclusion of such a layer over both faces of a paper base sheet certain advantages are attained.

As a photoconductive material zinc oxide has been found to give good results and has proved to be a desirable material from an economic standpoint. This does not preclude the use, however, of other photoconductors such as zinc sulfide, cadmium sulfide, mercuric sulfide, titanium dioxide, gallium triselenide, tetragonal lead monoxide, anthracene, anthraquinone, paraterphenyl paradiphenyl benzene, acyl hydrazones, and like photoconductors. The types of zinc oxides best used are those prepared from metal according to the French process, and such are procurable from the New Jersey Zinc Company and also from St. Joseph Lead & American Zinc Co.

Apparently the type of paper and weight of paper used forms no material part of the invention and the choice of paper is dictated by the end use desired. Preferably the paper is white, well formed and smooth and has reasonably good sizing such as normally found in a tablet or bond-type paper. With zinc oxide used as the photoconductive layer, and using the resins indicated to prepare the dielectric film, the copy sheets finally produced are also white.

Any of the binders well known in the art may be employed in the preparation of the photoconductive layer. Starch and natural resin binders may be used, such as Essex gum 1390 (Penick and Ford, an ether derivative of starch) and Penford Gum 280 (Penick and Ford, a hydroxy alkyl ether derivative of starch). Also usable is a polyvinyl acetate emulsion (Elvacet 81-900, Du Pont). A solvent base lacquer-type binder such as Pliolite S-7 (butadiene-styrene copolymer of the Goodyear Tire & Rubber Co.), and Saran, and like binders are also employable. The pigment to binder ratio may be varied according to type of binder chosen, and usually is anywhere from 20:1 (for very efficient binder) to 1:1 (for a less efficient binder). Plasticizers or wetting agents can be used if necessary.

Coating weight requirements are variable and are determined to some extent by the type of paper base sheet employed. On a normal bond or tablet paper, coating weights as low as 3 pounds/ream applied from a blade-type coating give satisfactory coverage and the necessary photoconductive effects. On a super calendered, label base paper, coating weights as low as 2 pounds/ream have been noted to give the necessary photoconductive effects. There apparently are no upper limits to the photoconductive coating weight, except the limitations dictated by economy, convenience and appearance. For instance, coating weight may go as high as 10 pounds/ream or more on a roughly finished paper.

The amount of conductive salt to be incorporated into the photoconductive layer will depend somewhat upon the conductivity required of the particular system. However, the amounts usually needed, if at all, are small. Weights up to about 30 percent of the weight of the photoconductive material in the photoconductive layer may be used beneficially, and there apparently is no real advantage gained in including conductive salts in an amount exceeding about 35 percent of the weight of the photoconductive material.

Numerous dielectric resins can be used as a film superimposed over the photoconductive layer to accept electrostatic image charge. The dielectric film should be transparent or at least translucent or light permeable, so as to permit penetration of light to the underlying photoconductive layer with excitation of this layer and production of electrical conductivity. In addition to the resins indicated in the examples, other resins such as polyvinyl butryal, acrylic polymers, silicone resins, and polyethylenes are employable.

With respect to the illumination of the photoconductive layer, the light source used to excite the material will depend on the type of photoconductive material employed. White zinc oxide, for instance, has a special sensitivity between 3,200 and 4,200 A. The response sharply peaks around 3,850 A. Therefore, a light source emitting 3,850 A. wave length would give the best electrical conductivity response to white zinc oxide. However, the response can be made to extend through the visible spectrum with the proper selection of organic dyes. Several combinations of dyes can be added to the zinc oxide or other photoconductive material to make it respond to all wave lengths in the visible spectrum, which will make possible the use of ordinary light as an activating source. The electrical conductivity of a photoconductor is generally increased with the intensity of light, and for a given light source the maximum conductivity obtainable is dependent upon the period of illumination. Illumination was found most effective for a paper coated on both sides, if done on both sides, however, with a strong enough light source, illumination of one side can excite a photoconductive layer superimposed over both sides of a paper base sheet.

Exposure time depends on the intensity of the light. The higher the light intensity the shorter is the exposure time necessary. The exposure to light may be for a fraction of a second, or for a few days. Excess and long exposures to light do not affect the performance of the product. However, the quality of the print is adversely affected if the product which is already exposed to light is kept in dark for an appreciable amount of time. This is because holding the product in dark results in an increase in its resistivity and a decrease in its conductivity.

In preparing the copy sheets, the drying of the sheets may be done by any conventional means, for instance, they may be air dried.

While several embodiments of the invention have been set forth, it should be apparent that variations are possible without departing from the invention. It is desired to cover all variations and modifications as would be apparent to one skilled in the art, and that come within the scope of the appended claims.

We claim:

1. A coated product applicable for electrographic printing comprising a base; a continuous photoconductive layer extending over at least one side of said base having a photoconductor distributed therein for imparting photoconductivity; a water-soluble conductive salt dispersed throughout said photoconductive layer; and a continuous dielectric coating extending over said photoconductive layer adapted to receive an image-defining electrostatic charge.

2. A coated copy sheet for electrographic printing comprising a paper base sheet, a continuous photoconductive layer extending over at least one side of said sheet having a photoconductor distributed therein for imparting photoconductivity; a water-soluble conductive salt dispersed throughout said photoconductive layer; and a continuous dielectric coating extending over said photoconductive layer adapted to receive an image-defining electrostatic charge.

3. A coated copy sheet for electrographic printing comprising a paper base sheet; a continuous photoconductive layer, having a photoconductor distributed therein for imparting photoconductivity, extending over both sides of said sheet; and a continuous dielectric coating superimposed over the photoconductive layer on one side of the sheet only adapted to receive an image-defining electrostatic charge; the photoconductive layer extending over at least one side of said base sheet including a water-soluble conductive salt dispersed therein.

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