Dec. 9, 1969 G. RITZERFELD ET AL 3,483,027

METHOD OF MAKING CHARGEABLE IMAGE STRUCTURES

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Fig.2

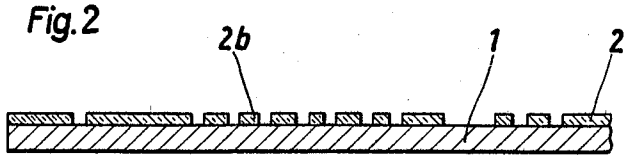


Fig.1

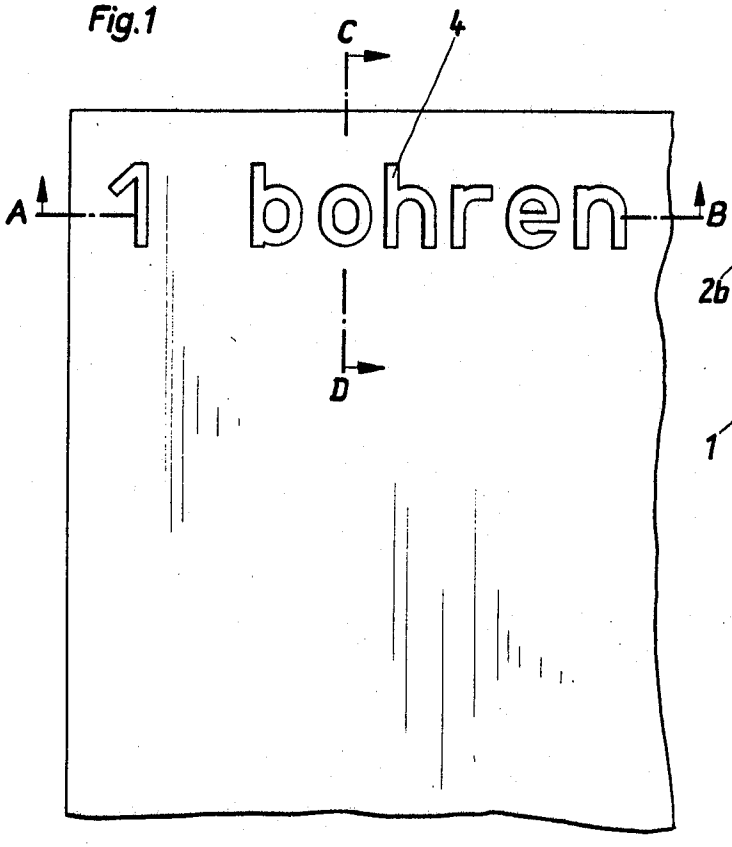
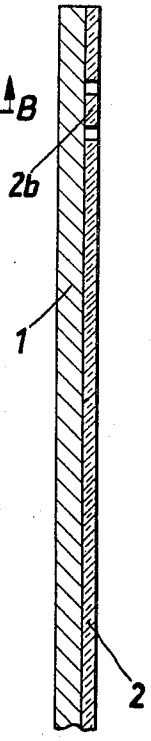


Fig.3

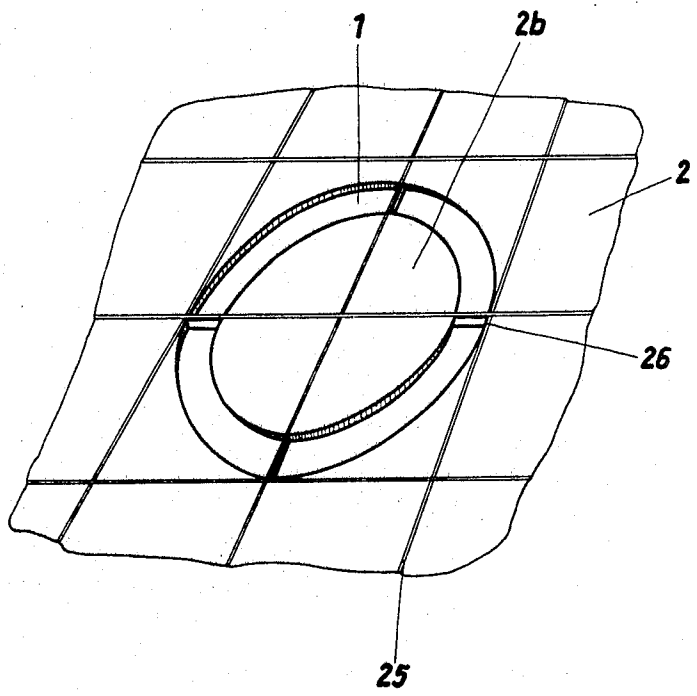


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Fig.4



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Fig.5

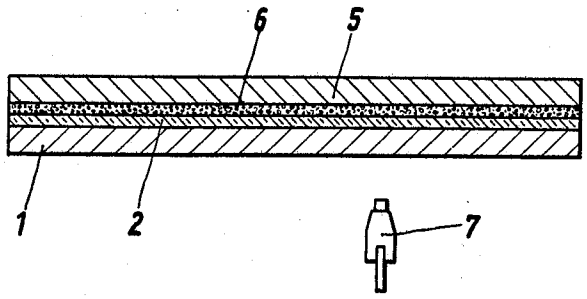


Fig.6

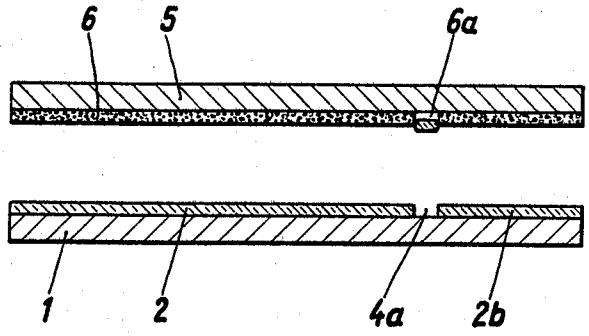
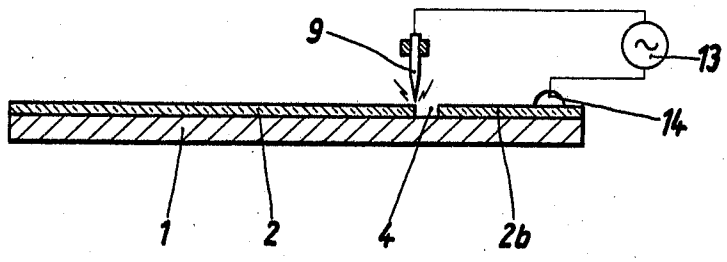


Fig.7



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METHOD OF MAKING CHARGEABLE IMAGE STRUCTURES

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Fig.8

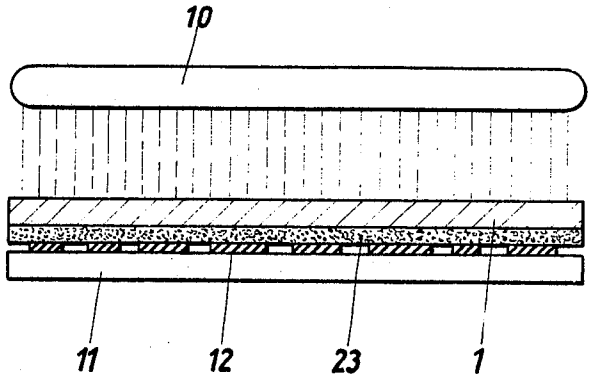
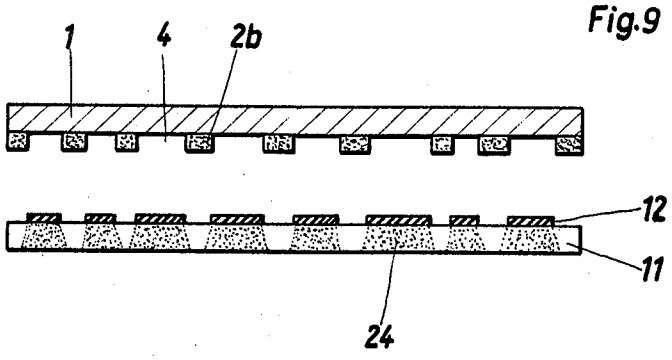


Fig.9



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Fig. 10

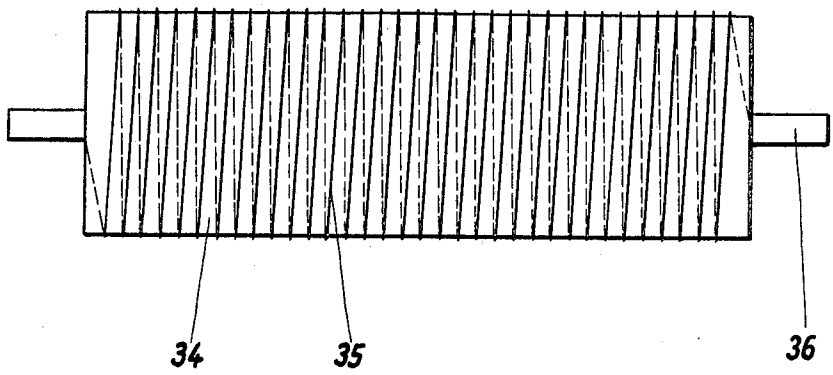
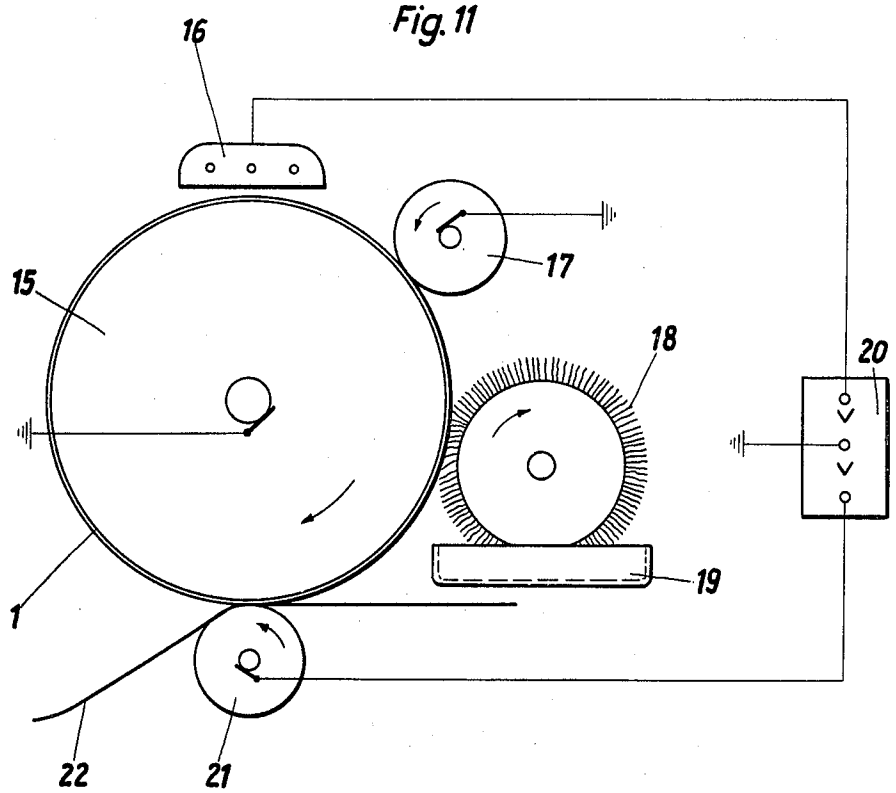


Fig. 11



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METHOD OF MAKING CHARGEABLE IMAGE STRUCTURES

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Int. Cl. B44d 1/18
U.S. Cl. 117—212 4 Claims

ABSTRACT OF THE DISCLOSURE

An electrostatically chargeable printing form is produced by removing from a printing form blank which includes a composite printing surface layer consisting essentially of a dielectric, electrostatically chargeable material covered by a layer of electrically conductive material selected portions of the layer of electrically conductive material so as to expose corresponding underlying portions of the dielectric material, the thus exposed portions of the dielectric material forming an electrostatically chargeable image.

The present invention relates to chargeable image structures and a method of making the same, more particularly, the present invention is concerned with producing printing forms which can be electrostatically charged so that on the dielectric, electrostatically chargeable portions of the printing form a toner or the like can be adhered.

More particularly, the present invention is concerned with printing forms and the method of producing the same, according to which the electrostatically chargeable image-forming printing portions of the printing form are produced without application of light.

In a manner known per se, a toner is then applied and will adhere to the electrostatically charged dielectric, image-forming portions of the printing surface but will not adhere to the electrically conductive portions of the printing surface which are not electrically charged.

Such toner is well known per se, and generally consists of a pulverulent material preferably having a particle size of between 20 and 60 microns and consists of a mixture of low melting synthetic and/or natural resins or waxes per se or mixtures thereof with pigments and dyestuffs. In most cases carbon black is used as the dyestuff and for improvement of the coloring effect, nigrosine bases may be added. Thus, the toner may consist for instance of an intimate mixture of candelilla wax to which 5% carbon black and 2% nigrosine have been added.

The printing form with the toner adhering to the charged dielectric portions thereof is then contacted in conventional manner with a copy sheet on which a copy of the image is to be formed, for instance a paper sheet, and the image which is thus formed on the paper sheet may be fixed thereon in conventional manner.

It is an object of the present invention to provide a method for producing electrostatic printing forms which can be carried out in a particularly simple and effective manner.

It is a further object of the present invention to provide an electrostatic printing form and a method for producing the same which will permit in a simple and effective manner to remove electric charges from the image-free electrically conductive portion of the printing form.

Other objects and advantages of the present invention will become apparent from a further reading of the description and of the appended claims.

With the above and other objects in view, the present

invention contemplates a method of producing an electrostatically chargeable printing form, which method comprises the step of removing from a printing form blank which includes a composite printing surface layer consisting essentially of a dielectric, electrostatically chargeable material covered by a layer of electrically conductive material, selected portions of the layer of electrically conductive material so as to expose corresponding underlying portions of the dielectric material, the thus exposed portions of the dielectric material forming an electrostatically chargeable image.

The present invention also includes an electrostatically chargeable printing form which comprises, in combination, a printing surface formed of abutting portions of electrically conductive material and of electrostatically chargeable dielectric material, the latter portions forming an image to be printed, and linear conductors interconnecting the surface portions of electrically conductive material so as to facilitate withdrawal of an electric charge therefrom.

According to the present invention, the dielectric surface of the printing form blank is covered with an electrically conductive layer and the electrically conductive layer is then selectively removed by mechanical, chemical or physical, particularly electrical methods at the image-forming portions of the printing form.

Preferably, according to the present invention, the removal of the conductive layer at the image-forming portions of the printing surface is carried out in such a manner that thin conductive bands or linear conductors or a network of conductive linear bridges remains in order to permit discharge or withdrawal of an electric charge from the islands-forming residual portions of the electrically conductive surface layer.

It is important that the printing foil as a whole or at least the surface layer thereof, below the electrically conductive layer, consists of a dielectric material which is very well suited to be electrostatically charged and which possesses a high electric resistance. The entire printing foil below the conductive layer, or the dielectric surface of the printing foil may be formed of a foil of synthetic material for instance a synthetic foil consisting of a cellulose triester. However, it is also possible to form the printing foil of paper or of a paper sheet which has been coated or otherwise covered with a layer of synthetic material. In any event, the outermost surface of the printing form blank, prior to producing thereon the electrostatically chargeable printable image, will consist of a thin layer of electrically conductive material.

The electrically conductive layer may consist, preferably, of metal or of an alloy, whereby it is desirable that the metal should have a position in the electrochemical series which is as far removed from hydrogen as possible, so that the metal can be easily etched. This is the case, for instance, with respect to magnesium, aluminum, cadmium or zinc. However, it is also within the scope of the present invention to form the electrically conductive surface layer of the printing form blank of other material such as electrically conductive lacquers or inorganic compounds such as metal sulfides.

Such electrically conductive lacquers are described, for instance, in "Werkstoffkunde der Hochspannungsvakuumtechnik," by W. Espe, volume 2, page 349.

Suitable metal sulfides include the sulfides of lead, copper, iron, tin, zinc and cadmium.

For the etching of the metallic, electrically conductive layer of the printing foil, preferably acid or acidic salts having a pH of preferably between 3 and 5, or bases or basic salts having a pH of between 8 and 11 are used.

Very good results with respect to the etching of the electrically conductive metal foil are achieved with buf-

fered mixtures according to Soerensen and Clark, for instance, for the pH range of between 3 and 5 mixtures of hydrochloric acid and sodium citrate, for the pH range of between 8 and 9 mixtures of primary potassium phosphate and secondary sodium phosphate, and for the pH range of between 9 to 11 mixtures of sodium borate and sodium hydroxide.

It is particularly advantageous to form the thin electrically conductive layer on the dielectric surface of the printing form by vapor deposition in a thickness of about 0.1 micron. If an aluminum layer, for instance an aluminum layer formed by vapor deposition, is used as the conductive metallic layer, then etching of the same at the image-forming portions of the printing form can be carried out, for instance, with amino-sulfuric acid, or with sodium carbonate solution.

The forming of the electrostatically chargeable, exposed dielectric, image-forming portions of the printing form surface can be carried out by placing against the electrically conductive rear face of the printing foil an etching sheet which is either impregnated with etching materials or carries a layer of etching material. The etching of the conductive rear face of the printing foil, i.e., the removal of selected portions of the conductive surface layer therefrom, can be carried out by exposing the contacting printing foil and etching sheet (with the electrically conductive surface layer of the printing form blank and the etching material-containing surface of the etching sheet in contact with each other) to pressure, heat or moisture at the selective portions which are to form the printable image. This can be carried out by inserting the printing foil blank and the etching sheet into a typewriter so that the typewriter keys will exert an impact on the front face of the printing foil which impact will be conveyed from the front face of the printing foil to the front face of the etching sheet, thereby releasing etching liquid at the selected portions of the etching sheet which are thus exposed to pressure, and the thus released etching liquid will etch away corresponding portions of the thin electrically conductive metal layer which covers the dielectric rear face of the printing foil.

It is also within the scope of the present invention to use an etching sheet which contains on one surface a layer having incorporated therein small frangible hollow bodies or capsules which contain an etching material or etching liquid. The etching sheet is then placed in contact with the printing form blank so that the electrically conductive surface layer on top of the dielectric portion of the printing form blank contacts the capsule-containing layer of the etching sheet. When pressure then is applied to the thus formed stack of printing form blank and etching sheet at selected portions thereof which correspond to the image which is to be printed, then at such selected portions the frangible hollow bodies will break and etching liquid will be freed for etching away the corresponding portions of the contacting electrically conductive surface layer of the printing form blank.

According to another embodiment of the present invention, the above-described etching layer of the etching sheet which contains frangible hollow bodies more or less filled with etching liquid, is replaced by a layer of sponge-like structure, formed for instance of a synthetic material, and the etching material is embedded in the sponge-like layer. Here again, upon application of pressure to selected portions of the superposed printing form blank and etching sheet, the etching material of the sponge-like layer will be squeezed out of the sponge-like layer at the selected portions thereof which are exposed to such pressure or impact, and will contact the adjacent electrically conductive metal or the like surface layer of the printing form blank, etching away the corresponding portions thereof, so that the underlying dielectric layer of the printing form blank will be exposed at the portions thereof which correspond to the portions of the etching sheet which have been subjected to such pressure or impact.

The application of pressure or impact may be carried out for instance by operation of a typewriter, however, it would be also possible to apply such pressure or impact against selected portions of the etching sheet by other means, such as ball point pens, pencils, etc.

A pulverulent mass consisting of frangible hollow bodies or microcapsules filled or partially filled with an etching liquid or the like is known to those skilled in the art and is commercially available, for instance, from the National Cash Register Company, Dayton, Ohio.

An etching sheet with a sponge-like layer having an etching agent incorporated therein, can be produced, for instance, in the following manner:

10 parts of a mixed polymerizate, consisting of about 80% by weight of vinyl chloride and about 20% by weight of vinyl acetate are ground together with 25 parts by weight glycerol, 5 parts by weight water and 10 parts by weight trisodium phosphate.

The thus formed mixture is diluted with 55 parts of acetone.

The surface of a paper sheet is made etch-resistant by applying thereto a dispersion of polyethylene-glycol or polyisobutylene, and the acetone-diluted mixture is then applied in a thickness of between 10 and 20 microns of the polyethylene-glycol or polyisobutylene surface of the paper sheet. After evaporation of the solvent, there is obtained in this manner on the paper sheet a surface layer of finely porous structure in which the etching agent is incorporated.

It is also possible to utilize an etching sheet which contains as etching layer on one surface thereof a composition consisting essentially of an etching liquid, silica gel and an etch-resistant adhesive, for instance a polyvinyl alkyl ether which layer may be transferred by pressure, impact or heat for selected portions of the etching sheet to the electrically conductive surface layer of the printing form blank, which is to be etched. Thereby, at selected portions of the electrically conductive layer of the printing form which correspond to the portions which have been exposed to pressure, impact or heat, the electrically conductive layer will be etched away and corresponding portions of the underlying dielectric, electrostatically chargeable layer of the printing form will be exposed. Thereafter, etching agent which still adheres to the printing form is removed by washing or the like. A layer of this type may consist, for instance, of a composition formed of 50 parts by weight glycerol, 20 parts by weight trisodium phosphate, 10 parts by weight water, 5 parts by weight Aerosil (a trademark product of the firm Degussa) as the silica gel, and 5 parts polyvinyl alkyl ether. A specific ether is: Lutonal M40 (a trademark product of the firm BASF) as polyvinyl methyl ether.

According to another embodiment, the method of the present invention is carried out by removing selective portions of the electrically conductive surface layer of the printing form blank by exposing these portions to a series of sparks formed by high voltage alternating current. For this purpose, the electrically conductive surface layer of the printing form is electrically connected to one terminal of a source of high voltage alternating current while the second terminal is formed by a movable electrode terminating in a more or less pointed end portion which may be passed along the electrically conductive surface of the printing form, thereby producing thereon, in the indicated manner, a substantially linear image.

It is also within the scope of the present invention to form the surface layer of the printing form which is superposed upon the dielectric, electrostatically chargeable portion thereof, of an electrically conductive material of low melting point, or of a material of low melting point which can be chemically reacted so as to become electrically conductive, and thereafter, to remove selectively portions of the easily melting surface layer by application of heat so that at these selectively removed surface portions the

dielectric, electrostatically chargeable layer of the printing form will become exposed.

The easily melting material which can be chemically converted into a conductive material and of which the surface layer of the printing form blank may be formed, may be an inorganic or organic tin compound, for instance sodium hexahydrostannate of the formula $Na_2[Sn(OH)_6]$ which melts at 140° C., or tri-p-tolyltinhydroxide of the formula $CH_3C_6H_4SnOH$ which melts at 108° C. This low melting tin compound is then, after removal of selective portions of the layer formed thereof by application of heat, converted into the electrically highly conductive tin dioxide by a conventional reduction process.

After thus forming the printing form according to the present invention so that the surface thereof will consist of alternating portions of dielectric, electrostatically chargeable material, and electrically conductive portions, the printing form surface is charged so that an electrostatic charge will be retained by the electrostatically chargeable portion of the printing form surface. After charging the printing form surface, it is important to remove electric charge from the electrically conductive portions thereof. This might present difficulties, if such individual electrically conductive portions of the printing surface are completely surrounded by dielectric surface portions.

In order to overcome this difficulty, the present invention provides the forming of a network or the like of fine linear conductors which are not attacked by acid or alkalis and which will serve to conductively interconnect the individual electrically conductive portions of the printing surface which remain after removal of selective portions of the electrically conductive surface layer, for instance by etching. The linear conductors may consist for instance of printing ink which generally possesses a sufficient electric conductivity and is also sufficiently resistant against the etching agents, whether basic or acidic which might be applied for removing selected portions of the electrically conductive surface layer of the printing form blank. The term printing ink is meant to denote the commercially available inks for printing books and the like which broadly consist of mineral oil, organic oil, carbon black and graphite, which are etch-resistant, in other words, which will not be attacked by acids or alkali substances within the pH ranges contemplated for etching of the electrically conductive surface layer in accordance with the present invention.

According to another embodiment of the present invention, the island-forming electrically conductive surface portions which remain after removal of selected portions of the conductive surface layer so as to expose the underlying dielectric surface corresponding to these selected portions, are electrically conductively interconnected by a network formed of thin lines of a metal or metal salt which will not be etched under the prevailing operating conditions. Such network may be applied for instance by vapor deposition and may consist, for instance, of gold, platinum, or iron or aluminum oxide which has been heated to glowing temperatures.

It is also within the scope of the present invention, to charge the printing form so as to electrostatically charge the exposed dielectric surface portions thereof, and then to remove electric charge from the electrically conductive portions of the printing form surface by contacting the printing form surface with a member having point-shaped or linear-shaped electrically conductive surface portions which upon contact with the remaining electrically conductive surface portions of the printing form will discharge the same without, however, discharging the electrostatically charged dielectric surface portions of the printing form. This discharging of the electrically conductive, image-free portions of the printing form is carried out prior to application of a toner thereto.

The method of the present invention can be carried out with an electrostatially chargeable printing form foil which consists of a dielectric material, for instance a dielectric synthetic material unto which, by vapor deposition a thin metallic surface layer has been applied.

Furthermore, the electrostatically chargeable printing form foil may consist of or may include a layer of dielectric material, such as polyvinyl chloride, polyethylene, polystyrene, polyvinyl acetate or polyethylene terephthalate, on the free surface of which a thin layer of a metal sulfide, such as lead, copper, iron, tin, zinc or a cadmium sulfide layer has been formed by vapor deposition.

It is also possible to use a printing form foil which consists of a dielectric material such as a cellulose triester for instance cellulose triacetate, onto which a metallic surface layer, for instance aluminum or zinc has been applied by vapor deposition and which is provided with a thin linear structure of electrically conductive acid and alkali resistant material such as printer's ink, which linear structure will serve for discharging the remaining electrically conductive surface portions, after selected portions of the conductive surface which correspond to the image to be printed have been removed.

The novel features which are considered as characteristic for the invention are set forth in particular in the appended claims. The invention itself, however, both as to its construction and its method of operation, together with additional objects and advantages thereof, will be best understood from the following description of specific embodiments when read in connection with the accompanying drawings, in which:

FIG. 1 is a plan view of a printing foil consisting of a dielectric foil having an electrically conductive layer on one face thereof, with portions of the electrically conductive layer which correspond to the image to be printed removed therefrom;

FIG. 2 is a cross-sectional view of the printing foil according to FIG. 1 taken along the line A–B;

FIG. 3 is a cross-sectional view of the printing foil of FIG. 1 taken along the line C–D;

FIG. 4 is a schematic perspective view of the surface of the printing foil, showing particularly the network of linear conductors which serves for discharging the remaining electrically conductive portions of the printing form surface;

FIG. 5 is a schematic elevational view illustrating an arrangement of printing form blank and etching sheet which permits etching and thus removal of selected portions of the conductive layer of the printing form by pressure, such as is applied for instance by typing;

FIG. 6 is a schematic cross-sectional view of the arrangement of printing foil and etching sheet as shown in FIG. 5 after pressure has been applied and the two sheet members have been separated from each other;

FIG. 7 is a schematic cross-sectional illustration of an arrangement for removal of selected portions of the electrically conductive layer by application of high voltage alternating current;

FIG. 8 is a schematic elevational cross-sectional view of an arrangement for removal of selected portions of the electrically conductive layer of the printing foil, which portions correspond to the image-forming portions of an original, by application of heat;

FIG. 9 is a schematic cross-sectional view of the arrangement of FIG. 8 after exposure of the image-forming dielectric surface portions of the printing form and separating of the latter;

FIG. 10 is a schematic elevational view of a conductive member which may be used for discharging the remaining electrically conductive surface layer portions after selected portions thereof, corresponding to the image to be printed have been removed therefrom; and

FIG. 11 is a schematic elevational view of an entire electrostatic printing arrangement.

The dielectric layer of the electrostatic printing form may be formed of any easily electrostatically chargeable dielectric material, such as electric insulating material having a greater resistance than $10^{13}\Omega cm.^3$. Further characteristics of a dielectric material which is easily chargeable and lends itself for forming the dielectric layer of the printing foil are high surface resistance, high dielectric constant and high voltage breakdown resistance. Materials possessing a combination of these desirable characteristics are primarily thermosetting and thermoplastic synthetic materials such as polyamides, polystyrenes, polyvinyl chlorides, polyvinyl acetates, polycarbonates and cellulose triesters.

Referring now to the drawing, and particularly to FIGS. 1–3, an electrostatic printing form is shown as comprising dielectric foil **1** and an electrically conductive layer **2** partially covering one surface of foil **1**. While the electric body is shown schematically as having the thickness of a foil, it is noted that the dielectric body having a partially exposed surface, the remainder of the surface being covered by portions of electrically conductive layer **2**, may be of any desired thickness. At the portions **4** of the printing form surface, which portions correspond to the image which is to be printed, the electrically conductive layer **2** has been removed, for instance by etching. Thereby island-forming residual portions of the electrically conductive layer **2** will remain which are completely surrounded by exposed surface portions of the dielectric material. Such island-forming conductive portions are indicated in FIGS. 2 and 3 by reference numeral **2***b*.

In order to discharge these discrete electrically conductive portions **2***b*, as illustrated in FIG. 4, the surface of the conductive layer **2** has superposed thereon a network **25** of narrow linear conductors. It would also suffice to apply to the conductive surface a plurality of parallel linear conductors. These linear conductors may be applied, for instance by imprinting. Printer's ink is a suitable material for the linear conductors since the electric conductivity of printer's ink suffices to prevent electric charging of these conductors. Underneath the network or parallel linear bodies or the like of, for instance printer's ink, similarly shaped portions of the conductive layer will be protected from being etched and thus will be retained as linear conductors **26**. Thereby it is achieved that the electric charge from discrete portions **2***b* can be withdrawn via conductive bridges **26** which interconnect discrete portions **2***b* with the remainder of conductive layer **2**.

FIG. 5 illustrates a method of forming the printing surface corresponding to an image to be printed by removing by etching selected portions of conductive layer **2**, which selected portions correspond to the image which is to be printed. According to FIG. 5, the printing foil consisting of dielectric foil **1** and electrically conductive surface layer **2** is placed against a contact sheet or etching sheet. The etching sheet consists of a carrier sheet **5** and a surface layer **6** which contains etching liquid. Surface layer **6** comprises either microcapsules which contain the etching liquid, or the etching liquid is absorbed in the sponge-like structure of layer **6**. The material of which layer **6** is formed should be resistant against the etching liquid and this requirement is primarily fulfilled by synthetic materials such a polytetrafluoroethylene. Upon subjecting selected portions of the etching sheet to pressure or impact, the capsules or hollow frangible bodies will be broken and destroyed and thereby will release etching liquid, or such pressure or impact will press the etching liquid absorbed by a sponge-like structure of layer **6** to the surface thereof. It will be noted that printing foil and etching sheet are juxtaposed in such a manner that conductive layer **2** of the printing foil will contact etching liquid-containing layer **6** of the etching foil.

As illustrated in FIG. 5, the impact of a typewriter key **7** is used for forcing the etching liquid of portions of layer **6** which correspond to the configuration of the surface of typewriter key **7**, into contact with conductive layer **2**. Thereby, the corresponding portion of conductive layer **2** will be dissolved by etching and removed and a corresponding portion **4***a* of the surface of the dielectric foil **1** will be exposed. Reference numeral **2***b* again illustrates in FIG. 6 a discrete remaining portion of conductive layer **2** which portion **2***b* is entirely surrounded by exposed surafce portions of dielectric layer **2**.

During the inscribing of the printing form it may become necessary from time to time to carry out minor corrections. For this reason, it is desirable to extend the etching process for a period of several minutes, so that such corrections can be carried out before the etching is completed.

It has been mentioned above that weak acids or bases may be used for etching away portions of the electrically conductive layer which covers the dielectric surface of the printing form.

The etching process can be extended for longer periods of time in an even more effective manner by embedding the etching liquid or etching agent in a composition of high viscosity, for instance by increasing the viscosity of the etching liquid by the admixture of silica gel and of an adhesive. Such composition may easily be incorporated in the sponge-like layer of the etching sheet or, if the viscosity of the composition is sufficiently high, the same may be applied per se as the etching layer **6** of the contact or etching sheet. Such composition may, for instance, consist of an intimate mixture of 50 parts glycerol, 20 parts trisodium phosphate, 10 parts water, 5 parts silica gel, such as is available for instance under the trade name Aerosil, and 5 parts of a polyvinyl alkyl ether.

It is achieved by forming the etching layer of such a composition that by pressure or impact a considerably larger quantity of the weakly etching substance is transferred from etching layer **6** of the etching sheet onto conductive layer **2** of the printing foil. The extension of the time during which such composition will carry out the etching away of conductive layer **2** is caused by the diffusion of the etching liquid which thus will only be relatively slowly carried into contact with the metal surface **2**.

FIG. 7 illustrates, by way of example, the forming of a printable image by removal of selected portions of conductive layer **2**, which selected portions correspond to the image which is to be printed, in a physical manner, namely by application of sparks of high voltage alternating current to the selected portions of conductive surface layer **2** of the printing foil.

As illustrated, electrically conductive layer **2** is connected by means of electrode **14** to one terminal of source **13** of high voltage alternating electric current. The second terminal is formed by the pointed end portion of movable electrode **9** which is passed along the conductive surface **2** so as to outline the image which is to be printed. By spark formation between electrode tip **9** and conductive layer **2**, the portion of conductive layer **2**, directly underneath the electrode tip **9** will be burned off so that these image-forming portions **4** at the surface of the dielectric portion **1** of the printing foil will be exposed.

FIGS. 8 and 9 illustrate how heat can be utilized in order to produce an electrostatic printing foil in accordance with the present invention. Dielectric foil **1** of the printing foil is provided according to FIG. 8 with an electrically conductive and easily melting layer **23** which may consist for instance of a mixture of wax and light permeable, electrically conductive tin dioxide SnO_2.

Tin dioxide is a relatively good electric conductor with a specific electric resistance of about $8\times10^{-3}\Omega cm.^3$. An original **11** of absorbent material contacts layer **23** so that at least the image-forming portions **12** of the original **11** are in direct contact with layer **23**. Infrared rays emanating from source **10** pass first through light-permeable

or infrared rays-permeable foil **1** and through the other intermediate layers to image-forming portions **12** at which the infrared rays are absorbed causing heating of image-forming portions **12**. Due to the heating of image-forming portion **12**, the immediately superposed portions of easily melting layer **23** will be molten by heat convection and due to the strong absorbent properties of original **11**, as shown in FIG. 9, portions of the easily melting layer **23** which were directly juxtaposed to the heated image-forming portions **12** will be practically completely absorbed by original **11** so that the conductive surface layer **23** is interrupted at the image representing portions **4**. Easily melting layer **23** preferably has a thickness of only between about 1 and 3 microns.

The easily melting layer **23** may also consist of a chemical precursor of tin dioxide, for instance of the inorganic sodium hexahydrostannate which melts at 140° C. or of the organic tri-p-tolyltinhydroxide which melts at 108° C. These precursor layers, after removal of the portions thereof which correspond to the image-forming portions **12** of the original can then be reduced to form tin dioxide.

The chemical precursors of the oxide may also be chlorides such as tin tetrachloride which with water will form tin dioxide in accordance with the formula:

$$SnCl_4+5H_2O\rightarrow SnO_2+HCl+3H_2O$$

Tin tetrachloride is a gel-like substance also known under the name "tin butter" which melts at about 60° C.

The discharge of the discrete or island-forming remaining portions **2***b* of the electrically conductive surface layer of the printing foil, which are shown in FIGS. 2, 3, 4 and 9 may also be accomplished by contact with a discharge roller such as is shown by way of example in FIG. 10.

The discharge roller comprises a rubber cylinder **34** about which a thin metal wire **35** having a thickness of between about 0.1 and 0.2 mm. is spirally wound so that upon rolling of the discharge roller over and in contact with the printing form all of the island-forming discrete residual portions **2***b* will be contacted by one or the other of the wire windings. The ends of the wire windings are connected with the electrically conductive shaft **36** of the roller so that the electric charge can be grounded.

Printing cylinder **15** is covered by printing foil **1** which is formed as described hereinabove, namely so that the image-forming portions which are to be printed are represented by a dielectric surface while the image-free portions form an electrically conductive surface. The printing form is electricaly charged by means of the corona current formed by sparking electrode **16**. The discrete or island-forming residual electrically conductive surface portions are then discharged by contact with discharge roller **17**. The pulverulent toner is applied to printing form **1** by means of brush roller **18** and the toner will adhere only to the electrostatically charged portions of the printing form. The toner is supplied to brush roller **18** from container **19**. The thus-formed toner or pulverulent image which covers the image-forming portions of printing foil **1** is then transferred by means of transfer roller **21**, electrostatically in a manner known per se, onto paper sheet **22**. Subsequent fixing of the toner or pulverulent image to its paper sheet support, for instance by melting, is also carried out in conventional manner and therefore not illustrated. Finally, FIG. 11 also illustrates schematically the electric connection between spray electrode **16** and transfer roller **21** with a high voltage source **20**. The electric circuit is closed by grounding the source of high voltage current, the printing cylinder **15** and discharge roller **17**.

The following examples are given as illustrative only, the present invention, however, not being limited to the specific details of the examples.

EXAMPLE I

For producing a hand drawn printing form, a printing form blank consisting of a cellulose-triester foil carrying on one face thereof a thin layer of zinc sulfide, formed by vapor deposition, is used.

The zinc sulfide layer must be sufficiently thin so that it is still light permeable to the extent of about 20%.

The image or writing which is to be printed and which has to correspond to exposed portions of the cellulose-triester foil, is produced by hand by means of a stylus or another suitable, more or less pointed scraping tool by means of which the conductive zinc sulfide layer is removed from the image-forming portions of the operating face of the printing foil.

EXAMPLE II

Mechanical removal of selected portions of the conductive layer of a printing foil can also be carried out in the following manner.

A printing foil is used such as is described in Example I which, however, in addition, includes an imprinted raster or the like of fine lines which consist of printer's ink and are arranged at a distance of about 1 mm. from each other.

The zinc sulfide layer of the printing foil is contacted with the adhesive face of an adhesive foil. Such adhesive foils consist preferably of a carrier foil of hydrated cellulose having a thickness of about 60 microns and carrying a layer of a polyvinyl alkyl ether of sufficiently high viscosity so that the same will adhere to the zinc sulfide layer only upon application of considerable pressure.

Upon superposing the two foils with the adhesive layer of the adhesive foil contacting the zinc sulfide layer of the printing foil, and applying pressure, for instance by means of a typewriter or ball point pen, followed by separation of the printing foil from the adhesive foil, it will be found that the portions of the zinc sulfide layer which were exposed to such pressure will have been adhered to the adhesive foil and thus will have been removed from the dielectric surface of the printing foil.

The raster of printer's ink lines is imprinted on the cellulose-triester foil, before the conductive zinc sulfide layer is formed by vapor deposition so that the same will not be removed together with pressure exposed portions of the zinc sulfide layer by separation of the printing foil from the adhesive foil.

EXAMPLE III

Removal of selected portions of the conductive surface layer of the printing foil blank may be carried out in a chemical manner, for instance with a foil such as is described in Example II wherein, however, instead of a layer of zinc sulfide, an aluminum layer has been formed by vapor deposition.

The aluminum layer of the printing foil is then contacted by the active layer of an etching or contact sheet. This contact sheet consists preferably of a carrier sheet of thick condenser paper having a thickness of about 15 microns and on one face thereof an active layer of frangible etching capsules having a diameter of between 20 and 40 microns which are made commercially available by the National Cash Register Company. Upon superposing of the etching layer or active layer of the etching sheet onto the electrically conductive layer of the printing foil and inscribing the outer face of the carrier sheet of either the printing foil or the etching sheet by pressure, for instance by means of a stylus, a ball point pen or typewriter, the capsules whch are directly exposed to such pressure will break and release etching liquid which will etch away corresponding portions of the aluminum surface layer of the printing foil so that at the portions of the printing foil which correspond to the area of application of pressure the dielectric surface will be exposed, with the exception of those portions thereof which are covered by the imprinted line raster of printer's ink or the like. Thereafter, the thus-formed printing foil is rinsed

with water in order to remove therefrom salts which are formed by the etching process as well as residual portions of the etching liquid.

EXAMPLE IV

In another manner, the selected portions of the electrically conductive surface layer of the printing foil may be chemically removed by contacting a painting foil as described in Example III with a contact or etching sheet which carries an etching layer consisting of a mixture of 10 parts of a mixed polymerizate of about 80% vinyl chloride and 20% vinyl acetate, 25 parts glycerine, 5 parts water and 10 parts trisodium phosphate. Upon applying pressure and further proceeding as described in Example III, a printing foil will be produced having image-forming surface portions consisting of exposed dielectric, electrostatically chargeable material, and image-free surface portion formed by the residual portion of the electrically conductive layer.

EXAMPLE V

It is also possible to remove selected portions of the electrically conductive layer of the printing foil by proceeding generally as described in Example III, however, using as the active layer of the etching sheet a mixture of 50 parts of glycerol, 20 parts of trisodium phosphate, 10 parts of water, 5 parts of silica gel, for instance Aerosil, and 5 parts of a polyvinyl alkyl ether.

EXAMPLE VI

For producing a printing foil by removal of selected portions of the conductive surface layer, corresponding to the image-forming portions which are to be printed, by physical, i.e. electrical means, it is advantageous to use a printing foil blank for instance of the type described in Example I wherein, however, the conductive layer is formed by vapor deposition of aluminum. The conductive aluminum layer is electrically connected to one terminal of a source of high voltage alternating current, while the second terminal of the current source is connected to a movable stylus-shaped electrode, whereby at least a portion of the movable electrode, spaced from the pointed tip thereof is covered by a layer of insulating material. Upon passing the pointed exposed tip of the movable electrode along the aluminum layer, it will be found that the current flowing between the pointed end of the movable electrode and the aluminum layer will always have to pass through air and oxide layers. Thereby spark formation will be caused which in turn will result in burning away the portion of the aluminum layer at the point of contact with the movable electrode. In order to improve the safety of this method, it is desirable that the alternating current which is used thereby should be of high frequency and for this reason it has been found advantageous to use as a source of the high voltage a Tesla transformer.

It will be understood that each of the elements described above, or two or more together, may also find a useful application in other types of printing foils differing from the types described above.

While the invention has been illustrated and described as embodied in a dielectric, electrostatically chargeable printing foil, it is not intended to be limited to the details shown, since various modifications and structural changes may be made without departing in any way from the spirit of the present invention.

Without further analysis, the foregoing will so fully reveal the gist of the present invention that others can by applying current knowledge readily adapt it for various applications without omitting features that, from the standpoint of prior art, fairly constitute essential characteristics of the generic or specific aspects of this invention and, therefore, such adaptations should and are intended to be comprehended within the meaning and range of equivalence of the following claims.

What is claimed as new and desired to be secured by Letters Patent is:

1. Method of producing an electrostatically chargeable printing form, comprising the step of removing from a printing form blank which includes a composite printing surface layer consisting essentially of a dielectric, electrostatically chargeable material covered by a layer of electrically conductive material, selected portions of said layer of electrically conductive material so as to form on said printing form blank a printing surface consisting of exposed portions of said dielectric material corresponding to said removed selected portions of said layer of electrically conductive material with the remaining portion of said layer of electrically conductive material being interconnected and surrounding the exposed portions of said dielectric material so that an electric charge can be easily withdrawn from said interconnected remaining portion of said layer of electrically conductive material, the thus exposed portions of said dielectric material forming an electrostatically chargeable image.

2. Method of producing an electrostatically chargeable printing form, comprising the steps of arranging in superposed relationship a printing form blank including a composite printing surface layer consisting essentially of a dielectric, electrostatically chargeable material covered by a layer of electrically conductive material adapted to be etched, and an etching sheet having a surface layer adapted upon activation to etch contacting portions of said electrically conductive layer, with said electrically conductive layer contacting said surface layer of said etching sheet; and activating selected portions of said surface layer of said etching sheet so as to etch and thereby remove corresponding portions of said electrically conductive layer, thereby exposing corresponding underlying portions of said dielectric material of said printing form blank, the thus exposed portions of said dielectric material forming an electrostatically chargeable image.

3. Method of producing an electrostatically chargeable printing form, comprising the steps of arranging in superposed relationship a printing form blank including a composite printing surface layer consisting essentially of a dielectric, electrostatically chargeable material covered by a layer of electrically conductive material adapted to be etched, and an etching sheet including a surface layer of sponge-like characteristics having embedded therein an etching liquid adapted upon release from said sponge-like layer to etch said electrically conductive layer, with said electrically conductive layer contacting said surface layer of said etching sheet; and subjecting selected portions of said sponge-like surface layer of said etching sheet to pressure so as to release the etching liquid therefrom, the latter etching and thereby removing corresponding portions of said electrically conductive layer, thereby exposing corresponding underlying portions of said dielectric material of said printing form blank, the thus exposed portions of said dielectric material forming an electrostatically chargeable image.

4. Method of producing an electrostatically chargeable printing form, comprising the steps of removing from a printing form blank which includes a composite printing surface layer consisting essentially of a dielectric, electrostatically chargeable material covered by a layer of electrically conductive material, selected portions of said layer of electrically conductive material so as to expose corresponding underlying portions of said dielectric material, the thus exposed portions of said dielectric material forming an electrostatically chargeable image; and interconnecting the residual portions of said layer of electrically conductive material with linear conductors so as to facilitate removal of an electric charge from said residual portions of said layer of electrically conductive material.

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