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SATORU HONJO ET AL

3,745,002

METHOD OF PREPARING A PRINTING MASTER BY XEROGRAPHY

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Fig. 1

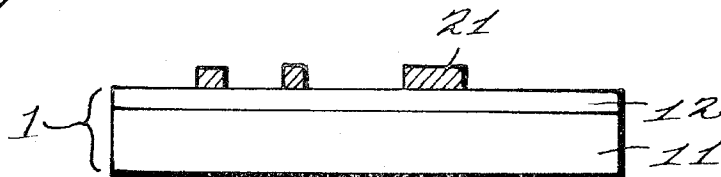


Fig. 2

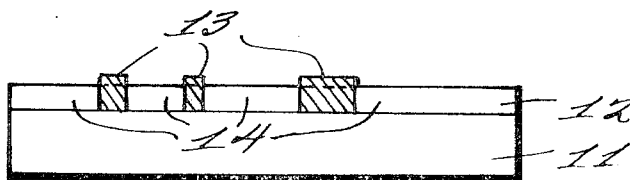


Fig. 3

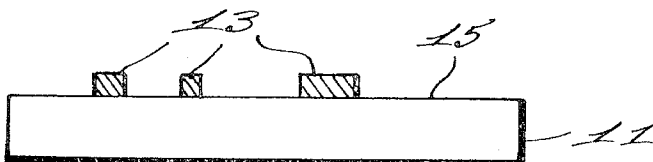
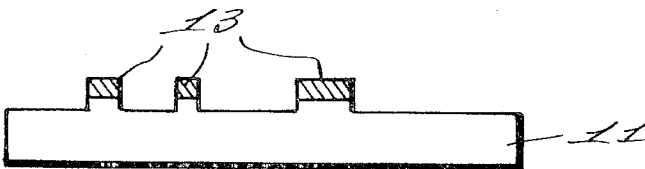


Fig. 4



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METHOD OF PREPARING A PRINTING MASTER BY XEROGRAPHY

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4 Claims

ABSTRACT OF THE DISCLOSURE

A method of producing an etch resist pattern by xerography consisting of the following steps: forming on a metal substrate a photoconductive insulating coating comprising an intimate mixture of a photoconductive powder and an electrically insulating resin binder containing chemically active functional groups which can react with isocyanate groups; providing an electrostatic latent image on said coating; developing said latent image with a toner comprising a masked polyisocyanate compound; heating the developed plate to an elevated temperature sufficient to regenerate the isocyanate thus causing a reaction between the resin binder in the photoconductive coating and the polyisocyanate whereby the resin binder is completely cured and becomes insoluble in organic solvents, and finally removing the photoconductive coating at the areas where no toner deposition occurred and thus exposing the metal substrate.

This invention relates to a new method of xerography, and especially, to a method of preparing a printing master by xerography.

Xerography, in its most common manner of practice, comprises imparting a uniform charge on a photoconductive insulating layer provided on an electrically conductive support under a subdued light by means of corona discharge, exposing said layer to a light image to be reproduced to form an electrostatic latent image, and finally applying a toner material onto said latent image having an electrostatic charge of desired polarity to render the image visible. The obtained toner image may be permanently fixed directly on the photoconductive layer or may be transferred onto a suitable transfer member. A new application has been developed by utilizing a chemically active toner material which can react with an ingredient contained in the photoconductive layer. A typical example of such application is disclosed in Japan patent publication No. 13,470/63, or in U.S. Pat. No. 3,226,227 whereby a toner image comprising an ingredient which promotes curing of the resinous material in photoconductive coating, or which can bond with an ingredient in the coating is formed on the photoconductive coating by xerography. The developed recording material is then heated to carry out an imagewise curing of the coating, thus providing an etch resist pattern.

Conventionally, the typical combination of materials has been polysiloxane resin binder in the photoconductive coating and aluminum oxide, or aluminum salts of organic acids as toner, in which case, however, the silicone resins not only exhibited an insufficient adhesion to a variety of metal substrates, but were difficult to form a photoconductor coating of a high light sensitivity. Besides, the hardened coating showed a poor resistance to chemical reagents used for etchant. Due to these shortcomings the process has not yet been commercialized.

Therefore, the principal object of the present invention is to provide a new combination of resinous binder and toner material which can overcome or improve the above described shortcomings, and thus to provide a

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new method of preparing a printing master by xerography.

Such object has proved to be accomplished by forming on a metal substrate photoconductive insulating coating comprising an intimate mixture of a photoconductive powder and an electrically insulating resin binder containing chemically active functional groups which can react with isocyanate groups, providing an electrostatic latent image, developing this image with a toner comprising a masked polyisocyanate compound which is sometimes referred to as isocyanate generator, heating the developed plate to an elevated temperature sufficient to regenerate the isocyanate thus causing a reaction between the resin binder and the toner material, whereby the resin binder is completely cured and becomes insoluble in organic solvents, and finally removing the photoconductive coating only at the areas where no toner deposition occurred thus exposing the metal substrate.

The above described process has many advantages including a strong affinity of the photoconductive coating with a variety of metallic substrates, a high resistance of the cured coating to chemical reagents, and employment of electrophotographic coatings having superior electrophotographic properties. Now the process will be explained in more detail referring to the accompanying drawings.

FIG. 1 illustrates a cross-sectional view of an electrophotographic material having on its photoconductive coating a toner image. The recording material 1 comprises a conductive substrate 11 and a photoconductive insulating coating 12 provided on 11. The substrate 11 comprises metals in this invention, including zinc, magnesium, aluminum, copper, and etc. The photoconductive coating 12 comprises an intimate mixture of a finely-divided photoconductor such as zinc oxide, cadmium sulfide, titanium dioxide, lead oxide, or other calcogenite compounds of zinc, cadmium and lead, and a resinous binder. The coating may contain as minor ingredient spectral sensitizers for the photoconductor, or chemical sensitizers. The resinous binder used must contain such functional groups as to be able of reacting with an isocyanate group. Such groups are primary and secondary hydroxyl and amino radicals. Suitable resinous materials include various types of alkyd (drying and non-drying oil modified, phenolformaldehyde resin modified, styrene or acrylester modified, rosin modified, and etc.), epoxyesters, (for example, epoxyester of dehydrated castor oil fatty acid) epoxides, vinyl polymers containing monomers having hydroxyl groups (for example, polyvinylbutyral, copolymers, or terpolymers comprising a monomer selected from styrene, alkylacrylates, alkylmethacrylates, vinyl chloride, vinyl acetate, or ethylene, and comonomer selected from hydroxyalkylacrylate, hydroxyalkylmethacrylate, and allyl alcohol; the polymer may also contain acidic monomer such as acrylic acid, methacrylic acid, itaconic acid, crotonic acid, or maleic anhydride). Mutually compatible combinations of these resins are also used, or in some cases resinous materials which are insoluble in the solvent to be used to dissolve the photoconductive coating after development may be incorporated as a minor component.

These resinous material contain in their molecular structures primary or secondary hydroxyl groups which can enter into condensation reactions with the isocyanate radicals generated from the toner materials at temperatures ranging from 20 to 150° C. It should be noted that these resins serve as excellent binder material for electrophotographic coating, providing coatings having faster photographic speeds than polysiloxane resins do. Further, they are superior to polysiloxane as regards the adhesion

to metallic substrates and capability of forming coatings on which the electrostatic charge attenuates quite slowly in many insulating organic liquids which may be used as carrier liquid for liquid developer. The photoconductive coating 12 normally comprises 40 to 80 volume per-

cents of a photoconductive powder in its total volume and its coating thickness lies between several and several ten microns.

The electrophotographic coating is uniformly charged in a subdued light, then exposed to an image of light and shadow to be reproduced whereby the light-struck area loses the surface charge, and thus an electrostatic latent image is formed.

Next, the exposed coating is subjected to a development operation by using a toner comprising polyisocyanate generator to convert the latent image into a material image. Any known development method may be employed, among which the liquid development or electrophoretic development can give a developed image of highest quality. The development image is designated as 21 in FIG. 1.

An isocyanate generator which is a quite important material characterizing the present process is a compound in which the isocyanate group is temporarily blocked or masked by a suitable component attached to the isocyanate below a certain temperature above which the added component dissociates to regenerate the active isocyanate. Typical isocyanate generators include polyisocyanates masked with the following components; phenol, diethyl-malonate, alkylacetoacetate, acetylacetone, secondary aromatic amine, tertiary alcohol, amide, lactum, etc. Among these, phenol masked polyisocyanate is most popular, one of which is commercially available for Bayer A.G. (West Germany) under the trade name "Desmodur AP Stable."

As for isocyanate compounds, aromatic isocyanates are preferred because of their high reactivities. The isocyanate generator is suitably pulverized to prepare a toner for dry developing operations such as magnetic brush, cascade, or powder cloud development; or it may be dissolved in a suitable organic solvent, then the resulting solution is dispersed in an electrically insulating, nonpolar liquid which cannot dissolve the generator; the resulting dispersion may be used in liquid development. In the case of Desmodur AP Stable, ethyl acetate, or methyl ethyl ketone, is suited as solvent, and the dispersion carrier liquid may be isoparaffinic, normal paraffinic or cycloaliphatic hydrocarbons, halogenated hydrocarbons, etc. The resulting dispersion has proved to exhibit stable electrophoretic properties for a long period of time. Coloring agents or other charge control agents may also be added to the masked isocyanate. The colored toner makes it easy to judge the developed image quality with the unaided eyes.

FIG. 2 shows the cross-sectional view of the electrophotographic material in the state after the developed toner image 21 is impregnated into the photoconductive coating 12 and then the polyisocyanate is regenerated by heating whereby the resinous binder in 12 is completely cured at the toner-deposited areas. 13 and 14 designate the cured and uncured regions of the coating, respectively.

If the impregnation of the toner into the coating is not complete, the curing will proceed only at the surface of the coating, thus causing an undesirable result.

The impregnation of the toner image 12 can be accomplished either by heating the material to an temperature above the melting point but below the dissociating point of the isocyanate generator, or by exposing the material to a solvent vapor of the generator.

In the case of phenol masked product above illustrated, the suitable range of temperature for toner impregnation is 140 to 170° C.

The curing reaction is carried out at 170 to 180° C. with the same product, and under such elevated temperatures a reaction counterpart having a low reactivity such

as secondary hydroxyl group can even enter into condensation reaction with the regenerated isocyanate rather rapidly.

In FIG. 3 the uncured region is removed by a suitable solvent including esters, ketones, aromatic hydrocarbons, etc. To prevent the danger of inflammability of the processing solvent one may incorporate or use chlorinated hydrocarbons, or chlorofluorinated. 15 in FIG. 3 designates the exposed substrate metal.

In FIG. 4 the exposed substrate has been etched by a suitable etching solution such as an aqueous ferric chloride solution, or other acidic etching baths.

One way carry out additional operations to improve the image quality of the developed image. Representative examples of such additional operations are pre-bathing of the latent image bearing material and the rinsing of the developed material prior to the removing operation of the uncured coating. The former serves to decrease background, while the latter, in addition to the decrease of background, improves the uniformity of the developed image.

EXAMPLE I

Preparation of an electrophotographic recording material. On a zinc plate there was spray-coated a mixture comprising 100 parts by weight of photoconductive zinc oxide, 50 parts of styrene modified alkyd resin varnish (non-volatile content 50%), and 40 parts of toluol to give a dried thickness of about 5 microns (coating weight on dry base 18 grams/m²).

Preparation of a toner (developer). 10 parts by weight of Desmodur AP Stable (manufactured by Bayer A.G. in West Germany; the material comprises phenol masked condensate made from 3 mol of tolylene diisocyanate and 1 mol of trimethylolpropane) was dissolved in 1000 parts of butyl acetate. 30 parts of the solution was dispersed with the aid of ultrasonic wave into 1000 parts of a carrier liquid comprising 980 parts of kerosene and 20 parts of cottonseed oil.

Preparation of a printing master by electrophotography. The photoconductive coating prepared above readily dissolved in toluol. The dark-adapted recording material was exposed to a negative corona and accepted a uniform electrostatic charge. The accepted potential immediately after the termination of the corona charging was about 200 volts. The coating was contact exposed to a positive transparency with an incandescent light. After the transparency was peeled off, the coating was soaked with an isoparaffinic solvent "Isopar H" (manufactured by Esso Standard Oil Co.), and then developed with the developer prepared above. Since the particles of Desmodur AP Stable acquired a positive electrostatic charge in the dispersion, they deposited on the charge-remaining area, forming a positive reproduction.

The plate still held a thin film of the developer which was rinsed with an isoparaffinic solvent "Isopar E" (manufactured by Esso Standard Oil Co.). Then the plate was dried by applying a warm air of about 40° C. Next, the plate was left in an air oven kept at 140° C. for 10 minutes, then the temperature was raised to 180° C. Under this condition the plate was kept for 10 minutes. Thus the curing reaction completed. The plate was immersed in toluol with mild stirring whereby the toner-deposited area remained unchanged but at the background area the photoconductive coating slowly dissolved off. The resulting resist pattern proved to stand various acidic baths including aqueous ferric chloride.

EXAMPLE II

An electrophotographic material was prepared in a similar manner as was described in Example I except that an epoxyster of dehydrated castor oil fatty acid having an oil length of 40% was used in place of the styrenated alkyd resin.

A cascade developing material was prepared by mixing nitrocellulose coated silica granules and a finely-divided

Desmodur AP Stable of 20 micron mean diameter. With the use of these materials a similar satisfactory result was obtained.

EXAMPLE III

To a zinc plate there was applied a layer comprising 100 parts by weight of photoconductive zinc oxide, 20 parts by weight of copolymer containing 60% of butyl methacrylate, 25% of styrene, 13% of hydroxyethylacrylate and 2% of acrylic acid, and 5 parts by weight of acrylic ester modified alkyd resin (hydroxyl value 30). The electrophotographic material thus formed was treated in a similar manner as described in Example I except that a mixture of 50 parts of toluol and 50 parts of ethyl acetate was used in place of the toluol. A similar result as Example I was obtained.

What is claimed is:

1. A method of producing an etch resist pattern by xerography comprising; forming on a metal substrate an inorganic photoconductive insulating coating comprising an intimate mixture of a photoconductive powder and an electrically insulating resin binder containing chemically active functional groups which can react with isocyanate groups, providing an electrostatic latent image on said coating, developing said latent image with a toner comprising a masked polyisocyanate compound, impregnating the inner portion of the photoconductive coating with the developed toner material, heating the developed plate to an elevated temperature sufficient to regenerate the isocyanate thus causing a reaction between the resin binder in the photoconductive coating and said polyisocyanate whereby the resin binder is completely cured and becomes insoluble in organic solvents, and finally removing the photoconductive coating at the areas where no toner deposition occurred and thus exposing the metal substrate.

2. The method as claimed in claim 1, which is characterized by that, prior to regeneration of the masked isocyanate, the developed toner material is allowed to sufficiently impregnate into the inner portion of the photoconductive coating by heating above the melting point but below the regenerating temperature of said masked isocyanate.

3. The method as claimed in claim 1, wherein said masked polyisocyanate is a phenol masked polyisocyanate.

4. The method as claimed in claim 1, wherein said resin binder is alkyd resin, epoxyster of dehydrated castor oil fatty acid, vinyl copolymer containing hydroxyalkyl acrylate, hydroxyalkyl methacrylate or allyl alcohol, or a compatible combination thereof.

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117—17.5; 96—33, 36, 36.3; 101—457, 458, 459, 463