Patented Nov. 17, 1953 2,659,670

UNITED STATES PATENT OFFICE

2,659,670

METHOD OF DEVELOPING ELECTROSTATIC IMAGES

Harold E. Copley, Worthington, Ohio, assignor, by mesne assignments, to The Haloid Company, Rochester, N. Y., a corporation of New York

No Drawing. Application June 6, 1950, Serial No. 166,549

3 Claims. (Cl. 95—1.9)

1

This invention relates to electroscopic powders for the development of electrostatic images, such as the electrostatic latent images formed on electrophotographic plates, and the electrically-charged insulating images on electroprinting plates and the like.

In the process of electrophotography, or xerography, as described for example in U. S. Patent No. 2,297,691, issued to Chester F. Carlson, a layer of photoconductive insulating material is given a uniform electrostatic charge over its surface and is then exposed to a light image to dissipate the charge on the layer in proportion to the amount of light reaching each part of the layer, thereby leaving an electrostatic latent image corresponding to the light image. The image is then developed and rendered visible by depositing a finely-divided powder on the layer, the powder being attracted to the charged areas and arranging itself in a configuration corresponding to the electrostatic image. The powder image may then be fixed on the layer or, preferably, transferred to a sheet of paper or other material to which it is subsequently affixed. Thus, if the powder is formed of a fusible material, such as a fusible resin, the image may be transferred to a sheet of paper and affixed to it by heating the paper above the melting point of the resin and then allowing it to cool.

Some variations and improvements have been made in certain steps of the process of electrophotography described, one of which comprises the use of a developing composition formed of two components. One of these components is a finely-divided dyed or pigmented material (hereinafter called the toner) which will adhere to the electrostatic image, and the other component is a granular material (hereinafter called the carrier (which serves to carry the finely-divided toner over the plate and deposit it where required. The composition of the toner and of the surface of the carrier are so adjusted as to place them in different positions in the triboelectric series. Upon being mixed together, the carrier and toner impart to each other opposite electrostatic charges. Thus, if the carrier surface is of a composition which is closer to the positive end of the triboelectric series than the toner, the carrier will acquire a positive charge on its surface from rubbing and contact with the toner and the toner acquires a negative charge. As a result of the mixing operation, the toner particles, which are many times smaller than the carrier particles, adhere to and coat the surface of the carrier particles due to the electrostatic attraction between them. During development, as the powder coated carrier particles roll or tumble over the electrophotographic plate carrying an electrostatic image of opposite polarity to the charge on the toner, toner particles are pulled away from the carrier by the charged image and deposit on the plate to form a powder image, while the partially denuded carrier particles pass off the plate.

2

While frictional charging of an electrophotographic plate as described in the above-mentioned Carlson patent is feasible, it has been found that improved results can be obtained by charging the plate from an ion source, such as an electric discharge wire or series of needles. In this charging method a fine wire, for example, is raised to a potential of several thousand volts in relation to the grounded backing of the electrophotographic plate to generate a corona discharge from the wire to the plate coating. As the plate is passed under the discharge wire an electrostatic charge is deposited on the surface of the coating of photoconductive insulating material. With such charging methods it has been found that the most uniform and consistent results are obtained if the corona wire is held at a positive potential with respect to the electrophotographic plate, and a positive charge is thereby deposited on the plate coating.

Upon exposure of a positively-charged electrophotographic plate to a light image a positively-charged electrostatic image is produced on the plate. In order to effect development of this image with a toner-carrier combination, it is preferable, and usually necessary, to use a combination in which the toner acquires a negative charge from the carrier.

The present invention contemplates a toner composition which is especially suited for the development of electrophotographic and other electrostatic images, and particularly of electrically positive images when used with a suitable carrier which imparts a negative charge to the toner.

In addition to the specific requirements of the electrophotographic and electrostatic developing processes, a universally useful toner must meet a large number of additional exacting requirements. Since the toner must be rendered available in finely-divided form for incorporation in a carrier, or in some instances for use alone without carrier, it is essential that it be a solid at room temperature and at such elevated temperatures as are normally encountered in storage and use. However, in order to permit the powder images to be affixed by heat to paper or other organic materials, the toner must be fusible at temperatures below those which paper and other sheet materials are damaged or discolored when heated to such temperatures for a short period of time.

In order that the image shall be permanent after affixing to the final surface, it is necessary that the toner composition, after fusing, be insoluble in water and shall not be rendered sufficiently tacky by contact with water to cause blocking or adhesion between sheets. However, it is desirable that the toner be soluble in one or more common organic solvents to enable the cleaning of electrophotographic plates which have been repeatedly used to remove any accumulated film of toner. It is also sometimes desirable, particularly with plastic materials which are easily distorted or damaged by heat, to use an organic solvent to temporarily dissolve or soften the toner to affix a powder image to such materials without the use of heat.

Another requirement is that the fixed image shall be permanent and stable under conditions ordinarily encountered, that it shall not decompose or be bleached by light nor readily attacked by microorganisms. The completed image should also be relatively hard but sufficiently tough to be resistant to chipping and cracking under conditions of handling and use. The toner must also be free of any reactive material, such as acids, which deleteriously react with the paper or other bases to cause deterioration even after years of storage of the completed copies.

It is, of course, necessary that the toner have a certain color value, either by virtue of the color of the bonding material, or by the incorporation of dyes or pigments into the bonding material. For general use in copying documentary material and drawings, a dense black is required, although it is an added advantage that the bonding material be sufficiently colorless itself so that it may be pigmented or dyed to any color desired.

The toner composition must be capable of reduction to a fine powder of a few microns in diameter by available manufacturing equipment. The fused toner must also have suitable flow properties to permit the fusing of images without any substantial tendency of the fused powder particles to "ballup" or to spread out on the sheet. The material should also be preferably of a thermoplastic nature, rather than thermosetting, in order that the composition can be fused during manufacture and still be fused again to affix the image to the final surface.

An important application of electrophotography is in the application of images to lithographic plates and lithographic paper masters, such as those used in offset duplicating machines. In this application, the powder image is transferred to a grained zinc or aluminum offset plate surface or to a paper offset plate, such as the "Duplimat" paper masters sold by Addressograph-Multigraph Corporation, Cleveland, Ohio. The transferred powder image is fused to the offset plate after which the plate is attached to the press or duplicating machine and run in the conventional offset lithographic process in which the plate is wet with water to render the non-image areas repellant to ink, and then inked with lithographic ink which adheres only to the fused powder image. Heretofore, such images have been applied by elaborate photomechanical methods involving the coating of a grained zinc plate with a bichromated albumin which is light sensitive, and exposing the coated plate to an intense arc light under a specially prepared negative for several

minutes after which the plate is developed with an ink and the unexposed albumin removed with water. The electrophotographic process makes possible the rapid application of printing images both to metal and paper offset plates without the necessity of a special negative nor involved processing.

The composition of the present invention meets the varied and exacting requirements given above and comprises an electroscopic developing powder, or toner, which is capable of producing permanent images on paper, cloth, plastic and metal surfaces, and is also capable of forming printing images which are readily wettable by lithographic inks and are capable of bonding to both metal and paper offset plates to form durable printing plates capable of printing many thousands of copies when used for offset printing and duplication.

The preferred composition of the toner of the present invention comprises a combination of synthetic and natural resins, together with a pigment. The materials are so compounded that each particle of toner comprises a coloring material or pigment embodied in the resinous base.

The preferred resinous components comprise phenol formaldehyde resin modified or reacted with a fresh natural resin, such as rosin or colophony, and brought to a neutral state. The phenol formaldehyde condensation product can be melted together with the natural resin and then neutralized with a polyhydric alcohol, or the condensation product can be produced in the presence of the natural resin, and then neutralized.

The phenolic condensate is believed to enter into chemical combination with the rosin during heating. The resulting composition, upon neutralization with a polyhydric alcohol, appears to be a chemically and physically homogeneous high molecular weight compound. Reaction is completed during manufacture of the resin to yield a reaction product which is not subject to further curing upon heating, but is a permanently fusible or thermoplastic material.

Resins of varying hardness and melting point are possible by varying the proportions of phenol formaldehyde resin and natural resin. The preferred range of proportions is between 1 and 8 parts of colophony to 1 part of phenol formaldehyde resin. The mixture is heated slowly in an autoclave until the melting point does not rise further, the final heating preferably taking place at 200 to 250° C. The product is then esterified by adding sufficient glycerol, glycol or other polyhydric alcohol to reduce the acid number below 20 and heating for several hours to complete the reaction.

One of the preferred resins of the type described has a relatively light color, a softening point between 118 and 125° C., a melting point between 142 and 149° C. and an acid number between 11 and 20. However, the proportions of the components can be varied within the limits described to yield resins of higher and lower melting points which can also be used successfully.

According to a preferred method of preparing an electroscopic developer or toner, the resin is intimately mixed with a finely-divided pigment, the mixture is fused and stirred, and allowed to cool an harden. The solid composition is then broken up and pulverized by extensive ball milling or by micropulverizing to yield a final product having substantially all particles under 30 microns in diameter, and no substantial mass of particles under 0.1 micron.

Example

In one instance 20 parts by weight of resin having a melting point in the range 142 to 149° C. was dry-milled in a pebble mill with 1 part of "Raven Bead" carbon black. A few irregularly-shaped bent sheet metal pieces were included in the mill to scrape caked resin off the walls. As the milling proceeded the color of the mixture became more uniform and intense until after about four hours no further change appeared to take place and the milling was stopped.

The milled mixture was then removed and heated in a pan until it became fluid and took on the consistency of a thin paste. During heating, the mixture was stirred constantly to minimize the heating time. After stirring the molten mixture thoroughly for five minutes, it was cooled and solidified into a solid block. The block of material was first broken into pea-size lumps and then micronized in a No. 5 Mikro-Atomizer (manufactured by Pulverizing Machinery Co., Summit, New Jersey). This machine reduces granular materials to a fine powder by attrition within a turbine-like rotor housing. The stream of powder and air from the pulverizer was collected, except for the ultrafine sizes, in a cyclone separator. The particles collected ranged in size between 0.1 and 20 microns with a preponderance of the particles being approximately 5 microns in diameter.

The resulting toner mixes readily with a carrier to produce a two-component developer. By mixing 1 part toner with 20 parts of 30–50 mesh glass beads which are coated with a resin composition which is triboelectrically positive to the toner, a developer for positive electrostatic images is obtained. By mixing with a carrier which is electrically negative to the toner, such as 30 to 60 mesh ammonium chloride crystals, a developer for negatively-charged electrostatic images may be produced.

The present toner, when used in either a positive or negative developer mixture, produces dense black powder images with substantially no powder deposition on uncharged background areas. These images may readily be transferred to paper or other sheet materials by an electrostatic transfer process, or by pressure contact with a dampened sheet and affixed to the final surface by heating the sheet in an oven or between hot surfaces for a few seconds in order to bring the powder and the sheet surface above the melting point of the toner composition, and preferably above 160° C. The fixed image is found to adhere tenaceously to paper, metal and plastic surfaces to form a dense black glossy image resembling printed images and in some cases approaching the appearance of engraved printing. The images are durable and cannot be smudged by rubbing nor chipped by bending or folding of the sheet. They have a durability and life determined only by the life of the sheet material to which they are applied and do not fade nor change with age. Moreover, the images do not contain any material which causes deterioration of a paper base.

When applied to offset lithographic paper mats the fused images are capable of accepting lithographic inks and printing thousands of images, the life of the image normally exceeding the life of the mat itself. The images also can be fused to the surfaces of grained zinc and aluminum offset plates to which they adhere tenaceously and form durable printing masters.

Instead of carbon black, other pigments such as other forms of carbon, mineral pigments such as chrome yellow and ultramarine blue, organic pigments, and organic dyes, such as Calco oil blue B5199, a hydrocarbon soluble dye produced by Calco Chemical Division of American Cyanamid Company, Bound Brook, New Jersey, may be incorporated into the resin base, singly or in combination. From 3 to 15% by weight of pigment added to the resin yields good results. Less than 3% undesirably reduces the density of the image while above 15% renders the composition less easily fused onto the final surface to form a strongly bonded image. Dyes, if used, are preferably used in smaller proportions depending upon their color value. Calco oil blue in proportions of 3% by weight of the resin is suitable.

While the present invention, as to its objects and advantages, has been described herein as carried out in specific embodiments thereof, it is not desired to be limited thereby but it is intended to cover the invention broadly within the spirit and scope of the appended claims.

What is claimed is:

1. A method of producing an electrophotographic print from an electrostatic image comprising depositing a finely divided developer material on a surface bearing an electrostatic latent image in configuration conforming with such image, transferring deposited material in said configuration to a paper web and fusing the material to said web at a temperature below the char point of paper, the developer material consisting of a finely divided thermoplastic composition fusible below the char point of paper and comprising a colored pigment visible against the background of paper and uniformly distributed throughout a binder composed of a thermoplastic substantially non-tacky rosin-modified phenol-formaldehyde resin.

2. A method of producing an electrophotographic print from an electrostatic image comprising depositing a finely divided developer material on a surface bearing an electrostatic latent image in configuration conforming with such image, transferring deposited material in said configuration to a paper web and fusing the material to said web at a temperature below the char point of paper, the developer material consisting of a finely divided thermoplastic composition having a particle size between 0.1 and 30 microns in diameter and fusible below the char point of paper and comprising a colored pigment visible against the background of paper and uniformly distributed throughout a binder composed of a thermoplastic substantially non-tacky rosin-modified phenol-formaldehyde resin.

3. A method of producing an electrophotographic print from an electrostatic image comprising depositing a finely divided developer material on a surface bearing an electrostatic latent image in configuration conforming with such image, transferring deposited material in said configuration to a paper web and fusing the material to said web at a temperature below the char point of paper, the developer material consisting of a finely divided thermoplastic composition having a particle size between 0.1 and 30 microns in diameter and fusible between 142 and 149° C. and comprising a colored pigment visible against the background of paper and uniformly distributed throughout a binder composed of a

thermoplastic substantially non-tacky rosin-modified phenol-formaldehyde resin.

HAROLD E. COPLEY.

References Cited in the file of this patent

UNITED STATES PATENTS

Number	Name	Date
1,133,083	Baekeland	Mar. 23, 1915
1,902,461	Novotny	Mar. 21, 1933
2,297,691	Carlson	Oct. 6, 1942
2,362,627	Glycofrides	Nov. 14, 1944
2,378,366	Swain et al.	June 12, 1945

FOREIGN PATENTS

Number	Country	Date
259,030	Great Britain	Oct. 7, 1926
558,654	Great Britain	Jan. 14, 1944