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[54] **METAL COATED METAL CARRIER PARTICLES**
FOR ELECTROSTATIC DEVELOPERS
4 Claims, No Drawings
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117/17.5, 117/227, 117/100
[51] Int. Cl..... **G03g 9/02**
[50] Field of Search..... **252/62.1**

ABSTRACT: In an electrostatic printing process employing a developer mixture comprised of electrically conductive carrier particles and electrostatically attractable toner particles, the effect of humidity of the air on the electrical conductivity of the carrier particles is substantially reduced by coating the carrier particles with a thin surface coating of a metal of the platinum group of the metals of Group VIII of the Periodic Table of Elements.

METAL COATED METAL CARRIER PARTICLES FOR ELECTROSTATIC DEVELOPERS

BACKGROUND OF INVENTION

1. Field of Invention

The present invention relates to electrostatic printing and more particularly to an electrostatic printing process employing an improved developer mixture.

2. The Prior Art

In an application for an electrostatic printing system, Ser. No. 386,182, filed July 30, 1964 and now abandoned, for John B. Kennedy Jr., which is assigned to a common assignee, there is described a method for electrostatic screen printing wherein a developer mixture of large conductive carrier particles having relatively small toner particles adhering thereto by triboelectric forces is brought into contact with an electrically charged base electrode whereby the conductive carrier particles are charged therefrom so that a repulsion effect is established with sufficient strength to cause the developer mixture to be repelled from the base electrode. A screen or stencil which has apertures arranged in a pattern is presented in the path of the developer mixture, the size of the aperture being selected so that the carrier particles are larger than the apertures while the toner is smaller than the apertures. The apertures in the screen mechanically stop the impelled carrier particles while the momentum of the toner causes these particles to detach from the carrier particles and pass through the screen and continue onward to impinge upon the surface of the article to be printed located above the screen and spaced therefrom, the areas of impingement of the toner particles on the substrate corresponding to the pattern on the screen. The image body thus formed is then fixed by the application of heat or vapor or the like fusion means which will cause the toner particles to be retained on the surface of the article.

When the article surface is of a conductive material, it is charged oppositely to the toner particles for controlling the paths thereof from the screen to the substrate. When the article surface is of a nonconductive nature, a backing or back electrode bearing a predetermined potential is placed at the rear of the article and on a side opposite to the side of the article facing the screen and base electrode.

The above described electrostatic printing process has the advantage that neither pressure nor contact between the printing element and the subject material being printed is required.

During printing operations, in accordance with this procedure, the particles of the developer mixture oscillate back and forth between the electrodes. The rate of oscillation of the developer particles will vary depending upon the electrical conductivity of the carrier particles. It has been observed that developer particles comprised of carrier particles of relatively high electrical conductivity oscillate vigorously and those of low electrical conductivity oscillate sluggishly. The rate at which toner is delivered to the substrate to form a print of satisfactory quality varies with the vigor of the oscillation of the developer particles. Thus, if the developer particles oscillate vigorously, solid areas can be printed to a predetermined optical density in substantially less time than with sluggishly oscillating particles. For example, using vigorously oscillating developer particles, solid areas can be printed using black toner to an optical density of 1.4 in 50 to 100 milliseconds. Sluggishly oscillating developer particles deliver toner at a much slower rate, about 300 milliseconds or more being required to print to the same density.

One cause for the variance in electrical conductivity of the carrier particles appears to be changes which occur in the ambient relative humidity in the printing area. An increase in the ambient relative humidity, for example, causes a decrease in the electrical conductivity of the carrier particles. Thus, one drawback to printing with the above described electrostatic

technique is that the quality and speed of printing will often vary with the ambient relative humidity.

SUMMARY OF THE INVENTION

In accordance with the practice of the present invention, the variance in the performance of the developer particles due to changes in the ambient relative humidity in the printing area is substantially reduced by employing in the electrostatic printing process carrier particles which have been coated with a thin surface coating of a conductive metal which is inert to water vapor, and is selected from the platinum group of metals of Group VIII of the Periodic Table of Elements.

The developer mixture of the present invention provides sharp, detailed and dense reproductions. At a given relative humidity, coated carrier particles prepared in accordance with the present invention are relatively unaffected by the humidity of the air. The coated particles have higher conductivities than otherwise equivalent uncoated particles and oscillate more vigorously between the electrodes and the screen of the electrostatic printing apparatus. As a result, developer particles are delivered to the screen at a higher rate, and printing at any given density is generally accomplished in less time than with uncoated carrier particles.

PREFERRED EMBODIMENTS

The developer mixture of the present invention is comprised of large conductive carrier particles coated with a metal of the platinum group of metals of Group VIII of the Periodic Table of Elements, having a plurality of smaller toner particles adhered thereto by the triboelectric effect.

The carrier particles used in the present invention are composed of an electrically conductive material separated in the triboelectric series from the material of the toner. The carrier and toner are held together by the electrostatic forces produced upon contact between them by the triboelectric effect. Conductive materials suitable for use as carrier particles in the developer mixtures of the present invention include iron, nickel, aluminum, cobalt, copper, and their alloys.

The thickness of the Group VIII metal coating on the surface of the carrier particle can be in the order of several monoatomic layers or more.

The conductive carrier may be provided with a surface coating of a metal of the platinum group by any of the various means known to the art, such as evaporation in vacuum, cathode sputtering, chemical deposition, such as chemical displacement, electroless plating, and the like. Metals of the platinum group which may be used for coating the carrier particles include platinum, palladium, ruthenium, rhodium and iridium.

To obtain surface coated carrier particles using chemical deposition techniques, such as chemical displacement, the carrier particles, such as nickel particles, are immersed in a heated dilute acid solution containing about 0.05% to about 5% of a Group VIII metal salt based on the weight of the carrier particles. A color change in the coating solution is indicative of the completion of the displacement reaction. After the coating reaction is completed, the coated carrier particles are then separated from the coating solution and washed to remove extraneous impurities and other contaminants which may adhere to the carrier particles. The washed carrier particles and dried and, in this form, are mixed with toner particles and used for electrostatic printing.

Carrier particle sizes of 25 to 250 microns are satisfactory for producing good, clear, dense prints. It will be apparent to those skilled in the art that the lower limit of particle size is determined by the apertures contained in the screens utilized in the electrostatic printing apparatus.

The carrier particles should be present in the developer mixture in an amount sufficient to respond to the electric field and to carry sufficient amount of toner through such field to the screen. It has been found that the amount of toner mixed with the carrier particles can vary from about 0.5% to 6% by

weight of the carrier particles. Generally speaking, toner concentrations in the order of about 2% by weight prove to be satisfactory.

The words "toner" and "toner particles" are employed herein to designate particles smaller than the apertures of the screen, capable of adhesion to the carrier particles by a force less than that developed upon impact of the carrier particles against the screen, and capable of forming a pattern effect upon the substrate. In usual practice, the toner particles are of a different color than the substrate which is being printed. The toner may be negatively or positively charged. Toner particles may be charged triboelectrically by mixing them with carrier particles. The polarity of charge the toner particles acquire is dependent upon both the properties of both the toner and carrier material. Preferably, toners are used which, when mixed with iron or nickel carrier particles, exhibit a negative charge. Negatively charged toner particles are preferably of nonconductive materials. Commercially available types are manufactured by the Xerox Corporation, and sold under the trade name XEROX COPIER TONER. These nonconductive toner particles, such as XEROX 914 COPIER TONER, are comprised of pigmented resin particles having a particle size of from about 1 to about 30 microns, and preferably have an average particle size of about 17 microns and consist of a finely divided uniform mixture of pigment in a nontacky polystyrene resin. The polystyrene resin is present in the toner composition in a predetermining amount, i.e., at least about 50% of the entire composition, optionally blended or mixed with a polybutyl methacrylate, such as polymerized n-butyl methacrylate. The pigment is present in the toner in a sufficient quantity to cause it to be highly colored whereby it will form a clearly visible image on the substrate on which it is electrostatically deposited. Thus, for example, in the case where lettering and the like is desired on corrugated paperboard, the pigment will be a black pigment such as carbon black or other minutely divided carbonaceous pigment. Toner capable of assuming a charge which is positive with respect to a reference is commercially available from Interchemical Printing Inks and is designated XRL 8969.

To illustrate the manner in which the invention may be carried out, the following example is given. It is to be understood, however, that the example is for the purpose of illustration, and the invention is not to be regarded as limited to any of the specific materials or conditions recited therein.

EXAMPLE

One hundred and twenty milliliters of concentrated H_3PO_4 was diluted with 300 milliliters of deionized water containing 10 drops of 1% sodium lauryl sulfate solution and the diluted acid solution was mixed with 1 liter of a dilute HCl solution containing 5 grams $PdCl_2$ /liter. The mixed solution was heated to 85° to 90° C. and 5000 grams of nickel powder was added to the heated solution. The properties of the nickel powder were as follows:

CHEMICAL COMPOSITION	
Co	0.41%
Cu	0.0037%
Fe	0.010%
S	0.0165%
C	0.008%
Ni	balance

SCREEN ANALYSIS	
Mesh Size	%
+150	1.0
-150 to +200	94.2
-200	4.8
Apparent density:	4.33 gm./cc.

The solution containing the nickel powder was heated with stirring for about 20 minutes. At this time, the color of the solution changed from brown to green and a dense white precipitate appeared indicating the palladium coating of the nickel powder was completed.

The coated nickel powder was washed with deionized water followed by washing with a solution of 150 milliliters of a 5% solution of EDTA (ethylene diamine tetra acetic acid disodium salt) dissolved in 500 milliliters of concentrated NH_4OH diluted to 1 liter with deionized water. This washing was followed by a further washing of the palladium coated nickel powder with a 50% NH_4OH solution using a vacuum filter. Washing was continued until the blue coloring in the washings caused by the ammonia-nickel complex disappeared. The washed palladium coated nickel powder was then dried at 300° F. for 1 hour.

An indication of the conductivity of the palladium coated nickel particles was then determined using the following procedure.

A conductivity measuring cell was constructed from a glass cylinder 3.25 inches high and 1.0 inches in diameter. Copper foil electrodes 0.75 inch wide were suspended from a rubber stopper inserted in the top of the cylinder with external leads connected to a resistance meter. The cell was filled with the palladium coated nickel powder and the resistance measured. The resistances of the palladium coated nickel powder exposed to a variety of atmospheric conditions, as well as control particles, i.e., nickel particles which were not coated with palladium, designated by the symbol "C", are summarized in the table below.

TABLE

Test No.	Atmospheric Condition	Resistance (Ohms)
1	Palladium coated nickel particles placed 5 days in desiccator	less than 50
2	Palladium coated nickel particles exposed 1 year to room atmosphere	less than 50
C ₁	Uncoated nickel particles placed 5 days in desiccator	more than 1 million
C ₂	Uncoated nickel particles exposed 11 week to room atmosphere	more than 1 million

The palladium coated nickel particles were mixed with XEROX 914 COPIER TONER and used as a developer mixture for the electrostatic printing of line copy through a patterned screen. The diffuse reflection optical density of the printing was typically in the range of from 1.4 to 1.8 as determined using a Macbeth RD100 Reflection Densitometer. To obtain an optical density of 1.4 required 100 milliseconds using the palladium coated nickel carrier particles at a relative humidity of 12%.

By way of contrast, when untreated nickel particles were used as carrier particles in an identical electrostatic printing process, about 200 to 300 milliseconds were required to achieve an equivalent optical density.

What we claim is:

1. A developer mixture for developing electrostatic images, said mixture being comprised of a mixture of carrier particles, the outer surface of which is coated with a metal of the platinum group of metals of Group VIII of the Periodic Table of Elements selected from the group consisting of platinum, palladium, ruthenium, rhodium and iridium, and electrostatically-attractable nonconductive toner particles, the carrier particles being composed of an electrically conductive material separated in the triboelectric series from the material of the toner, said toner particles being electrostatically charged through triboelectric action by contact with the carrier particles to adhere electrostatically to the coated surface of said carrier particles, the carrier particles being larger than the toner particles.

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2. The developer mixture of claim 1 wherein the carrier particle has a particle size of about 25 to 250 microns, and the toner particles have a particle size of about 1 to 30 microns.

3. The developer mixture of claim 1 wherein the metal coat-

ing is palladium.

4. The developer mixture of claim 1 wherein the carrier particle is nickel.

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