ELECTRICALLY INSULATING CARRIER PARTICLES

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Field of Search ............ 252/62.1, 117/93.1 R, 93.1 GD, 117/93.1 CD, 100 C, 100 M, 17.5, DIG. 6, DIG. 8, 204/168

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ABSTRACT

Carrier particles useful in developing electrostatic charge patterns are provided with a thin layer in insulating material by glow discharge treatment.

6 Claims, No Drawings
This invention relates to electrophotography, and more particularly, to magnetically attractive carrier particles useful in the magnetic brush type development of electrostatic images. Electrophotographic processes and techniques have been extensively described in both the patent and other literature, for example, U.S. Pat. Nos. 2,221,776; 2,277,013; 2,297,691; 2,357,809; 2,551,582; 2,825,814; 2,833,658; 3,220,324; 3,220,831; 3,220,833 and many others. Generally, these processes have in common the steps of employing a normally insulating imaging element which is prepared to respond to imagewise exposure with electromagnetic radiation by forming an electrostatic charge image. The electrostatic latent image is then rendered visible by a development step in which the charged surface of the photodecative element is brought into contact with a suitable developer mix.

One method for applying the developer mix is by the well-known magnetic brush process. Such a process generally utilizes apparatus of the type described, for example, in U.S. Pat. No. 3,003,462 and customarily comprises a nonmagnetic rotatably mounted cylinder having fixed magnetic means mounted inside. The cylinder is arranged to rotate so that part of the surface is immersed in or otherwise contacted with a supply of developer mix. The granular mass comprising the developer mix is magnetically attracted to the surface of the cylinder. As the developer mix comes within the influence of the field generated by the magnetic means within the cylinder, the particles thereof arrange themselves in bristle-like formations resembling a brush. The bristle formations of developer mix tend to conform to the lines of magnetic flux, standing erect in the vicinity of the poles and lying substantially flat when said mix is outside the environment of the magnetic poles. Within one revolution the continually rotating tube picks up developer mix from a supply source and returns part or all of this material to the supply. This mode of operation assures that fresh mix is always available to the surface of the photodecative element at its point of contact with the brush. In a typical rotational cycle, the roller performs the successive steps of developer mix pickup, brush formation, brush contact with the photodecative element, brush collapse and finally mix release.

In magnetic brush development of electrostatic images the developer is commonly a triboelectric mixture of fine toner powder comprised of dyed or pigmented thermoplastic resin with coarser carrier particles of a soft magnetic material such as "ground chemical iron" (iron filings), reduced iron oxide particles, or the like.

The magnetic brush conductivity of iron and similar ferromagnetic carrier particles can be useful in magnetic brush development in that a conducting magnetic brush serves effectively as a development electrode, and as a consequence, the fringing field created by an electrostatic latent image is modified and solid area development is achieved. However, solid area development by such a means has the disadvantage of very narrow exposure latitude and hence conducting carriers are to be avoided if one desires to take advantage of fringing field effects to increase exposure latitude. Accordingly, there is a need for a magnetic brush developing composition which is capable of producing good images within a broad range of exposure latitude.

Resinous coatings on iron or other magnetic brush carrier granules can increase the surface resistance and the tendency toward fringing development. However, application of a coating of insulating resin of sufficient minimum thickness to effect the required reduction in surface conductivity is a difficult operation. The resin, whether applied from a melt, a hydroxol, or a dope, tends to solidify to a compound mass with the carrier particles, so that it is difficult to recover the coated iron in the desired form of discrete uniformly coated bits. Grinding or other forms of commination of such a compacted or agglomerated mass of particles will usually result in exposing a sufficient amount of the conducting surface of the underlying particles to largely negate the intended improvement in resistance. Thus, prior coating procedures involve multi-step processes which make it difficult to control the thickness of the material deposited on the underlying core and which generally do not result in a continuous film being formed on each individual particle. A further problem with prior coating techniques is that the outer layer of coated material is generally subject to wear during usage which results in a variation in the physical properties with time.

Accordingly, there is a need for improved carrier materials having a continuous film of controlled thickness of insulating material which is abrasion resistant. There is likewise a need for a simple process for forming a continuous film of insulating material on carrier particles which film is not subject to wear and which process can readily be controlled.

It is, therefore, an object of this invention to provide a novel method of preparing carrier particles having a continuous uniform electrically insulating polymeric coating thereon. It is another object of this invention to provide novel carrier materials having a high electric resistance.

An additional object of this invention is to provide novel carrier particles which have an outer polymeric coating which is resistant to wear.

It is a further object of this invention to provide magnetically responsive carrier particles having a thin, continuous layer of polymer coated thereon and which particles are useful in the development of electrostatic charge patterns.

Still another object of the invention is to provide new developer compositions suitable for use in fringing development of electrostatic latent images.

These and other objects and advantages are accomplished in accordance with this invention by the preparation and use of improved carrier particles having a relatively high electrical resistance. These particles are each comprised of a core material of appropriate size and shape over which is coated a thin, continuous layer of electrically insulating resinous material.

The core materials which can suitably be overcoated in accordance with this invention include a variety of materials such as magnetic and nonmagnetic materials. Typical nonmagnetic materials include, for example, glass beads or crystals or organic salts such as sodium or potassium chloride. The present invention is particularly well suited for use with cores of magnetic materials. The phrase "magnetic materials" as used herein encompasses a variety of magnetically attractable materials. Particularly useful materials would include ferrimagnetic materials such as metals of the first transition series, i.e., nickel, iron, cobalt, and alloys containing any or all of these metals. Other useful materials which will not be a net magnetic moment are the ferrimagnetic materials. Examples of such ferrimagnetic materials would include the ferrites, which are materials having the general formula MeFe₂O₄, where Me is a metal ion, as well as the mixed ferrites, which contain more than one species of metal ion in addition to iron, and the substituted ferrites, in which another metal replaces some of the iron. Also included in the phrase "magnetic material" are particles such as those described in copending Miller U.S. application Ser. No. 562,497, filed July 5, 1966, now abandoned, entitled ELECTROPHOTOGRAPHIC DEVELOPING COMPOSITIONS, and which are comprised of, for example, iron dispersed in a resin binder. Such magnetic materials are used as a core in accordance with this invention over which is coated a film-forming resinous material.

The core can consist of a solid particle of magnetic material or can be a nonmagnetic particle overcoated with ferrimagnetic materials as described in copending Miller U.S. application Ser. No. 659,030, filed Jan. 19, 1968, now abandoned, entitled METAL SHELL FILMS.

The core material used, whether magnetic or nonmagnetic, can vary in size and shape, with core materials having an average diameter of from about 1,200 to about 30 microns being useful. Particularly useful results are obtained with core materials of from about 600 to about 40 microns average diameter. The size of the core particles used, will, of course,
depend upon several factors such as the type of image ultimately developed, desired thickness of the polymeric coating, etc. The phrase "average diameter" as used herein is not meant to imply that only perfectly uniformly dimensioned particles can be used. This phrase is used to refer to the average thickness of particles when measured along several axes. Average diameter also refers to the approximate size of the openings in a standard sieve series which will just retain or just pass a given particle.

In accordance with this invention, the core particles are coated with a continuous film of resinous material. A thin layer of material is applied to the core particles by a procedure which we generally refer to as "glow discharge polymerization." In glow discharge polymerization, an organic vapor at about 0.5 to 5.0 mm. of mercury pressure is introduced into a chamber containing two parallel closely spaced electrodes. When a.c. or d.c. fields of the order of several hundred v/cm. are imposed on the parallel electrodes, a uniform discharge forms between the plates and polymeric films are deposited on articles coated between the electrodes. In general, this procedure involves introducing a concentration of a vaporizable or gaseous monomer or polymer precursor into a reaction chamber containing suitable core particles and subjecting the materials to activating electromagnetic radiation to cause the monomer or polymer precursor to undergo polymerization on the surface of the core particles. During this procedure, the particles are kept in motion by any suitable means. The apparatus involved in forming these thin polymer layers is quite simple, and is mainly comprised of a chamber which may be evacuated to a pressure of the order of about 0.1 to about 0.001 mm. of mercury. After evacuating the chamber, an unreactive gas such as helium is bled into the apparatus to increase the pressure to about 0.3 to 5.0 mm. of mercury. Within this chamber is located a means for containing and vibrating or otherwise thoroughly agitating the core particles to be coated. One suitable means for this purpose is an aluminum plate which is maintained at ground potential and which is held in an insulating holder that is capable of being vibrated so as to maintain the particles in a relatively fluidized state. Located above the plate holding the particles is a large high potential electrode typically prepared of stainless steel. This electrode is maintained in close proximity to the particles, usually at a distance of about ½ to about 2 cm. depending on the potential applied, etc. This electrode is connected to a power source capable of maintaining at least a 10 kilocycle a.c. field sufficient to produce an even glow. Of course, glow discharge is typical of many suitable arrangements which can be used to activate the vaporized monomer. Other useful means of activation would include direct current, electroded current radio frequency, microwave glow discharge, as well as ultraviolet radiation and electron bombardment.

Prior to forming a polymer coating on the core particles, it is often desirable to clean the particles. This can be done by introducing helium or other nonreactive gas into the system and subjecting the particles to glow discharge treatment. The helium is bled off and then the vaporized monomer or polymer precursor is introduced into the chamber at a pressure of about 0.5 to 5.0 mm. of mercury and once again subjected to a glow discharge. The vaporizable monomer or polymer precursors which are useful can be selected from a wide variety of materials. Suitable materials would include such monomers as trifluoromonochloroethylene, tetrafluoroethylene, octafluorobutene-2, vinyl fluoride, vinylidene fluoride, hexafluorocacetone, acrylonitrile, styrene, ethylene, vinyl chloride, vinyl ferrocene, methyl methacrylate, divinylbenzene, carbon tetrachloride, hexafluoroethane, etc., as well as materials which are not generally considered as polymer precursors such as benzene, naphthalene and anthracene. In general, any vaporizable vinyl monomer is suitable for use herein. In addition, mixtures of these or any other vaporizable polymer precursors which undergo polymerization in the presence of activating radiation can be used.

In accordance with the present techniques, extremely thin, continuous layers of electrically insulating materials can be applied to various core materials. In general, the amount of resin applied is usually in the range of from about 0.003 to about 4 percent by weight of the core material being coated with preferred materials having a resin coating of from about 0.03 to about 0.2 percent by weight of the core. The average thickness of the continuous film of polymer applied in accordance with this technique is in the range of from about 0.005 to about 4.0 microns, with a thickness of about 0.05 to about 0.2 microns being preferred.

Typically, the electrical resistance of the coated carrier particles of this invention is greater than about 10$^{10}$ ohms with preferred carriers having a resistance of greater than about 10$^{11}$ ohms. Generally, it can be stated that the higher the resistance of the carrier particle, the better the quality of the friction development obtained. Of course, above extremely high levels of resistance the increase in quality of friction development per unit increase of resistance becomes so small as to be negligible. For purposes of comparison, the resistance of various magnetically attractive carrier particles is measured in a standard magnetic brush resistance test. This test is conducted each time using a 1.5 gram quantity of the carrier particles. A cylindrical shaped bar magnet having a magnetic moment of 6.25 cm$^2$ is in area is used to attract the carrier and hold it in the form of a brush. After formation of the brush, the bar magnet is then positioned with the brush-carrying end approximately parallel to and about 0.5 cm. from a burnished copper plate.

The resistance of the particles in the magnetic brush is then measured between the magnet and the copper plate.

The resin layers formed on the carrier particles of the present invention are extremely durable and abrasion resistant. The improved abrasion resistance of the present polymer coatings appears to be a result of the considerable crosslinking which occurs during the discharge polymerization reaction used to coat the core materials.

Electroscopic developer compositions can be prepared by mixing from about 90 to about 99 percent by weight of the present carrier particles with from about 10 to about 1 percent by weight of a suitable electroscoptic toner material. The toner granules useful with the carrier are generally comprised of a resin binder and a colorant. Suitable toners can be selected from a wide variety of materials to give desired physical properties to the developed image and the proper triboelectric relationship to match the carrier particles used. Generally, any of the toner powders known in the art are suitable for mixing with the carrier particles of this invention to form a developer composition. When the powder selected is utilized with ferromagnetic carrier particles in a magnetic brush development arrangement, the toner granules charge the carrier by triboelectric attraction. The carrier particles acquire a charge of one polarity and the toner acquires a charge of the opposite polarity. Thus, if the carrier is mixed with a resin toner which is higher in the triboelectric series, the toner normally acquires a positive charge and the carrier a negative charge.

Useful toner granules can be prepared by various methods. Two convenient techniques for preparing these toners are spray-drying or melt-blowing followed by grinding. Spray-drying involves dissolving the resin, colorant and any additives in a volatile organic solvent such as dichloromethane. This solution is then sprayed through an atomizing nozzle using a substantially nonreactive gas such as nitrogen as the atomizing agent. During atomization, the volatile solvent evaporates from the airborne droplets, producing toner particles of the uniformly colored resin. The ultimate particle size is determined by varying the size of the atomizing nozzle and the pressure of the gaseous atomizing agent. Conventionally, particles of a diameter between about ¼ μ and about 25 μ are used, with particles between about 1 μ and about 10 μ being preferred, although larger or smaller particles can be used where desired for particular development or image considerations.

Suitable toners can also be prepared by melt-blowing. This technique involves melting a powdered form of polymer or
resin and mixing it with suitable colorants and additives. The resin can readily be melted or heated on compounding rolls which are also useful to mix or otherwise blend the resin and addenda so as to promote the complete intermixing of these various ingredients. After thorough blending, the mixture is cooled and solidified. The resultant solid mass is then broken into small pieces and finely ground to form a free-flowing powder of toner granules. The resultant toner granules usually range in size from about ¾ to about 25μ.

The resin material used in preparing the toner can be selected from a wide variety of materials, including natural resins, modified natural resins and synthetic resins. Exemplary of useful natural resins are balsam resins, colophony, and shellac. Exemplary of suitable modified natural resins are colophony-modified phenol resins and other resins listed below with a large proportion of colophony. Suitable synthetic resins are all synthetic resins known to be useful for toner purposes, for example, polymers, such as vinyl polymers and copolymers including polyvinyl chloride, polyvinylidene chloride, polyvinyl acetate, polyvinyl acetics, polyvinyl ethers, polycrylic and polymethacrylic esters, polystyrene, including substituted polystyrenes; polycondensates, e.g., polystyres, such as phthalate, terephthathic and isophthalic polystyres, maleinate resins and colophony-mixed esters of higher alcohols; phenol-formaldehyde resins, including modified phenol-formaldehyde condensates; aldehyde resins; ketone resins; polyaclaimes; polyurethanes, etc. Moreover, chlormated rubber and polyolefins, such as various polyethylene, polypropylene, polystyrobulylene, are also suitable. Additional toner materials which are useful are disclosed in the following U.S. Pat. Nos.: 2,917,460, Re 25,156; 2,788,288; 2,638,416; 2,618,552 and 2,659,670.

The coloring material additives useful in suitable toners are preferably dyestuffs and colored pigments. These materials serve to color the toner and thus render it more visible. In addition, they sometimes affect, in a known manner the polarity of the toner. In principle, virtually all of the compounds mentioned in the Color Index, Vol. I and II, Second Edition, 1956, can be used as colorants. Included among the vast number of suitable colorants would be such materials as Nigrosin Spirit soluble (C.I. 50415), Hansa Yellow G (C.I. 11680), Chromogen Black ETOO (C.I. 14465), Rhodamine B (C.I. 45170), Solvent Black 3 (C.I. 26150), Fuchsin N (C.I. 42510), C.I. Basic Blue 9 (C.I. 52015), etc.

The following examples are included for a further understanding of the invention and all indications of mesh sizes have reference to the U.S. Standard Sieve Series.

EXAMPLE 1

Nickel-plated spherical iron particles are prepared in accordance with the electrolysis plating technique of Example 2 of copending Miller application Ser. No. 799,967, filed Feb. 17, 1969, now abandoned, entitled HIGHLY CONDUCTIVE CARRIER PARTICLES. These core particles have a size such that they will pass through an 80 mesh screen and be retained by a 120 mesh screen and they have a resistance of 5 ohms as measured in the standard resistance test. Four grams of the nickel-clad iron particles are placed in an aluminum plate at ground potential and spread around such that they are contained in an area approximately 4.3 cm. × 4.3 cm. The aluminum plate is mounted in an insulating plastic holder capable of being vibrated so as to maintain the particles in a fluidized state. A high potential electrode comprised of a 7% × 7% cm. stainless steel plate is mounted approximately 1 cm. above the aluminum plate. The apparatus is placed within a vacuum chamber which is evacuated to a pressure of about 0.8 mm. of mercury. Helium is then bled into the apparatus to increase the pressure to about 2.0 mm. of mercury. Next, the core particles are cleaned by applying a 10 k.c. a.c. field sufficient to produce a glow at a current of 90 milliamperes across the electrodes for 5 minutes. The electrical equipment used to produce this field is comprised of an audio oscillator, a 200 watt audio amplifier and a step-up transformer. A 1,000 ohm current limiting resistor is placed in the lead to the high voltage electrode and the voltage drop across this resistor is recorded and used to calculate the current. The a.c. field is terminated and the chamber is evacuated again to about 0.8 mm. of mercury and gaseous tetrafluoroethylene is introduced into the chamber to increase the pressure to about 10 mm. of mercury. An electric field is again applied using a current of about 45 ma. for a period of 15 minutes. During the cleaning and coating operations, the particles are continually agitated. The resulting particles are free-flowing and have a thin, continuous layer of polymerized tetrafluoroethylene thereon. No agglomeration of particles occurs. As measured in the standard resistance test, the particles have a resistance of greater than 10 ohms. The carrier particles as produced above are mixed with 4 percent by weight of an electroscoptic toner material comprised of a polystyrene resin containing carbon black. The resultant developer mixture is applied to a handheld magnet to form a magnetic brush. This magnetic brush is then used to develop an electrostatic latent image carried on an electrophotographic element comprising a photoconductive layer having coated thereon an electroconductive layer containing an organic photoconductor and a polycarbonate binder. The developed image is transferred electrostatically to a white bond paper receiving sheet and fixed with heat. The developer gives good fringing development and good image quality. The process is repeated while varying the exposure over a range of greater than 20:1 using a constant exposure intensity. Satisfactory images are obtained over this entire exposure range.

EXAMPLE 2

Four grams of the nickel-clad iron particles of Example 1 are placed in the apparatus described in Example 1 and cleaned by exposure to glow discharge for 2 minutes using a current of 95 ma. in a helium atmosphere at a pressure of about 1.5 mm. of mercury. The pressure is reduced to about 0.8 mm. of mercury and acrylonitrile vapor is bled into the apparatus until the pressure rises to about 1.5 mm. of mercury. The particles are vibrated continuously while subjected to glow discharge for 30 seconds with a current of from 50 to 60 ma. The resultant free-flowing particles have a resistance as measured in the standard resistance test of about 10 ohms. The resultant carrier particles are mixed with 4 percent by weight of the toner material of Example 1 and used to develop an electrostatic image. A fringe developed image results which is of good quality.

EXAMPLE 3

Four grams of nickel-plated spherical iron particles similar to those described in Example 1 and having a particle size such that the will pass through a 150 mesh screen and be retained by a 200 mesh screen are exposed to a glow in the apparatus described in Example 1. The glow discharge treatment is conducted in a helium atmosphere at a pressure of 1.5 mm. of mercury for 5 minutes at a current of 95 ma. The particles are removed from the glow discharge apparatus and measured in the standard resistance test and found to have a resistance of 150 ohms as compared to 5 ohms prior to the glow discharge treatment. This increase in resistance of about 145 ohms indicates that apparently some surface oxidation occurs in the glow discharge treatment. The resultant material is used to form a developer mixture comprising 4 percent by weight of the toner of Example 1. The resultant developer mixture is used to develop an electrostatic image and is found to produce solid area development. Thus, it appears that the fringing development obtained in Examples 1 and 2 cannot be explained simply on the basis of oxidation of the core materials. The examples demonstrate that the procedures of the present invention are well suited for forming glow discharge coatings on carrier particles. However, the application of glow discharge coatings in accordance with this invention is not
limited to iron particles in that the conductivity of the particles to be coated plays no part in the procedures of this invention. Consequently, the coating or encapsulation procedures of this invention can be used on any metallic or nonmetallic core particle. In addition, as mentioned previously, suitable coatings may be applied by any system capable of activating a vaporized monomer, and the term glow discharge treatment is meant to include, for example, direct current, alternating current, electrodeless radio frequency and microwave glow discharge, as well as ultraviolet treatment and electron bombardment. Similarly, the materials for coating the core particles may include conventional monomers as well as vaporizable organic and inorganic molecules known to undergo glow discharge polymerization.

As described in the above examples, the core particles are maintained in an agitated state during the cleaning and coating procedures. It is desirable that the particles are maintained in this agitated state so as to insure that each particle receives a continuous coat without causing agglomeration of a plurality of particles. Although the separation of particles in the above examples is accomplished by a vibratory motion, it is evident that other methods of keeping the particles apart are equally useful such as fluidization with a gas, mechanical stirring or cascading the particles through the polymerizable vapors, etc.

The invention has been described in detail with particular reference to certain preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.

We claim:

1. A developer composition for use in developing electrostatic charge patterns comprising a mixture of electroscopic toner material and a particulate, free-flowing carrier vehicle, said carrier vehicle comprising individual particles each having a core having coated thereon a thin, continuous layer of a glow discharge polymerized material.

2. A developer composition for use in developing electrostatic charge patterns comprising a mixture of electroscopic toner material and a particulate, free-flowing carrier vehicle for said toner material, said carrier vehicle comprising individual particles each having a core of a magnetically responsive material overcoated with a thin, continuous, film of an electrically insulating glow discharge polymerized material.

3. A developer composition in accordance with claim 1 wherein said core contains a material selected from the group consisting of iron, nickel, cobalt, and alloys thereof and wherein said carrier vehicle has an electrical resistance of greater than about 10^5 ohms.

4. A developer composition for use in developing electrostatic charge patterns comprising a mixture of electroscopic toner material and a particulate, free-flowing carrier vehicle for said toner, said carrier vehicle comprising individual particles each having a core of a magnetically responsive material overcoated with a thin, continuous, film of an electrically insulating glow discharge polymerized material, said core containing a material selected from the group consisting of iron, nickel, cobalt, and alloys thereof, said glow discharge polymerized material being formed from a gaseous polymerizable material selected from the group consisting of trifluoromonochloroethylene, hexafluoropropylene, tetrafluoroethylene, octafluorobutene-2, vinyl fluoride, vinylidene fluoride, hexafluoroacetone, acrylonitrile, styrene, ethylene, vinyl chloride, vinyl ferrocene, carbon tetrachloride, hexafluorothane, methyl methacrylate, divinylbenzene, benzene, naphthalene, anthracene and mixtures thereof.

5. A developer composition as described in claim 3 wherein said film on said core is formed of a glow discharge polymerized monomer selected from the group consisting of tetrafluoroethylene, acrylonitrile, and vinylidene fluoride.

6. A developer composition as described in claim 3 wherein said toner material comprises from about 1 to about 10 percent by weight of said composition.
UNIVERSAL STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,669,885 Dated June 13, 1972

Inventor(s) John F. Wright and Bruce J. Rubin

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

In the Abstract, line 2, "in" should read "of".

Column 8, line 29, "3" should read "4".

Column 8, line 33, "3" should read "4".

Signed and sealed this 26th day of December 1972.

(SEAL)

Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents