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3,632,512

**METHOD OF PREPARING MAGNETICALLY
RESPONSIVE CARRIER PARTICLES**Howard A. Miller, Rochester, N.Y., assignor to Eastman
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2 Claims

ABSTRACT OF THE DISCLOSURE

Ferromagnetic carrier particles having uniform surface and triboelectric properties can be prepared by treatment of commercial iron powders in an aqueous acid solution, followed by removal of acid, rinsing and controlled drying to induce or exclude oxidation. The resultant particles can subsequently be overcoated with a thin, uniform, continuous film of a nonferrous material such as a metal or a resinous material. These carrier particles are useful for applying electrosopic toner material to electrostatic latent images.

This invention relates to electrophotography, and more particularly, to magnetically attractable carrier particles useful in the magnetic-brush type development of electrostatic latent images.

Electrophotographic imaging processes and techniques have been extensively described in both the patent and other literature, for example, U.S. Pats. Nos. 2,221,776; 2,277,013; 2,297,691; 2,357,809; 2,551,582; 2,825,814; 2,833,648; 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 photoconductive element which is prepared to respond to imagewise exposure with electromagnetic radiation by forming a latent electrostatic charge image. The electrostatic latent image is then rendered visible by a development step in which the charged surface of the photoconductive 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 can utilize apparatus of the type described, for example, in U.S. Pat. No. 3,003,462 and often 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 of the developer mix 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 continuously rotating cylinder picks up developer mix from a supply source and then 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 photoconductive 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 photoconductive 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 thermo-

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plastic 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 conductivity of the ferromagnetic carrier particles which form the "bristles" of a magnetic brush provides the effect of a development electrode having a very close spacing to the surface of the electrophotographic element being developed. By virtue of this development electrode effect it is to some extent possible to develop part of the tones in pictures and solid blacks as well as line copy. This ability to obtain solid area development with magnetic brush developing sometimes makes this mode of developing advantageous where it is desired to copy materials other than simple line copy. One difficulty with such counter-electrode development is that the exposure latitude obtainable is limited. Consequently, for certain applications, it is desirable to suppress the counter-electrode effect in order to obtain improved exposure latitude. One method of suppressing the counter-electrode effect is to use a carrier material which has a high electrical resistance.

Presently available commercial iron powders, however, are not at all uniform in regard to the properties of conductivity and resistivity. In general, the materials now available have too high resistivity to give good solid area development and are too conductive to entirely suppress the counter-electrode effect. One reason for the lack of uniformity in the electrical properties is that the particles carry surface dirt, such as grease, oil, and other contaminants. It has been suggested in the prior art that typical iron carrier particles can be treated with methanol, isopropanol, and other alcohols to rid the iron of grease, oil, etc. Iron so treated is generally referred to as "alcoholized iron."

However, the prior art has not recognized the heterogeneous nature of the intimate surface of the iron powders used in this art. In addition, no recognition has been given to the resulting complications in magnetic-brush processing which arise from using some of the presently available materials. The extraneous surface dirt found on the available iron particles is only part of the problem. In addition to the dirt, the iron particles invariably carry a non-uniform distribution of iron oxide and oftentimes pyrites such as iron sulfide, as well as other iron compounds. When materials of this type are used in conventional magnetic brushes, the iron carrier is in continuous motion and the constant friction of the particles against one another and against the various mechanical parts gradually remove bits of this nonuniform surface material. The attrition will, of course, vary from point to point on an iron particle depending on the nature of the deposit, its thickness, friability, adhesion to the underlying structure, and the like. Thus, with the available carrier materials, a progressive change occurs in the character of the iron surface during use. Correspondingly, the nature of the admixed toner also changes as it becomes contaminated with the fine particles which have separated from the surface of the carrier.

Accordingly, there is a need for iron carriers which will present a more nearly homogeneous surface and which will have stable triboelectric and other properties even during continued use. Furthermore, there is a need for iron carrier particles which will enhance the counter-electrode effect and thus improve the solid-area type development obtainable in magnetic brush processing. Also, there is a need for iron carrier particles which can repress the counter-electrode effect so that fringing development will be induced with its accompanying improvement in exposure latitude.

It is, therefore, an object of this invention to provide a new simple economic process for preparing magnetical-

ly responsive iron carrier particles having a homogeneous surface.

It is another object of this invention to provide a new process for preparing magnetically responsive carrier particles which process is adapted for forming particles of high surface conductivity or low surface conductivity, as desired.

A further object of this invention is to provide new developing compositions for use in magnetic brush development.

These and other objects and advantages are accomplished in accordance with this invention by the treatment of iron powder with an aqueous solution of acid followed by removal of residual acid and waste products evolved with subsequent controlled drying of the iron powder under preselected conditions of temperature, relative humidity and ambient atmosphere. In addition, the dried powder can be further treated by applying one or more thin continuous layers of an additional nonferrous material.

The carrier materials which are suitable for treatment in accordance with this invention include ferromagnetic materials such as iron powder in various forms. The phrase "iron powder" as used herein is meant to include a wide variety of particulate, magnetically responsive material the surface of which can be readily oxidized and includes material in such forms as reduced iron oxide bits; particles produced by atomization of molten metal and subsequent cooling of the droplets; particles produced by grinding, milling, filing, turning, etc.; as well as particles of iron alloys having oxidizable iron on the surface thereof such as stainless steel and iron alloys containing nickel and/or cobalt. The ferromagnetic carrier particles used can vary in size and in shape with useful results being obtained with average particle sizes of from about 1200 to about 40 microns. Particularly useful results are obtained with average particle sizes from about 600 to about 60 microns. The size of the carrier particles used will, of course, depend upon several factors, such as the type of images ultimately developed, the desired thickness of any subsequent coatings, etc.

Commercially available iron powder is first subjected to an acid treatment in accordance to this invention. This acid treatment can be carried out using a dilute aqueous solution of the acid. A wide variety of acids can be used such as sulfuric, hydrochloric, nitric, and other mineral acids. Sulfuric acid is a preferred material, by virtue of the fact that it is inexpensive, readily available, and only slightly volatile. In addition, certain organic acids, such as acetic acids, e.g., trichloroacetic acid, etc., are also useful in certain applications. In general, the acid concentrations which are useful can vary from about 1-normal to about 3-normal. Higher or lower acid concentrations can sometimes be useful because of the quantity of iron being treated, the average particle size or other such variables. The step of acid treatment of the iron particles is in no way restricted to any particular method of applying the acid. For example, spraying, percolation, and/or other means can conveniently be used to accomplish the acid treatment step. One very convenient procedure is to form a slurry of the iron powder in dilute acid for a period of time which will vary with the nature and concentration of the acid used, the agitation applied, the required degree of attack by the acid, the particle size of the iron powder, as well as the character and thickness of the surface material which is to be removed. When using commercial iron powders of average size, from about 100 microns to about 400 microns, it is generally sufficient to agitate the iron powder in a 5% aqueous solution of, for example, sulfuric acid for about one minute at about 25° C.

If necessary to stop the reaction of the acid on the carrier powder, an alkaline solution can be added to the acid slurry. Alternatively, the reaction can be checked by dilution with cold water. However, it is generally simpler and more efficient to start with an acid concentration of

the appropriate value such that the reaction rate will be sufficiently slowed down at the end of the treatment period, so as to facilitate settling of the iron powder and removal of the supernatant liquid. As mentioned above, the acid concentration required will vary with different iron powders, depending on the amount used and the average particle size, the nature of the surface on the starting material, etc.

Despite the harmful effects of the various surface contaminants found on commercial iron powders, such contaminants constitute only a very small fraction of the total weight of the powder. In most cases, the reduction in weight resulting from removal of undesired surface contaminants and incidental solution of elementary iron in the treatment of commercial iron powders by the method of this invention, is of the order of about 1 to about 2% by weight or less. Treatment need not be extended beyond the degree necessary to remove the heterogeneous surface contaminants. No further reduction in surface contaminants nor improvement in surface uniformity is observed by continuing treatment until the loss of metallic iron is about 2% by weight. Preferably, the metallic iron lost by dissolution should be less than about 1% by weight of the iron powder. In fact, unduly prolonged treatment not only results in needless consumption of acid and dissolution of iron but, in some instances, can produce deleterious results, by exposing occluded particles of acid-insoluble material.

After processing the iron powder in the aqueous acid solution, the acid is removed and the iron is washed by percolation or other means to insure removal of any residual acid. A large part of the material removed from the surface of the powder is often insoluble and consequently, decantation washing is a preferred method of eliminating both the residual acid and the suspended products of the reaction. A simple decantation procedure can be carried out by slurring the iron in clean cold water followed by a settling period to permit the iron particles of suitable carrier size to settle to the bottom of the liquid. After settling the supernatant liquid is rapidly decanted such that the unwanted contaminants are carried off with the liquid. This washing operation can be repeated until the rinse water is clear or until an established level of residual turbidity is reached.

The process of this invention can be used to prepare iron particles having very high surface conductivity. The highly conductive particles, made in accordance with this invention, show surface resistance values several orders of magnitude lower than the best of the commercially available iron powders when measured in magnetic brush conformation under standardized testing conditions. For purposes of comparison, the resistance of the carrier particles is measured in a standard resistance test. This test is conducted each time using a 15 g. quantity of carrier material. A cylindrically shaped magnet having a circular end of about 6.25 square centimeters 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. In general, the uncoated conductive particles made in accordance with this invention have a resistance of less than about 50 ohms, with especially preferred materials having a resistance of less than about 20 ohms.

Metallic iron is a very good electrical conductor and the clean elemental iron surface of the carrier iron prepared by this process of this invention results in a highly conductive iron powder as mentioned above. However, iron is also a highly reactive metal and readily oxidizes in air. Therefore, it is of utmost importance when making highly conductive carrier material by this invention to repress oxidation during the washing and drying steps as well as during subsequent storage. The repression of oxidation can be accomplished in any of several ways. One useful way

to repress oxidation is by the addition of an antioxidant or reducing agent to the wash water and particularly to the last several quantities of wash water. A variety of known antioxidants or reducing agents can be used to inhibit oxidation in the subsequent drying operation. For example, one-half percent of hydrazine sulfate or sodium nitrite is usually quite effective for this purpose. Oxidation can also be minimized by the use of one or a succession of rinses in a water-miscible organic solvent such as acetone or a lower alcohol like methanol, ethanol and isopropanol. Such solvents remove the residual water from the iron and speed subsequent drying. Additionally, the temperature and relative humidity of the drying air should also be carefully controlled. One reason for the careful control is that warming of the iron powder will encourage oxidation while similarly, if the iron is cooled too rapidly such that the temperature drops below the dew point, condensation of water on the iron will also encourage surface oxidation. Thus, when preparing conductive carriers, it is necessary that drying be carried out under temperature and relative humidity conditions which discourage the formation of surface oxide.

In general, the iron powder processed according to this highly conductive embodiment of the invention can be dried by agitating continuously in a current of warm air. Generally, the temperature of the air is in the range of from about 15° to about 40° C. with a preferred temperature of from about 20° to about 30° C. In addition, the drying temperature should be kept above the dew point of the ambient atmosphere to avoid unnecessary condensation. Furthermore, the relative humidity of the drying air should be kept low. Generally, good results can be obtained with relative humidity values of less than about 30% and preferably the relative humidity is less than about 20%. Under these conditions of temperature and humidity, the resulting powder shows very high surface conductivity. If, however, even higher surface conductivities are required, the iron can be dried in an inert, substantially oxygen-free atmosphere such as hydrogen, nitrogen, etc. After drying, the iron must be protected from oxidation until ready for use. This can be readily accomplished by storing it in an inert atmosphere in a sealed container. When used, the carrier particles are mixed with a toner material of suitable triboelectric properties which toner provides a physical coating that effectively lessens any further oxidation on the carrier during use. As a result, it is possible to maintain the improved surface conductivity of the carriers of the invention during extended periods of use in magnetic brush apparatus.

Of course, it is also possible to stabilize the improved surface conductivity of particles prepared in accordance with this invention by additional surface treatment of the carrier. One particularly useful surface treatment involves overcoating each carrier particle with a thin continuous layer of a nonferrous electrically conducting metal which is more resistant to aerial oxidation than iron. The materials useful for coating or plating onto the present conductive carriers are typically nonferrous metals which are substantially more resistant to surface oxidation than iron and iron-alloy. Suitable coating materials having a resistance to aerial oxidation greater than that of iron include those metals in Groups VIa, VIII, Ib and IIb of the Periodic Table (Cotton and Wilkinson, *Advanced Inorganic Chemistry*, 1962, page 30). Particularly useful metals are cadmium, chromium, copper, gold, nickel, silver, zinc, and the platinum group elements which include ruthenium, rhodium, palladium, osmium, iridium and platinum as well as mixtures of alloy of any of these. Most of these metals are more electronegative than the iron starting material which property is advantageous in certain coating procedures. With other coating procedures, the metals more electropositive than iron can be useful such as chromium, zinc and cadmium.

The useful conducting metals all have a greater corrosion resistance or resistance to aerial oxidation than does

iron. The terms "corrosion resistance" or "resistance to aerial oxidation" all have reference to the ability of a metal to withstand oxidative-type corrosion which impairs electrical conductivity. In general, the type of corrosion which should be avoided is continuous aerial oxidation or rapid aerial oxidation which substantially reduces the electrical conductivity of a metal. In particular, these terms have reference to corrosion induced by exposure to air, carbon dioxide, water, ozone, etc., and do not have particular reference to the chemical attack of solutions of strong acids or bases, etc. Coatings of this type are further described in H. A. Miller U.S. application Ser. No. 799,967, filed Feb. 17, 1969, co-filed herewith, and entitled *Highly Conductive Carrier Particles*. The metal coated carrier particles of this invention generally have a resistance of less than 10 ohms with preferred materials having a resistance of less than 1 ohm.

Conductive carrier as described above are excellent for use in magnetic-brush development wherein it is desired to obtain a development electrode effect thus producing solid area development. However, if solid area development is not desired, then it is necessary to suppress this development electrode effect. The simplest way to accomplish this result is through the use of highly insulating carrier particles. When insulating carrier particles are used, the development electrode effect is suppressed and fringing development occurs.

In accordance with this invention, high resistance iron carrier particles can be provided by acid washing and rinsing, as referred to above, followed by treatment to provide a uniform, adherent iron oxide surface of high resistivity on the individual particles. However, in accordance with this embodiment of the invention, subsequent washings to remove residual acid and waste products are conducted without the addition of any antioxidant material. After water washing, the iron is drained to remove surplus moisture and then dried without subsequent solvent treatment. The drying is conducted at elevated temperatures so as to induce formation of surface oxides. Good results are obtained with drying temperatures of from about 40 to about 80° C. During the drying operation, the damp powder is mixed gently in order to keep the temperature and water content relatively uniform throughout the mass of powder. During drying, the color of the iron gradually change from gray to brown. After drying, the treated powder exhibits a very high level of surface resistivity. The optimum drying conditions (i.e., temperature, agitation, humidity, etc.) needed to produce the desired thin, uniform oxide coatings will be dependent upon the particular iron powder used as a starting material. Simple experimentation will readily show which conditions are optimum for a particular powder chosen. In general, good results are obtained with air drying temperatures in the range of from about 40 to about 80° C. with a preferred temperature being in the range of from about 45 to about 60° C. The relative humidity of the drying air can vary widely with good results being obtained at values of 40% R.H. and above. Preferably, the drying air has a relative humidity of 60% and above. Oxide-coating particles can be prepared in this manner having electrical resistance ranging up to greater than about 10⁹ ohms.

When high resistance carrier particles of the above type are mixed with an appropriate toner material, the resultant developer composition is found to greatly reduce the development electrode effect of a magnetic brush. In addition, such a developer composition induce fringing development with the accompanying increase in exposure latitude. The iron oxide coating on these carriers can also be overcoated with a thin plastic film to further increase the resistance of the carrier and thereby inducing greater fringe development. In particular, the particles can be overcoated with continuous, uniform layers of film-forming electrically insulating resinous material. The polymers or resinous material useful in overcoating the carrier

particles of this invention can be selected from a variety of substances. Useful resins must be film-forming and, in general, they are electrically insulating such that when coated in desired amount they will impart the requisite degree of electrical resistance to the carrier particles. Useful resins include those capable of being cured, hardened, or otherwise insolubilized such that when a subsequent resin layer is applied there is no substantial permeation of a resin layer into an adjacent layer. Suitable resins include thermosetting resins which harden upon the application of heat as well as light sensitive resins which harden upon exposure to actinic radiation. Also combinations of resins having diverse inherent solubility characteristics can be used. The different types of useful resins can be used alone or in various combinations.

Useful light sensitive or light-hardening resins would include polymeric derivatives of cinnamic acid such as polyvinyl cinnamate, cinnamoylated polystyrene, ethylene vinyl cinnamate copolymer, cellulose cinnamate, N-(cinnamoylphenyl)-methane derivatives of hydroxylated polymers (e.g., partially hydrolyzed polyvinyl acetate cellulose acetate, etc.), epoxy resins esterified with cinnamoyl chloride and the like. Polyvinyl cinnamate succinate and polyvinyl cinnamate phthalate would be particularly easy to use in that they can be coated from an aqueous solution. In addition, photocrosslinkable compositions comprising an unsensitive resin and a light sensitive crosslinking agent are useful. Such compositions could comprise an alcohol soluble nylon-type polyamide with, for example, benzophenone as an initiator, etc.

Useful thermosetting or heat-hardening resins include a wide variety of materials with formaldehyde condensation products being exemplary of readily available materials. Particularly useful materials are formaldehyde condensation products formed with urea, melamine or with various phenols such as xylenol, cresol, trimethylphenol, phenol, soligenin, etc. Other resins can also be used such as the thermosetting epoxy resins, polyester-styrene resins and the like.

Other useful resins would include cellulose resins, such as cellulose nitrate, cellulose acetate butyrate, etc., and lower alkyl methacrylate polymers having from 1 to 4 carbon atoms in the alkyl moiety, etc. In general, film-forming polyesters, polyolefins, polyamides, polycarbonates, etc., can all be used provided they are applied from suitable liquid vehicles which will not soften any previously applied layer. Methods for applying multiple layers of such resins are disclosed in co-pending Miller U.S. application, Ser. No. 799,968, filed Feb. 17, 1969, co-filed herewith, and entitled High Resistance Carrier Particles. Of course, single layers of useful polymeric materials are also useful. Resin overcoated particles prepared in this manner generally have an electrical resistance of greater than about 10^{12} ohms.

Electroscopic developer compositions can be prepared by mixing from about 90 to about 99% by weight of the present acid-washed magnetically responsive carrier particles with from about 10 to about 1% by weight of a suitable electroscopic toner material. The toner used with the carrier particles of this invention 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 toner power selected is utilized with ferromagnetic carrier particles in a magnetic-brush development arrangement the toner clings to 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.

Toner powders suitable for use in this invention are typically prepared by finely grinding a resinous material and mixing with a coloring material such as a pigment or a dye. The mixture is then ball milled for several hours and heated so that the resin flows and encases the colorant. The mass is cooled, broken into small chunks and finely ground again. After this procedure the toner powder particles usually range in size from about 0.5 to about 25 microns, with an average size of about 2 to about 15 microns.

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 including polyvinylchloride, polyvinylidene chloride, polyvinyl acetate, polyvinyl acetals, polyvinyl ether and polyacrylic and polymethacrylic esters; polystyrene and substituted polystyrenes or polycondensates, e.g., polyesters such as phthalate resin, terephthalic and isophthalic polyesters, maleinate resin and colophony-mixed esters of higher alcohols; phenol-formaldehyde resins, including colophony-modified phenol formaldehyde condensates, aldehyde resins, ketone resins, polyamides and polyadducts, e.g., polyurethanes. Moreover, polyolefins, such as various polyethylenes, polypropylenes, polyisobutylenes and chlorinated rubber are suitable. Additional toner materials which are useful are disclosed in the following U.S. patents: 2,917,460; Re. 25,136; 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 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 ET00 (C.I. 14645), 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

A 2500 g. quantity of a commercial iron powder (Glidden Iron 388, Glidden-Durkee Div. SCM Corp.) is poured into 1500 ml. of 2 N sulfuric acid solution over a 10-second period. The iron powder used has a particle size such that it will pass through a 140 mesh screen and be retained by a 170 mesh screen. The resistance of the iron carrier as measured in the standards resistance test referred to above is 2400 ohms. After addition of the iron to the sulfuric acid, stirring is continued for 60 seconds whereupon the reaction mixture is diluted to 4000 ml. with cold tap water. The mixture is allowed to settle for 10 seconds and then the brown, supernatant liquid is decanted along with a considerable quantity of black greasy scum on the surface. Decantation rinsing is repeated 8 more times with 2000 ml. volumes of water. The slurry is agitated after each addition of rinse water so as to briefly suspend all iron powder. After suspension, the powder is allowed to settle and the supernatant liquid is again decanted along with suspended dirt and other unwanted materials. After the final water rinse, the iron is drained and rinsed 4 times with 600 ml. volumes of anhydrous methanol with thorough mixing after each addition followed by a settling period of 10 seconds prior

to decantation. Following the final alcohol rinse, the drained iron is suction filtered on a Büchner funnel and the resulting damp powder is dried in a thin layer ($\frac{1}{16}$ inch or less) on a glass sheet. The powder is mixed continuously during drying with heat being provided by infrared radiation from two 250 watt infrared bulbs at a distance of about 45 cm. from the powder. The two infrared bulbs provide sufficient heat to prevent the powder from being cooled excessively by evaporation of the residual methanol. The ambient air is at a temperature of about 21° C. and a relative humidity of slightly less than about 40%. Upon drying, the resistance of the powder was measured in the standard test referred to above and found to be 16 ohms. The dry powder weighs 2468 grams which represents a total loss of about 1.3% in dirt, surface oxide, pyrites, etc., as well as extremely finely divided iron powder decanted in washing. A magnet placed in all of the dirt, etc., removed from the starting iron attracted only a minute amount of material indicating that only very little of the material lost is actually iron. Next, two magnetic brush developer compositions are prepared from the acid-washed iron and with an equal quantity of untreated starting material. The two carriers are each mixed with 3% by weight of a black, styrene co-polymer toner, having a particle size of from 1-5 microns. The toner material charges positively on the carrier particles. The two developer mixtures are tested in a magnetic-brush development apparatus. The apparatus for testing comprises a cylindrical aluminum tube arranged to rotate axially in a horizontal position about a fixed permanent magnet. The permanent magnet has its poles oriented such that when the magnetic particles are present, a magnetic brush is formed on top of the cylinder. In the test procedure, this apparatus is run for 15 minutes with the magnetic brush in contact with an electrophotographic element comprised of a conductive support coated with a photoconductive layer of an organic photoconductor in a resin binder. The developer formed using the untreated carrier particles shows considerable tendency to leave a scum or deposit on the photoconductor after repeated use; whereas, the developer containing acid-treated carrier showed very little tendency to leave a scum. In addition, when the two carrier particles are tested in the same apparatus using no toner, the acid-treated carrier particle produces no visible deposit during the test; while the untreated carrier deposits a black layer having a density of about 0.8. The two developer mixtures are then used to develop an electrostatic latent image carried on a photoconductive element as described above. The developer containing the acid-treated carrier gives better overall image quality with more solid area development while showing less sensitivity to variations in the electrical potential applied to the magnetic brush.

EXAMPLE 2

A quantity of 454 g. of high density electrolytic iron powder (Glidden 475, Glidden-Durkee Div. SCM Corp.) is poured rapidly with stirring into 250 ml. of a 5% hydrochloric acid solution in a 1 liter beaker. The iron powder has a particle size such that it will pass through a 60 mesh screen and be retained by a 120 mesh screen. In addition, the resistance of this iron powder as measured in the standard resistance test described above is 640,000 ohms. The slurry of iron powder and hydrochloric acid is mixed continuously for 2 minutes at which time the reaction of the acid on the iron powder subsides. The acid-treated iron is then rinsed 4 times by decantation with 750 cc. of a 0.5% solution of sodium nitrite in distilled water. After the last water rinse, the iron is drained and rinsed twice with anhydrous ethanol. Excess alcohol is then removed by filtration using a Büchner funnel for 10 minutes. The damp powder is rapidly dried by sprinkling it repeatedly through a current of dry air at a temperature of approximately 30° C. and a relative humidity of less than 30%. The powder is fully dried within about 4 minutes. The yield is 450 grams. After drying, the acid-treated

powder is measured for resistance in the standard resistance test and found to be 0.2 ohm. Next, the acid-treated carrier particles are placed in the mechanical magnetic-brush apparatus as described in Example 1. The apparatus is run using the treated carrier particles for a period of 15 minutes. At the end of this period no visible scum is deposited on the electrophotographic element used. An equivalent quantity of uncoated control carrier material when used in the test apparatus for 15 minutes produces a deposit on the photoconductive element which measures 0.25 in density using a standard densitometer. Next, the acid-treated carrier and the control carrier are mixed with 5% portions of a blue toner powder and again subjected to the standard scumming test. The developer prepared with the acid-washed carrier particles produced a slight amount of scum which is barely visible; whereas, the control developer produces a large amount of scum which is readily visible. In addition, the control developer when in use is subject to a large degree of toner throw-off while the developer of the present invention exhibits considerably less toner throw-off. The two developer compositions are then used to develop an electrostatic latent image carried on an electrophotographic element. The developer containing the acid-washed carrier gives good image quality with excellent solid area development both with and without bias on the magnetic brush. The control developer gives some image development; however, the solid areas are developed in a very uneven manner. The hue of the two developed images shows the image formed from the control developer to be less saturated than the image formed from the developer containing the acid-washed carrier. The developer containing the acid-treated carrier is then placed in an open 1 liter beaker and held for 3 weeks under average room conditions (about 20° C. and 45% relative humidity). At the end of this period, the developer is measured for resistance and found to be substantially unchanged from the resistance value at the start of the test period. In addition, when this developer is tested again for image development, the results obtained are substantially the same as those obtained when using a freshly prepared developer composition in accordance with this example.

EXAMPLE 3

A 5 kilogram quantity of spherical iron particles, of a size that will pass through a 150 mesh screen and be retained by a 200 mesh screen, is poured into 3 liters of a 1:15 dilution of concentrated nitric acid at 20° C. The mixture is slurried for 2 minutes and then diluted to 10 liters with tap water at about 5° C. The diluted mixture is allowed to settle for about 10 seconds and the supernatant liquid and suspended contaminants are decanted. The initially black iron powder appears silver-gray in color after this acid treatment. The acid-treated iron is then subjected to 5 decantation rinses using tap water at 20° C. whereupon the surplus water is drained from the iron powder by suction in a Büchner funnel. The damp iron powder is spread out to a thickness of about 1 inch in a plastic tray and allowed to dry. Four 250 watt infrared bulbs are positioned approximately 50 cm. from the tray to warm the powder during drying. During the drying operation, the iron is turned over continuously while maintaining an average depth of about 2½ cm. As the powder dries, it turns progressively more brown in color. The weight of the dry product is 4986 grams. After drying, the resistance of the material is measured and found to be 2×10^9 ohms as compared to 2.8×10^6 ohms for the starting material. A hand-held bar magnet is then used to attract the treated carrier material. The amount of carrier material which is picked up by the bar magnet is measured and the magnet is cleaned and repeated again using the starting iron particles. It is found that the bar magnet will attract 5% by weight more of the treated carrier material than the untreated material. Next, two developer compositions are prepared using the treated

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carrier and the control carrier. Each developer contains 4% by weight of a black toner powder having an average particle size of 2 microns and comprising a nigrosine colorant in a styrene polymeric binder. The two developer compositions are then used in the mechanical brush apparatus described in Example 1. The acid-treated carrier containing developer produces images of good quality with excellent fringe development being obtained. In addition, a wide exposure latitude is obtained with the developer containing acid-treated carrier. The control developer gives only very limited exposure latitude and only slight fringing development.

EXAMPLE 4

A 200 g. quantity of iron powder in the form of flat iron leaflets having a particle size such that they will pass through a 60 mesh and be retained by an 80 mesh screen is placed into the bottom of a glass tube having an inside diameter of about 3 cm. and about 60 cm. long. One liter of 10% trichloroacetic acid solution is pumped upward through the iron in the tube. The solution is circulated through the iron powder 4 times in 5½ minutes. Suspended dirt and other contaminants are trapped in a wool-felt filter before recirculation of the solution. The acid is then replaced with cold tap water which is forced upward through the bed of iron powder at a rate sufficient to remove unwanted small particles of contaminants without carrying away any appreciable amount of the screened carrier material. The water flow rate is approximately 1 liter per 100 seconds. After 15 minutes of washing, the wet material is transferred to a suction funnel to remove surplus moisture. The top of the funnel is provided with a plastic cap to exclude air and nitrogen is pumped into the cap at a rate sufficient to prevent collapse of the cap. After 30 minutes, the nearly dried powder is removed and finally dried rapidly by sprinkling it repeatedly through a current of dry air at about 20° C. and a relative humidity of about 40%. The resistance of the final product as measured in the standard test as described above is 37 ohms compared to 1200 ohms for the starting material. Equal quantities of the starting material and the acid-treated material are used to prepare developer compositions, each containing 3% by weight of the black toner of Example 1. When used to develop electrostatic latent images, both developers give solid area development in a standard magnetic brush apparatus; however, the developer with the acid-treated highly conductive carrier produces substantially better solid area fill-in and is less sensitive to changes in the electrical bias of the magnetic brush than is the control developer.

EXAMPLE 5

A 1600 g. quantity of commercial iron powder in the form of flattened grains (Glidden Iron 412, Glidden-Durkee Div. SCM Corp.) is acid-treated as follows. The starting iron powder has a nominal particle size such that it will pass through a 60 mesh screen and be retained by a 120 mesh screen; however, the powder has an extremely large portion (about 15%) of much more finely divided material. The starting material is placed on a 120 mesh plastic screen and sprayed with an acid solution comprising 200 cc. of concentrated sulfuric acid and 3 liters of tap water at about 15° C. The iron is spread out evenly over an area of about 700 sq. cm. and sprayed uniformly with the acid at a rate of about 25 ml. per second under about 10 pounds pressure through a plastic spray nozzle. The force of the spray jet helps to separate small contaminants and force them down through the plastic screen. Next, the powder is rinsed with a 0.2% solution of hydrazine sulfate. After about 10 liters of the rinse solution has been sprayed over the iron, the material is drained, rinsed free of surplus water by spraying with 2 liters of isopropanol and dried in a current of dry air at a temperature of about 32° C. and a relative humidity of about 35%. The velocity of the air is maintained at

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a sufficient rate to produce continuous movement of the powder during drying. In addition, further agitation is provided by brushing the iron during the drying step with a small brush. After the iron is completely dry, the air is turned off, but manual brushing action is continued for 3 minutes to assist in sifting out any particles having a size smaller than 120 mesh. The resistance of the treated material is measured and found to be 7 ohms as compared to 900 ohms for the starting material. Next, the carrier material is mixed with 3% by weight of a yellow, styrene base toner which charges negatively with respect to the iron carrier particles. The resulting developer composition is used to develop positively charged electrostatic latent images carried on an electrophotographic element. Excellent solid area development is obtained and the resultant image is of a high quality and has a brilliant yellow hue. A control developer prepared with the same yellow toner and the starting iron carrier, which has been screened to reduce the number of fine particles, gives images of poor quality having substantially less solid fill-in and considerably less hue saturation. This loss of color brightness appears to be caused by loose dirt and oxide on the surface of the control carrier material, which dirt mixes with toner and is transferred to the electrostatic image. The control developer is also undesirable in that it is much more sensitive to change in bias potential on the magnetic brush.

EXAMPLE 6

Two kilograms of iron treated as in Example 1 above are coated with a thin continuous layer of nickel by electroless plating for 30 minutes at about 95° C. in a bath of the following composition:

Nickel(ous)chloride $\text{N} \cdot \text{Cl}_2 \cdot 6\text{H}_2\text{O}$ —67.5 g.
Sodium citrate $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$ —123.0 g.
Ammonium chloride NH_4Cl —75.0 g.
28% ammonia solution—150.0 ml.
Sodium hypophosphite $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ —16.5 g.
Water to make 1500.0 ml.

The nickel-plated powder is removed from the bath and washed with six changes of cold water, rinsed three times with ethanol, suction filtered and dried at room temperature. The resistance of the dry powder is measured in the standard resistance test and found to be less than ½ ohm. The nickel-coated carrier is then used to prepare a developer composition as in Example 1. Electrostatic latent images developed with this developer show excellent solid area fill-in.

EXAMPLE 7

A 700 g. quantity of a stainless steel iron powder having a particle size such that it will pass through a 200 mesh screen and be retained by a 325 mesh screen is treated with acid in the same manner as in Example 1 using 500 ml. of a 1:19 aqueous solution of sulfuric acid followed by 12 decantation rinses with 1500 ml. quantities of water at 38° C. After the last water rinse, the residual water is drained out by placing the iron in a suspended cotton sack for 15 minutes. The iron is then placed in a shallow glass tray and dried with a current of air at room temperature while keeping the level of the iron at about 1¼ cm. depth and turning over the iron every two or three minutes with a hand spatula. During the course of drying, the iron acquires a gray color. The final product is measured in the standard resistance test and found to have a resistance of 10 megohms as compared to 22,000 ohms for the starting material. The result carrier is used to prepare a developer composition and used to develop an electrostatic latent image as in Example 1. Good fringing development is obtained using this developer. A similar developer composition prepared using the control carrier and the toner of Example 1 gives neither good solid area nor good fringing development.

A one kilogram quantity of iron powder as prepared in Example 3 is mixed with 300 ml. of a 7% solution of polyvinylcinnamate light sensitive resin in methyl Cellosolve acetate. The powder is spread out on a glass surface and dried at room temperature. The dried powder is then exposed to a 35 ampere arc lamp for 10 minutes while continuously stirred to insure uniform exposure. This procedure is repeated four times resulting in four distinct resin coatings on each particle. The particles are then measured in the standard resistance test and found to have a resistance value of greater than about 10^{15} ohms. A developer composition is prepared with this carrier and used to develop an electrostatic latent image as in Example 1. Excellent fringe developed images are obtained over a wide range of exposures.

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.

I claim:

1. A process for preparing a magnetically responsive developer composition for use in developing electrostatic charge patterns comprising the steps of dispersing iron powder in a dilute aqueous mineral acid bath having a concentration of about 1 N to about 3 N, agitating the powder while in the bath, separating the powder from the bath, rinsing the powder with water, drying the wet powder in an oxygen-containing atmosphere at a temperature of from about 45 to about 70° C. whereby a thin uniform layer of iron oxide is produced on the surface of the individual particles of iron powder, overcoating each particle of iron powder with at least one thin, uniform layer of an electrically insulating, film-forming polymer to form magnetically responsive carrier particles having average particle sizes from about 1200 to about 40 microns and having an electrical resistance of greater than about 10^{12} ohms and mixing from about 90 to about 99% by weight of the resultant carrier particles with from about 10 to about 1% by weight of

an electroscopic toner material having a particle size smaller than that of the carrier particles.

2. A process for preparing a magnetically responsive developer composition for use in developing electrostatic charge patterns comprising the steps of dispersing iron powder comprised of particles having an average diameter of from about 60 to 600 microns, in a dilute aqueous mineral acid bath having a concentration of about 1 N to about 3 N, agitating the powder while in the bath, separating the powder from the bath, rinsing the powder with water, drying the wet powder in an oxygen-containing atmosphere at a temperature of from about 45 to about 70° C., whereby a thin, uniform layer of iron oxide is produced on the surface of the individual particles of iron, overcoating each particle of iron with at least one thin, uniform layer of an electrically insulating, film-forming polymer to form magnetically responsive carrier particles having an electrical resistance of greater than about 10^{12} ohms, said polymer being selected from the group consisting of cinnamate resins, cellulose esters, polyesters, polyolefins, polyamides, polycarbonates, formaldehyde condensation products and lower alkylmethacrylate resins and mixing from about 90 to about 99% by weight of the resultant carrier particles with from about 10 to about 1% by weight of an electroscopic toner material having a particle size smaller than that of the carrier particles.

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