An electrostographic imaging process comprising forming an electrostatic latent image on a surface and developing said image by contacting it with a developer mixture of finely-divided toner particles electrostatically clinging to the surfaces of carrier beads comprising nickel-zinc ferrite beads or manganese-zinc ferrite beads characterized as being substantially dense and uniform in size and shape with maximum roundness and sphericity and having substantially uniform electrostographic properties such as triboelectricity, magnetic permeability, and electrical conductivity, whereby at least a portion of the toner particles are attracted to and deposited on said surface in conformance to said latent image.

13 Claims, No Drawings
3,839,029

ELECTROSTATOGRAPHIC DEVELOPMENT
WITH FERRITE DEVELOPER MATERIALS

This is a division of application Ser. No. 160,893, filed July 8, 1971.

BACKGROUND OF THE INVENTION

This invention relates in general to electrostatography and in particular to a process for the preparation of ferrite materials and to the ferrite materials so prepared.

Ferrite materials are gaining ever increasing importance in the electronics industry and in the electrostatographic arts. Their use as low conductivity magnetic core materials and as carrier materials for photoconductive insulating materials is well known. Briefly, ferrites are described in general as compounds of magnetic oxides containing iron as a major metallic component. Thus, compounds of ferric oxide, Fe₂O₃, formed with basic metallic oxides having the general formula MFeOₓ or MFe₂O₄ where M represents a mono or divalent metal and the iron is in the oxidation state of +3 are ferrites. Ferrites are also referred to as ferrosilines since they have the same crystal structure of the mineral spinel Mg₆Al₂O₁₂. However, not all ferrites are magnetic such as, for example, ZnFe₂O₄ and CdFe₂O₄. This lack of magnetic property is due to the configuration of the ferrite lattice structure. Further, some ferrites, such as magnetobarite, BaFe₁₂O₁₉, which exhibit permanent magnetic properties are referred to as “hard” ferrites. A “hard” ferrite is difficult to magnetize and demagnetize and thus is the type of ferrite that is desirable in a permanent magnet. A “soft” ferrite has the opposite property; it is easily magnetized and demagnetized. The “softer” the ferrite material is, the better it is suited to various electrical devices in which magnetization must be reversed very often per unit of time. If one plots the characteristics of a “hard” ferrite and a “soft” ferrite on a graph in which the imposed magnetic field forms the horizontal axis and the total magnetization forms the vertical axis, one obtains a characteristic curve resembling a thick S known as a hysteresis loop. A “hard” ferrite has a wide hysteresis loop and a “soft” ferrite has a thin one. Since each traversal of a loop represents energy lost, a narrow loop is desirable in devices in which magnetization must be reversed frequently.

The ferrite materials of main interest in the electrostatographic arts are the soft ferrites. The soft ferrites may further be characterized as being magnetic, polycrystalline, highly resistive ceramic materials exemplified by intimate mixtures of nickel, manganese, magnesium, zinc, iron or other suitable metal oxides with iron oxide. Upon firing or sintering, the oxide mixtures assume a particular lattice structure which governs the magnetic and electrical properties of the resulting ferrite.

The formation and development of images on the surface of photconductor materials by electrostatic means is well known. The basic electrostatographic imaging process, as taught by C. F. Carlson in U.S. Pat. No. 2,297,691, involves placing a uniform electrostatic charge on a photoconductive insulating layer, exposing the layer to a light-and-shadow image to dissipate the charge on the areas of the layer exposed to the light and developing the electrostatic latent image by depositing on the image a finely divided electroscopic material referred to in the art as “toner.” The toner will normally be attracted to those areas of the layer which retain a charge, thereby forming a toner image corresponding to the electrostatic latent image. This powder image may then be transferred to a support surface such as paper. The transferred image may subsequently be permanently affixed to the support surface as by heat. Instead of latent image formation by uniformly charging the photoconductive layer and then exposing the layer to a light-and-shadow image, one may form the latent image by directly charging the layer in image configuration. The powder image may be fixed to the photoconductive layer if elimination of the powder image transfer step is desired. Other suitable fixing means such as solvent or overcoating treatment may be substituted for the foregoing heat fixing steps.

Several methods are known for applying the electroscopic particles to the electrostatic latent image to be developed. One development method, as disclosed by E. N. Wise in U.S. Pat. No. 2,618,552, is known as “cascade” development. In this method, a developer material comprising relatively large carrier particles having finely divided toner particles electrostatically coated thereon is conveyed to and rolled or cascaded across the electrostatic latent image bearing surface. The composition of the carrier particles is so selected as to triboelectrically charge the toner particles to the desired polarity. As the mixture cascades or rolls across the image bearing surface, the toner particles are electrostatically deposited and secured to the charged portion of the latent image and are not deposited on the uncharged or background portions of the image. Most of the toner particles accidentally deposited in the background are removed by the rolling carrier, due apparently, to the greater electrostatic attraction between the toner and the carrier than between the toner and the discharged background. The carrier and excess toner are then recycled. This technique is extremely good for the development of line copy images.

Another method of developing electrostatic latent images is the “magnetic brush” development process as disclosed for example, in U.S. Pat. No. 2,874,063. In this method, a developer material containing toner and magnetic carrier particles are carried by a magnet. The magnetic field of the magnet causes alignment of the magnetic carrier into a brushlike configuration. This “magnetic brush” is engaged with the electrostatic image-bearing surface and the toner particles are drawn from the brush to the latent image by electrostatic attraction. Thus, a developer mixture may be provided comprising a toner material and a carrier material which consists of particles which are magnetically attractive. Consequently, iron and magnetic ferrite materials have been employed as the carrier material in the electrostatographic arts.

Generally, in cascade or magnetic brush development typical carrier core materials include sodium chloride, ammonium chloride, aluminum potassium chloride, Rochelle salt, sodium nitrate, potassium chloride, granular zircon, granular silicon, methyl methacrylate, glass, silicon dioxide, flintshot, iron, steel, ferrite, nickel, carboburnum and mixtures thereof. Many of the foregoing and other typical carriers are described by L. E. Walkup in U.S. Pat. No. 2,618,551; L. E. Walkup, et al, in U.S. Pat. No. 2,638,416 and E. N. Wise in U.S. Pat. No. 2,618,552. Generally, an average carrier particle diameter between about 30 microns to
about 1,000 microns is preferred for electrostaticographic use because the carrier particle then possesses sufficient density and inertia to avoid adherence of electrostatic latent images during the cascade development process. In magnetic brush development, the ferrite carrier materials are generally homogenous, rounded or irregularly shaped particles having nominal particle sizes less than about 300 microns and more preferably between about 50 and 200 microns, the latter size range providing optimum image quality during extended use.

In the past, ferrite materials have generally been prepared by dry and wet methods. The dry method involves the intimate mixing of pure oxides or carbonates of the desired metallic constituents and causing the mixture to react at elevated temperatures to form the desired structure. This method requires extensive ball-milling of the oxides or carbonates, usually dispersed in a liquid, until an efficient degree of mixing is obtained. The mixture is usually then dried, granulated, pre-sintered to form the desired structure, reground to attain a suitable particle size distribution, pressed or compacted with a binder material, and finally sintered or refired at temperatures above the pre-sintering temperature. This method is undesirable in that it results in ferrite material of large crystallite or grain size having a high temperature coefficient of permeability or decreased temperature stability. The wet method generally involves the formation of an intimate mixture of the desired components by co-precipitation from solution. Usually, the components are dissolved as nitrates and co-precipitated as hydroxides, carbonates or oxalates. The product, after filtration and washing, is then prefired, reground, sized, compacted with a binder, and finally sintered or refired at temperatures above the pre-sintering temperature. This method also has the disadvantage of resulting in ferrite materials of large crystallite or grain size having a high temperature coefficient of permeability or decreased temperature stability. Both the dry and wet methods have the further disadvantage of requiring compaction of the product with a binder prior to final firing which is a time consuming, expensive step and which limits the firing temperature and also causes bead to bead agglomeration and sticking of beads to surfaces of sintering equipment.

Other techniques of producing magnetic powders are known such as preparing a powdered alloy and mechanically disintegrating the alloy to magnetic particles and blowing the magnetic particles through a reducing gas flame at a temperature sufficient to melt the particles to spherical form, and cooling and collecting the particles so obtained as disclosed in U.S. Pat. No. 2,186,659. Even though this technique can produce spherical particles, to avoid undesired reactions such as oxidation of the particles, a protective gas stream such as hydrogen or nitrogen is generally required. Further, the product coming from the ball mill must be baked in a compressed gas flame and the ball material caught in a liquid bath. In addition, the baked material thus produced must generally be mixed in a kneading machine with a binding medium, such as an artificial resin that can be solidified. After drying, the material must be compressed in a suitable manner.

Several methods of preparing a manganese-zinc ferrite are disclosed. For example, in U.S. Pat. No. 3,567,641 an oxide mixture is prepared, the mixture is pre-sintered at about 700°-900°C for about an hour, the pre-sintered mixture is wet ground with CaO, the material is pressed to shape and sintered at 1,100°-1,300°C for 1 to 4 hours in a low oxygen atmosphere, and then cooled in a substantially pure neutral atmosphere such as nitrogen. In U.S. Pat. No. 3,565,806 the ferrite material is produced by providing a mixture of the oxides, forming ferrite blanks from the oxide mixture, sintering the ferrite blanks at 1,200° to 1,300°C for about 4 to 20 hours, and during the last half of the sintering period the sintering occurring in an inert gas atmosphere containing less than 0.2 percent by volume of oxygen, and then cooling the sintered ferrite blanks to a temperature of about 300°C in the same inert atmosphere. However, both processes suffer from various disadvantages. For example, in U.S. Pat. No. 3,567,641 the process requires that the material be pre-sintered and then wet ground, then pressed into shape and also be cooled in a substantially pure neutral atmosphere. Likewise, in U.S. Pat. No. 3,565,806 it is required that ferrite blanks be formed from the oxide mixture and also that the sintered ferrite blanks be cooled in the same inert atmosphere. Since previously known ferrite preparation processes are deficient in one or more respects, there is a continuing need for an improved ferrite production process.

**SUMMARY OF THE INVENTION**

It is, therefore, an object of this invention to provide a ferrite manufacturing process and resulting products which overcome the above noted deficiencies.

It is another object of this invention to provide a ferrite manufacturing process which avoids problems of ferrite bead-to-bead agglomeration.

It is another object of this invention to provide a ferrite manufacturing process which avoids sticking of ferrite beads to surfaces of sintering equipment.

It is another object of this invention to provide a ferrite manufacturing process which provides improved ferrite particles of a desired size and controlled size distribution.

It is another object of this invention to provide a ferrite manufacturing process which provides improved ferrite carrier particles having more stable electrostaticographic properties.

It is another object of this invention to provide a ferrite manufacturing process wherein undesirable compaction or pressing of the spray dried bead particles prior to the sintering step is avoided.

It is another object of this invention to provide a ferrite manufacturing process wherein carrier materials having a substantially spheroidal shape may be prepared without the use of a binder material.

It is another object of this invention to provide a ferrite manufacturing process which is superior to known ferrite manufacturing processes.

The foregoing objects and others are accomplished, generally speaking, comprising preparing a slurry of ferrite forming metal oxides in a liquid, spray drying the slurry of metal oxides to form substantially spherical metal oxide beads which are significantly larger than the size of the metal oxide starting materials, and sintering the substantially spherical metal oxide beads to form ferrite beads under conditions which preserve the shape and particulate nature of the beads.

The desired metal oxide materials may be selected first on the basis of desired ferrite properties. In a preferred embodiment using a high speed mixer, the metal
oxide starting materials are slowly added to a make-up tank while a deflocculent is added so that the solids are continually wetted out. A smooth, homogenous slurry is generally formed after approximately ten minutes of agitation depending upon the equipment capacity and the size of the batch prepared. If the finished ferrite is to be composed of several components for use as a carrier particle, it is usually desirable to achieve an intimate mixture of the metal oxide starting materials by this slurry preparation process. The actual degree of mixing achieved may be controlled by the choice of equipment used and selection of specific equipment operating parameters and/or slurry conditions such as mixing speed, mixing time, viscosity and temperature. Where it is desired to obtain controlled particle size reduction during the mixing operation, then the choice of equipment will generally predominate. The metal oxide starting materials may be mixed in slurry form in any one of the following types of equipment such as ball-milling, vibrating pebble mill, high speed stirrer with counter turning rotor and blades, impeller mixer, high speed dispersator, and other conventional mixing equipment. As an alternative, one may dry mix the metal oxide starting materials and combine the dry mixture at a later time with a liquid medium. Following the slurring operation, it is generally preferred to screen the slurries prior to spray drying in order to eliminate any large solid particles which may be present as would plug the atomizer. A spray dryer designed for either spray nozzle atomization or spray machine-disc atomization or equivalent may be employed to dry the slurry of metal oxide starting materials. A particularly desirable type of spray machine is one that is essentially a closed pump impeller driven by a variable speed drive and is commonly termed a spinning atomizer, disc or wheel. The total system generally consists of a power-coolant-lubrication console, power cables, fluid transport hoses, and a variable speed motor drive with closed impeller. The high speed impeller uses the energy of centrifugal force to atomize the slurry. The particle size distribution obtained with this spray machine is generally narrow. In addition, product characteristics may be varied by the spinning atomizer design, speed and position in the chamber relative to air entrainment. Preferably, when employing the spinning atomizer, the spray dryer should have a large diameter configuration to avoid sticking of the atomized metal oxide particles to the dryer chamber walls. Slurries of metal oxides may be atomized using two-fluid nozzles where the atomizing force is pressurized air, single-fluid pressure nozzles where the atomizing force is the pressure of the slurry itself released through an orifice, and centrifugal atomization by a spinning wheel or other suitable atomization method. The atomizing pressures, or the speed of rotation in the case of wheel atomization, and the slurry feed rates may be varied as a partial control of particle size. It is also possible to control the particle size of the spray dried metal oxide beads by varying the percentage of solids in the feed slurry. The atomizing force and feed rate should be adjusted to the configuration, size and volumetric air flow of a given drying chamber in order that atomized particles do not contact drying chamber surfaces while still wet. In accordance with the process of this invention the percentage of solids in the feed slurry may be varied from about 15.0 to about 80.0 percent by weight of oxides slurried in the liquid medium. If a deflocculent material is added to the metal oxide slurry, the concentration of deflocculent may be varied from about 0.01 to about 2.0 percent by weight of the oxide solids. Although considerable latitude exists in regard to the metal oxide particle sizes employed for the slurry, metal oxide particles having an average particle size less than about 25 microns are preferred to avoid high settling rates in the slurry. It has been found that no binder material need be added to the feed slurry in order to preserve the shape and integrity of the atomized metal oxide beads formed during the spray drying and collecting steps of the process of this invention. The elimination of a binder material in the formation of spray dried metal oxide beads has been found to provide a denser and stronger ferrite material following sintering of the spray dried beads. The elimination of binder material from spray dried metal oxide beads is preferred because it has been found that binder material promotes bead-to-bead agglomeration or adherence during the sintering step. The spray dried metal oxide beads may be collected in drying chambers of suitable size. Spray dried metal oxide beads have been collected in a chamber 30 inches in diameter and 6 feet in height, with volumetric air flow of 250 cfm. With a system of this type, a product collection rate of about 50 pounds per hour may be maintained. The same metal oxide slurry may be dried in a chamber 12 feet in diameter and 20 feet in height, with volumetric air flow of about 12,000 cfm. When employing this latter system, a product collection rate of about 400 pounds per hour of spray dried metal oxide material may be maintained. It has been found that both types of dryer systems will produce a spray dried metal oxide product in the size range for a particular electrostaticographic use, for example, on the order of 50 to 500 microns. In addition, both co-current and counter-current drying systems yield satisfactory products. The temperature of the drying air may be varied from about 400°F to about 900°F at the inlet and from about 200°F to about 700°F at the outlet with satisfactory results.

When the sintered ferrite material is to be employed in the electrostaticographic art, it is desirable that the ferrite material when employed as a carrier possess certain basic properties. The ferrite carrier should have uniform electrostaticographic properties such as triboelectricity, magnetic permeability, and electrical conductivity as to meet machine performance requirements. The ferrite carrier should be substantially uniform in size and sufficiently dense individual beads in order to minimize possible bead sticking to the photo-receptor. The ferrite carrier should have uniform surface characteristics with a minimum of surface contamination. Finally, the ferrite carrier should be of a uniform shape with maximum roundness and sphericity. Any suitable type of sintering furnace may be employed in the sintering step of the process of this invention. Typical sintering furnaces include a static furnace, a rotary kiln, or a grate loaded bed furnace. The static furnace type will generally provide for long residence times. The rotary kiln type of sintering furnace generally provides uniform product reaction, consistent residence time and high capacity throughput. When employing a rotary kiln sintering furnace, a special media such as a flow promoting ingredient, for example, aluminum oxide, zirconium oxide, or other materials may be added in combination with the metal oxide beads to...
minimize or avoid bead-to-bead agglomeration and bead to furnace wall sticking. Preferably, the flow promoting ingredient is approximately the same size as the spray dried metal oxide beads because bead-to-bead agglomeration and bead to furnace wall sticking is substantially eliminated. Thus, if the spray dried beads are about 100 microns, the flow promoting ingredient should also be about 100 microns. Further, such a flow promoting ingredient may also influence the electrostatographic properties of the ferrite carrier material. In addition, to further avoid or minimize metal oxide bead sticking to rotary furnace walls, a scraping device may be employed individually or in combination with the flow promoting ingredient. In any event, the sintering of metal oxide beads should be under controlled conditions as to preserve the shape and particular nature of the beads while providing a uniform furnace residence time to produce maximum bead uniformity and desired properties.

Firing of the metal oxide spray dried beads at elevated temperatures to induce reaction of the ferrite components is generally carried out between 1,150° and 1,600°C. Actually, lower and higher temperatures may be used, but this is dictated by the processing time, the furnace materials of construction generally available, the ferrite formulation and the resulting strength of the fired bead. Generally, if a nickel-zinc ferrite carrier material is fired at 1,100°C for less than 1 hour, the carrier material may lack mechanical strength and sufficient magnetic permeability. On the other hand, firing about 1,600°C will generally place undue demands upon production equipment. If a low firing temperature is chosen, for example, 900°C, a longer firing time is generally required to achieve sufficient solid state reaction than if one chooses to fire at a higher temperature, for example, 1,400°C or 1,500°C. This is particularly important with respect to the resulting mechanical strength of the carrier material. To achieve the desired electrostatographic response, based on firing, the firing time and temperature relationship is important to establish the minimum firing conditions relative to the bead strength. Optimum electrostatographic ferrite carrier properties are obtained at sintering temperatures ranging from about 1,300°C to about 1,400°C with a residence time of about 10 to about 60 minutes. The preferred range of sintering temperatures is from about 1,150°C to about 1,500°C with a residence time of about 10 to about 180 minutes because the ferrite materials are magnetic, have a polycrystalline spinel structure, are highly resistive, and provide the maximum electrostatographic response. Satisfactory electrostatographic ferrite carrier properties are also obtained at sintering temperatures ranging from about 900°C to about 1,600°C with a residence time of about 5 minutes to about 5 hours. In any event, the sintering conditions should be sufficient to provide the desired polycrystalline spinel ferrite structure.

The firing atmosphere used is also important in that it influences oxygen content and thus the oxidation state of the metal ions present in the forming crystal structure. Here also, the conductivity of the ferrite carrier is influenced by an oxygen rich or deficient atmosphere. An example of the influence of the firing atmosphere is clearly demonstrated in the preparation of a ferrous-ferric ferrite from ferric oxide. When the material is fired in an oxidizing atmosphere, inferior magnetic properties are obtained whereas firing in a suitable reducing atmosphere provides acceptable magnetic properties.

Any suitable size of sintering furnace may be employed in the sintering step of the process of this invention. Rotary furnaces are preferred because they generally provide a consistent residence time, uniformity of product reaction, and high capacity throughput. Thus, 100 gram samples of metal oxide beads spray dried in accordance with the process of this invention may be successfully processed through a laboratory sized 3 inch laboratory tube rotary furnace. Several pound samples may be presintered at lower temperatures and successfully sintered in a pilot plant sized 5 inch diameter tube rotary furnace. Tonnage lots may be processed in a 12 inch diameter, gas fired, rotary furnace at rates of about 25 pounds per hour of product and at higher throughput rates. If pre-sintering is desirable, the pre-sintered conditions consist of pre-sintering the spray dried metal oxide beads in a rotary furnace at about 900°C to about 1,300°C with about a 10 to 15 minute residence time because these conditions provide bead strengthening and densification which assists in preservation of bead shape and integrity during the final sintering step. This sintering procedure provides sufficient reaction time to insure desired electrostatographic and magnetic properties of the ferrite carrier material. Following sintering, rotary cooling with about a 5 to 10 minute residence time generally provides continuous agitation of the ferrite bed during its transition from the firing temperature to that of the final cooling. This method of cooling minimizes bed agglomeration and further allows uniform discharge of a free flowing powder. Desired electrostatographic properties of ferrite carrier materials are also influenced by the cooling rate after firing. Magnetic permeability, electrical conductivity, and triboelectricity can be varied by varying the cooling rate. For example, the electrical resistivity is decreased by two to three orders of magnitude by rapid cooling such as a short period of 2 to 3 minutes.

Surprisingly, it has been found that no binder material or additive other than a deflocculent need be mixed with the feed slurry of the metal oxide starting materials. Spray dried spherical metal oxide beads formed without binder unexpectedly retain their shape and integrity during the spray drying, collecting, classifying, and sintering steps. The absence of binder material benefits the process in that the slurry is less apt to clog nozzle orifices under pressure and also, equally important, the drying temperature is not thereby limited.

That is, when a binder material is present, the drying temperature is usually limited to prevent loss of the binder by oxidation. In addition, the use of higher drying temperatures allows an increase in the slurry feed rate to the spray dryer. If, however, a binder is employed it may comprise any suitable fugitive film forming material. Typical fugitive film forming binder include polyvinyl alcohol, dextrin, lignosulfonates and methyl cellulose.

In accordance with the process of this invention it has been found beneficial to employ a deflocculent with the metal oxide slurry. Any suitable deflocculent may be employed. Typical deflocculents include the ammonium or sodium salt of polymethacrylic acid, pyrogallic acid, tannic acid and humic acid; and the ammonium or sodium salts of tripolyphosphate and hexametaphosphate. A deflocculent such as Darvan 7, which is the sodium salt of polyethylenimine acid and is available
from the R. T. Vanderbilt Company, generally promotes the preparation of a concentrated metal oxide slurry having a solids content of up to about 80 percent by weight in water based on the total weight of the slurry. Further, in spite of this remarkably high solids content, the metal oxide feed slurry may be pumped to the spray drier and atomized without clogging in a pressure nozzle or wheel atomizer. In addition, where about 50 to about 500 micron beads are desirable, the high solid content of the metal oxide slurry contributes to attainment of such particle sizes. Further, the high concentration of oxides reduces the equipment and energy requirements necessary to form the particles.

Any suitable pigmented or dyed electrostatic toner material may be employed with the ferrite carrier materials produced in accordance with the process of this invention. Typical toner materials include: gum copal, gum sandarac, resin, cumaroneindene resin, asphaltum, gilsonite, phenolformaldehyde resins, rosin-modified phenolformaldehyde resins, methacrylic resins, polystyrene resins, polypropylene resins, epoxy resins, polyethylene resins and mixtures thereof. The particular toner material to be employed obviously depends upon the separation of the toner particles from the ferrite carrier materials in the triboelectric series. As is well known in the art, sufficient separation should exist to permit the toner to electrostatically cling to the surface of the carrier. Among the patents describing electroscopic toner compositions are U.S. Pat. No. 2,659,670 to Copley; U.S. Pat. No. 2,755,308 to Landrigan; U.S. Pat. No. 3,079,342 to Insalaco; U.S. Pat. Reissue No. 25,136 to Carlson and U.S. Pat. No. 2,788,288 to Reimfrank, et al. These toner materials generally have an average particle diameter between about 1 and about 30 microns. Generally speaking, satisfactory results are obtained when about 1 part toner is used with about 10 to about 200 parts by weight of carrier.

Nickel-zinc ferrite and manganese-zinc ferrite carrier materials produced in accordance with the process of this invention are preferred because they have triboelectric properties which vary from 8 to 40 microcoulombs per gram of toner depending on the specific toner used. Generally, the triboelectric value of the ferrite carriers decreases as the amount of iron oxide present is increased. Increasing the iron contents beyond the stoichiometric amount of two moles per mole of divalent metal and firing at temperatures above 1,200°C includes the formation of divalent iron. The presence of divalent and trivalent iron causes an increase in the electrical conductivity of the ferrite materials. Thus, the extent of divalent iron formed and the conductivity of the ferrite and resulting developed electrostatic latent image background desired may be controlled within broad limits. Therefore, a ferrite carrier material having high electrical conductivity generally provides a developed electrostatic latent image with low background.

Generally, the ability to magnetically hold a ferrite carrier material of the nickel-zinc ferrite type in a magnetic brush configuration diminishes as the nickel to zinc ratio is decreased in the composition. At the various firing conditions, a significant loss in magnetic permeability is noted at nickel to zinc ratios of less than about 0.3. In electrostaticographic machine evaluations it is found that the nickel zinc ferrite carrier materials provide optimum electrostaticographic response when the nickel to zinc molar ratio of about 0.3 or greater is present in the ferrite formulations. In addition, ferrites represented by $M_1M_2Fe_3O_7\pm\delta$ prepared in accordance with the process of this invention have satisfactory electrostaticographic properties when employed as carriers for electrostaticographic developers when $M_1$ and $M_2$ comprise between about 0.1 to about 0.9 moles of metal oxide such as those described above and both $M_1$ and $M_2$ total 1.0, and x comprises about 1.4 to about 4.0 moles of iron. All the ferrite carriers exhibit magnetic permeability adequate for magnetic brush operation when sintered for about 5 minutes to about 5 hours at temperatures between about 900°C and about 1,600°C.

In accordance with the process of this invention, it is possible to form spherical metal oxide spray dried beads by atomizing and drying a slurry of metal oxide starting materials without the addition of a binder material. Thus, this process avoids the conventional requirement of mixing a binder material such as an artificial resin with a metal oxide slurry in order to form metal oxide beads that retain their particular shape and integrity after spray dried, prior to sintering, and also during sintering of the spray dried metal oxide beads to convert them to ferrites. In addition, this process avoids the step of pressing or compacting the metal oxide mixtures prior to sintering. Further, firing temperatures between about 900°C and about 1,600°C may be employed in sintering the spray dried metal oxide beads without substantial bead-to-bead agglomeration since no binder material is used. This process also permits storage of the spray dried metal oxide beads prior to their sintering without problems of caking, bead fracture, or significant loss of physical, chemical, and mechanical properties. In addition, sticking of beads to the surfaces of sintering equipment is substantially avoided. Ferrite materials produced according to this process have been found to possess improved uniformity of particle size and particle size distribution. The uniformity of particle size that may be obtained by the process of this invention has been found to provide ferrite carrier materials which have properties that are extremely desirable when employed in electrostaticographic development processes. This process further provides economic efficiency and simplicity in the production of ferrite materials. This process avoids agglomeration and clogging problems in processing equipment common to conventional methods of preparing ferrite materials. It also removes restrictions imposed on conventional methods of preparing ferrite materials. It is capable of producing extremely small particle size ferrite materials and ferrite materials of a desired size. This process is particularly advantageous in preparing ferrite materials ranging from about 50 to 500 microns. Finally, this process may be employed to form ferrite materials of various compositions and characteristics.

**DESCRIPTION OF THE PREFERRED EMBODIMENTS**

The following examples further define, describe and compare exemplary methods of preparing ferrite materials according to the process of the present invention. Parts and percentages are by weight unless otherwise indicated. The examples, other than the control examples, are intended to illustrate the various preferred embodiments of the present invention.
In the following examples, the unit employed for spray drying is Bowen Tower Laboratory Spray Dryer Manufactured by Bowen Engineering Incorporated, North Branch, N.J. This unit has a bottom chamber collector and a single cyclone collector. This chamber collector is 30 inches in diameter and the vertical chamber height is 6 feet. Nozzle atomization is upward with a maximum vertical particle path height of about 8 feet. The incoming air is heated by direct gas firing.

EXAMPLE I

A powdered metal oxide and water feed slurry comprising about 4,000 grams of about 64.5 percent ferric iron oxide, having a particle size of about 1 micron, about 12.8 percent zinc oxide, having a particle size of about 0.1 micron, and about 22.7 percent manganese oxide having a particle size of about 1 micron or smaller, and about 1,700 grams of water is prepared using a high speed dispersator. About 2 percent by weight of Elvanol 51-05, a polyvinyl alcohol available from E. I. DuPont Co. is added to the oxide slurry as a binder. About 65 milliliters of about 25 percent by weight solution of Darvan 7, the sodium salt of a polymethacrylic acid available from the R. T. Vanderbilt Company is added to the oxide slurry mixture. The slurry mixture is about 70 percent by weight of solids. The slurry is screened using 20 mesh sieves. This slurry is fed to the spray dryer at a feed rate of between about 145 and about 225 milliliters per minute, a drying air input temperature of about 525°F, and an outlet temperature of about 320°F. The type of atomizer is a two-fluid nozzle and the atomizing force is about 14 psig of air pressure. Spherical spray dried metal oxide beads of about 100 microns average particle size are obtained. It is observed, however, that clogging of the nozzles is found to occur. The occurrence of nozzle clogging is attributed to the presence of the polyvinyl alcohol binder material in the feed slurry. In addition, the air inlet temperature is limited due to the presence of the binder material.

EXAMPLE II

A powdered metal oxide and water feed slurry comprising about 4,000 grams of about 64.5 percent ferric iron oxide having a particle size of about 1 micron, about 12.8 percent zinc oxide having a particle size of about 0.1 micron, and about 22.7 percent manganese oxide having a particle size of about 1 micron or smaller, and about 1,700 grams of water is prepared using a high speed dispersator. About 2 percent by weight of Elvanol 51-05, a polyvinyl alcohol available from the R. T. Vanderbilt Company is added to the oxide slurry mixture. The slurry mixture is about 70 percent by weight of solids. The slurry is screened using 20 mesh sieves. This slurry is then fed to the spray dryer at a feed rate of between about 530 and about 640 milliliters per minute, a drying air input temperature of about 520°F, and an outlet temperature of about 280°F. The type of atomizer is a two-fluid nozzle and the atomizing force is about 12 psig of air pressure. Spherical spray dried metal oxide beads of about 100 microns average particle size are obtained. It is observed, however, that clogging of the nozzles is found to occur. The occurrence of nozzle clogging is attributed to the presence of the polyvinyl alcohol binder material in the feed slurry. The air inlet temperature is also limited due to the presence of the binder material so as to prevent oxidation of the binder material and thus the dryer chamber ceiling and core surfaces are wet and the beads are insufficiently dried.

EXAMPLE III

Example I is repeated except that the polyvinyl alcohol binder material is omitted. All other conditions are kept the same. It is found that spherical spray dried metal oxide beads of about 100 microns are obtained. It is also found that the nozzles do not clog. In addition, in a subsequent trial employing the same conditions herein, the drying air input temperature is increased to about 900°F thereby enabling a decrease in the processing time by increasing the slurry feed rate.

EXAMPLE IV

Example II is repeated except that the polyvinyl alcohol binder material is omitted. All other conditions are kept the same except that the drying air input temperature is increased to about 900°F, and the outlet temperature to about 400°F. It is found that spherical spray dried metal oxide beads of about 100 microns are obtained. It is also found that the nozzles do not clog and also that the ceiling and core surfaces are dry and the beads are dry.

EXAMPLE V

A powdered metal oxide and water feed slurry comprising about 3,000 grams of about 70.3 percent ferric iron oxide about 9.3 percent zinc oxide, and about 20.4 percent nickel oxide, and about 1,000 grams of water is prepared from a nickel-zinc ferrite presintered at 1,200°C, and ground to a particle size of less than 5 microns using a high speed dispersator. About 100 milliliters of about 25 percent by weight solution of Darvan 7, the sodium salt of a polymethacrylic acid available from the R. T. Vanderbilt Company is added to the oxide slurry mixture. The slurry mixture is about 73 percent by weight of solids. The slurry sieves are screened using 20 mesh sieves. This slurry is then fed to the spray dryer at a feed rate of between about 330 and about 380 milliliters per minute, a drying air input temperature of about 935°F, and an outlet temperature of about 400°F. The type of atomizer is a two-fluid nozzle and the atomizing force is about 12 psig of air pressure. Denser and more spherical spray dried metal oxide beads of about 100 microns are obtained. The nozzles do not clog or plug. The dryer surfaces are dry. The beads collected in the dryer chamber are a dry, free-flowing powder.

EXAMPLE VI

A powdered metal oxide and water feed slurry comprising about 3,000 grams of about 63.0 percent ferric iron oxide having a particle size of about 1 micron, about 26.4 percent zinc oxide having a particle size of about 0.1 micron, and about 10.6 percent nickel oxide having a particle size of up to 10 microns, about 750 grams of water is prepared from materials presintered at 1,200°C using a high. dispersator. About 100 milliliters of about 25 percent by weight solution of Darvan 7, the sodium salt of a polymethacrylic acid available from the R. T. Vanderbilt Co. is added to the oxide slurry mixture. The slurry mixture is screened using 20 mesh sieves. This slurry is then fed to the spray drier at a feed rate of between about 210 and about 240 millili-
ters per minute, a drying air input temperature of about 640°F, and an outlet temperature of about 360°. The type of atomizer is a two-fluid nozzle and the atomizing force is about 12 psig of air pressure. Denser and more spherical spray dried metal oxide beads of about 100 microns are obtained. No clogging or plugging of the nozzles is observed. The drier surfaces are dry. The beads collected in the dryer chamber are a dry, free-flowing powder.

EXAMPLE VII

A powdered metal oxide and water feed slurry comprising about 3,000 grams of about 70.3 percent ferric iron oxide having a particle size of about 1 micron, about 9.3 percent zinc oxide having a particle size of about 0.1 micron, and about 20.4 percent nickel oxide having a particle size of up to 10 microns, and about 1,000 grams of water is prepared from material presintered at 1,200°C using a high speed dispersator. About 100 milliliters of about a 25 percent by weight solution of Darvan 7, the sodium salt of a polyacrylamide acid available from the R. T. Vanderbilt Company is added to the oxide slurry mixture. The slurry mixture is about 73 percent by weight of solids. The slurry is screened using 20 mesh sieves. This slurry is then fed to the spray dryer at a feed rate of between about 330 and about 380 milliliters per minute, a drying air input temperature of about 935°F, and an outlet temperature of about 400°F. The type of atomizer is a two-fluid nozzle. Dense, spherical spray dried metal oxide beads of about 130 microns are obtained. The beads collected in the dryer chamber are a dry, free-flowing powder.

Analyses of the spray dried products of Examples I through VII is performed on statistically sampled portions. The analyses include microscopic examination and sieve analysis. It is found that substantially no breakdown of the unsintered beads occurs in any of the subsequent handling, classification, screening and feeding operations, even without binder material in the spray dried beads. As is apparent, these results have an effect on all other processing steps thereby allowing recycling of unfired spray dried beads in spray drying and permitting wider latitude of operational conditions in the firing step.

EXAMPLE VIII

Spray dried metal oxide beads prepared in accordance with the process of Example I are placed in a direct gas-fired rotary kiln having a 15 inch internal diameter and a length of about 12 feet, 6 inches. The feed rate to the rotary kiln is about 100 pounds per hour. Continuous operation is attempted with a temperature at the free end of the rotary kiln of about 900°C and a temperature at the discharge end of the rotary kiln of about 1,400°C. It is observed that flaming of the beads occurs and that equilibrium conditions such as the desired retention time of the beads in the rotary kiln are difficult to maintain during the firing due to sticking of the beads to the kiln walls. It is also difficult to establish a continuously moving bed of beads in the kiln without placing a scraper bar in the kiln. It is further observed that the ferrite product at the discharge end of the rotary kiln is not entirely a particulate, free-flowing powder and that bead-to-bead agglomeration is prevalent. It is postulated that the oxidation of the binder material may be the basis for bead sticking to the rotary kiln walls and bead to bead agglomeration.

EXAMPLE IX

Spray dried metal oxide beads prepared in accordance with the process of Example III are placed in the rotary kiln described in Example VIII. All other operating conditions are substantially the same. It is observed that equilibrium conditions can be more easily maintained. Minor to moderate bead-to-bead agglomeration and sticking of beads to the kiln walls is observed.

EXAMPLE X

Spray dried metal oxide beads prepared in accordance with the process of Example IV are placed in the rotary kiln described in Example VIII. All other operating conditions are substantially the same except that aluminum oxide particles having a diameter of about ¾ inch are added to the rotary kiln. Only minor bead-to-bead agglomeration and sticking of beads to the kiln walls is observed. A substantially continuously moving bed of beads can be maintained without rapping on the rotary kiln walls. Addition of the aluminum oxide assists the flow of the ferrite bed, prevents bead-to-bead agglomeration, and sticking of beads to the kiln walls.

EXAMPLE XI

Spray dried metal oxide beads prepared in accordance with the process of Example VII are placed in the rotary kiln described in Example VIII. All other operating conditions are substantially the same except that aluminum oxide particles having a diameter of about 100 to about 130 microns are included with the metal oxide beads. It is found that equilibrium conditions can be substantially maintained. Only minor bead-to-bead agglomeration and sticking of beads to the kiln walls is observed. A substantially continuously moving bed of beads can be maintained without rapping on the rotary kiln walls. It is concluded that addition of the aluminum oxide assists the flow of the ferrite bed, prevents bead-to-bead agglomeration and sticking of beads to the kiln walls. It is observed that the addition of the smaller particle size aluminum oxide also minimizes fracture of ferrite beads.

EXAMPLE XII

Spray dried metal oxide beads prepared in accordance with the process of Example VII are placed in the rotary kiln described in Example VII. All other operating conditions are substantially the same except that zirconium oxide particles having a diameter of about 100 to about 130 microns are included with the metal oxide beads. It is found that equilibrium conditions can be substantially maintained. Only minor bead-to-bead agglomeration and sticking of beads to the kiln walls is observed. A substantially continuously moving bed of beads can be maintained without rapping on the rotary kiln walls. It is concluded that addition of the zirconium oxide assists the flow of the ferrite bed, prevents bead-to-bead agglomeration, sticking of beads to the kiln walls, and minimizes fracture of ferrite beads. Also, the zirconium oxide advantageously increases the conductivity of the ferrite.

Using the values of the bulk densities of 98 pounds per cubic foot for the unfired metal oxide beads of Example VII and 156 pounds per cubic foot for the fired metal oxide beads of Example XI, an average diametrical shrinkage as a result of the firing is calculated to be
about 14 percent. Rotex screens of 177 microns and 77 microns are used for screening of the fired beads. No significant problem is encountered in screening the fired beads.

Although specific materials and conditions are set forth in the above exemplary processes of making ferrite materials by the process of this invention, these are merely intended as illustrations of the present invention. There are other ferrite materials, solvents, substitunents and processes such as those listed above which may be substituted for those in the Examples with similar results.

Other modifications of the present invention will occur to those skilled in the art upon a reading of the present disclosure. These are intended to be included within the scope of this invention.

What is claimed is:

1. An electrostaticographic imaging process comprising the steps of forming an electrostatic latent image on a surface and developing said electrostatic latent image by contacting said electrostatic latent image with a developer mixture comprising finely-divided toner particles electrostatically clinging to the surfaces of carrier beads having a particle size from about 30 to about 1,000 microns, each of said carrier beads comprising nickel-zinc ferrite beads comprising about 0.1 to about 0.9 moles of nickel, about 0.1 to about 0.9 moles of zinc, and about 1.4 to about 4.0 moles of iron, said carrier beads being further characterized as being substantially dense and uniform in size and shape with maximum roundness and sphericity and having substantially uniform electrostaticographic properties such as triboelectricity, magnetic permeability, and electrical conductivity, whereby at least a portion of said finely-divided toner particles are attracted to and held on said surface in conformance to said electrostatic latent image.

2. An electrostaticographic imaging process according to claim 1 wherein said developer mixture comprises about 1 part by weight of said toner particles and between about 10 and about 200 parts by weight of said nickel-zinc ferrite beads.

3. An electrostaticographic imaging process according to claim 1 wherein said toner particles have an average particle diameter between about 1 and about 30 microns.

4. An electrostaticographic imaging process according to claim 1 wherein said nickel-zinc ferrite beads have a triboelectric charging capacity of from about 8 to about 40 microcoulombs per gram of said toner particles.

5. An electrostaticographic imaging process comprising the steps of forming an electrostatic latent image on a surface and developing said electrostatic latent image by contacting said electrostatic latent image with a developer mixture comprising finely-divided toner particles electrostatically clinging to the surfaces of carrier beads having a particle size from about 30 to about 1,000 microns, each of said carrier beads comprising manganese-zinc ferrite beads comprising about 0.1 to about 0.9 moles of manganese, about 0.1 to about 0.9 moles of zinc, and about 1.4 to about 4.0 moles of iron, said carrier beads being further characterized as being substantially dense and uniform in size and shape with maximum roundness and sphericity and having substantially uniform electrostaticographic properties such as triboelectricity, magnetic permeability, and electrical conductivity, whereby at least a portion of said finely-divided toner particles are attracted to and held on said surface in conformance to said electrostatic latent image.

6. An electrostaticographic imaging process according to claim 5 wherein said developer mixture comprises about 1 part by weight of said toner particles and between about 10 and about 200 parts by weight of said manganese-zinc ferrite beads.

7. An electrostaticographic imaging process according to claim 5 wherein said toner particles have an average particle diameter between about 1 and about 30 microns.

8. An electrostaticographic imaging process according to claim 5 wherein said manganese-zinc ferrite beads have a triboelectric charging capacity of from about 8 to about 40 microcoulombs per gram of said toner particles.

9. An electrostaticographic imaging process comprising the steps of forming an electrostatic latent image on a surface and developing said electrostatic latent image by contacting said electrostatic latent image with a developer mixture comprising finely-divided toner particles electrostatically clinging to the surfaces of carrier beads having a particle size from about 30 to about 1,000 microns, each of said carrier beads comprising nickel-zinc ferrite beads comprising about 0.1 to about 0.9 moles of nickel, about 0.1 to about 0.9 moles of zinc, and about 1.4 to about 4.0 moles of iron, said carrier beads having been produced by preparing a slurry of ferrite forming metal oxides in a liquid, spray drying said slurry of said ferrite forming metal oxides to form substantially spherical metal oxide beads and sintering said substantially spherical metal oxide beads to form ferrite beads while maintaining the spherical shape and particulate nature of the beads, said carrier beads being further characterized as being substantially dense and uniform in size and shape with maximum roundness and sphericity and having substantially uniform electrostaticographic properties such as triboelectricity, magnetic permeability, and electrical conductivity, whereby at least a portion of said finely-divided toner particles are attracted to and held on said surface in conformance to said electrostatic latent image.

10. An electrostaticographic imaging process according to claim 9 wherein said metal oxide beads have been sintered at a temperature of between about 900°C and about 1,600°C for between about 5 minutes to about 5 hours.

11. An electrostaticographic imaging process according to claim 9 wherein said developer mixture comprises about 1 part of said toner particles and between about 10 and about 200 parts by weight of said carrier beads.

12. An electrostaticographic imaging process according to claim 9 wherein said nickel-zinc ferrite comprises a nickel to zinc molar ratio of at least about 0.3

13. An electrostaticographic imaging process comprising the steps of forming an electrostatic latent image on a surface and developing said electrostatic latent image by contacting said electrostatic latent image with a developer mixture comprising finely-divided toner particles electrostatically clinging to the surfaces of carrier beads having a particle size from about 30 to about 1,000 microns, each of said carrier beads comprising manganese-zinc ferrite beads comprising about 0.1 to
about 0.9 moles of manganese, about 0.1 to about 0.9 moles of zinc, and about 1.4 to about 4.0 moles of iron, said carrier beads having been produced by preparing a slurry of ferrite forming metal oxides in a liquid, spray drying said slurry of said ferrite forming metal oxides to form substantially spherical metal oxide beads and sintering said substantially spherical metal oxide beads to form ferrite beads while maintaining the spherical shape and particulate nature of the beads, said carrier beads being further characterized as being substantially dense and uniform in size and shape with maximum roundness and sphericity and having substantially uniform electrostogtographic properties such as triboelectricity, magnetic permeability, and electrical conductivity, whereby at least a portion of said finely-divided toner particles are attracted to and held on said surface in conformance to said electrostatic latent image.

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