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Hagenbach et al.

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[54] **ELECTROSTATIC IMAGING PROCESS USING NODULAR CARRIERS**

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Related U.S. Application Data

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[58] **Field of Search** .... 252/62.1; 96/1 R, 1 SD; 117/17.5

[56] **References Cited**

UNITED STATES PATENTS

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3,079,342	2/1963	Insalace	252/62.1
3,124,457	3/1964	Schwertz	117/17.5
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[57] **ABSTRACT**

An electrostatographic developer mixture comprising nodular carrier beads, the nodular beads having a number average size distribution in the range of 50 to 1,000 microns, and between about 95 to 99.5 weight percent, based upon the developer mixture, of finely divided toner particles electrostatically clinging to the surface of the nodular carrier beads. Such developer mixtures are useful in the development of latent electrostatographic images by cascade and magnetic brush development techniques.

12 Claims, No Drawings

ELECTROSTATIC IMAGING PROCESS USING NODULAR CARRIERS

This is a division of application Ser. No. 151,995, filed June 10, 1971, and now U.S. Pat. No. 3,767,598.

This invention relates in general to imaging systems and, more particularly, to improved imaging materials.

The formation and development of images on the surface of photoconductive materials by electrostatic means is well known. The basic xerographic 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 resulting latent electrostatic image by depositing on the image, a finely divided electroscopic material referred to in the art as "toner." The toner is attracted to those areas of the layer which retain a charge, thereby forming a toner image corresponding to the latent electroscopic image. This powder image may then be transferred, usually electrostatically, to a support surface such as paper. The transferred image may subsequently be permanently affixed to the support surface by heat, or other suitable fixing means such as solvent or overcoating treatment may be used instead.

Many methods are known for applying the electroscopic particles to the latent electrostatic image to be developed. One development method as disclosed by E. N. Wise in U.S. Pat. No. 2,618,582 is known as "cascade" development. In this method, developer material, comprising relatively large carrier particles having finely divided toner particles electrostatically clinging to the surface of the carrier particles, is conveyed to, and rolled, or cascaded across the latent surface bearing the latent electrostatic image. The charged portions of the surface have a charge of the same polarity as, but stronger than the carrier particles. Toner and carrier particles having opposite polarities are selected so that the toner particles cling to the carrier particles. In order to develop a negatively charged latent electrostatic image, a toner and carrier combination should be selected in which the toner is triboelectrically positive in relation to the carrier. Conversely, to develop a positively charged latent electrostatic image, a toner and carrier combination in which the toner is triboelectrically negative in relation to the carrier is used. This triboelectric relationship between the toner and carrier depends on the relative positions of the materials in the "triboelectric series." In this series materials are arranged in ascending order of ability to take on a positive charge. Each material is positive with respect to any material classified below it in the series; and negative with respect to any material above it in the series. As the mixture cascades or rolls across the image-bearing surface, the toner particles are electrostatically attracted from the carrier partially to the charged portions of the image bearing surface, whereas they are not electrostatically attracted to the uncharged or background portions of the image which they contact. The "cascade" development process has the distinct advantage that most of toner particles accidentally deposited on the background portion 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 particles and unused toner particles are then recycled. The cascade development process is extremely good for the development of line copy images, and is the most widely used commercial xerographic development technique. A general purpose office copying machine incorporating this technique is described in U.S. Pat. No. 3,099,943.

Another technique for developing electrostatic images is the "magnetic brush" process as disclosed, for example, in U.S. Pat. No. 2,874,063. In this process, a developer material containing toner and magnetic carrier particles is attracted to and is carried by a magnet. The magnetic field causes alignment of the magnetic carrier particles in a brush-like configuration. When this "magnetic brush" is brought into contact with an electrostatic image-bearing surface, the toner particles are attracted from the carrier particles of the "brush" to the charged areas of the image-bearing surface, but not to the uncharged areas. Since the charged areas have an imagewise configuration, the toner material clings to the surface in imagewise configuration, thus developing the latent image.

Many other methods, such as the "touchdown" development disclosed by C. R. Mayo in U.S. Pat. No. 2,895,847, are known for applying electroscopic particles to the latent electrostatic image to be developed. The development processes as described above, together with numerous modifications are well known to the art through various patents and publications and through the widespread availability and utilization of electrostatographic imaging equipment.

In automatic reproduction equipment, it is conventional to employ as the imaging plate, a photoconductor on a conductive substrate in the form of a cylindrical drum or a flexible belt which is continuously rotated through a cycle of sequential operations including charging, exposing, developing, transferring and cleaning.

The plate is usually given a uniform positive charge by means of a corona generating device of the type disclosed by L. E. Walkup in U.S. Pat. No. 2,777,957 which is connected to a suitable source of high potential.

It is then discharged in imagewise configuration by exposure to a light image corresponding to the original to be copied. The resultant latent image is then developed with toner, and the developed image is transferred to a proximate copy receiving surface such as paper, by electrostatically charging the paper to cause it to electrostatically attract the developed image. After image transfer, the residual powder and carrier particles are removed before the plate is reused in subsequent cycles. This is generally accomplished by imparting an opposite charge to the photoconductive surface thereby nullifying any electrostatic attraction between the surface and the particles then rubbing the surface to physically remove all the remaining particles and exposing it to light to fully discharge the surface.

Typical electrostatographic cleaning devices include the "web" type cleaning apparatus as disclosed, for example, by W. P. Graff, Jr., et al. in U.S. Pat. No. 3,186,838. In the Graff, Jr., et al. patent, removal of the residual toner and carrier particles from the plate is effected by rubbing a web of fibrous material against the imaging surface. These inexpensive and disposable webs of fibrous material are gradually advanced in pressure and rubbing or wiping contact with the imaging surface to present a clean surface to the plate whereby substantially complete removal of the residual powder and carrier particles from the plate is effected.

While ordinarily capable of producing good quality images, conventional developing compositions suffer deficiencies in certain areas. In the reproduction of high contrast copies such as letters, tracings and the like, it is desirable to select toner and carrier materials so that their mutual electrification is relatively large, the degree of such electrification being governed in most cases by the distance between their relative positions in the triboelectric series. However, when otherwise compatible electroscopic powder and carrier materials are separated from each other by too great a distance in the triboelectric series, the resultant images are very faint because the attractive forces between the carrier and toner particles compete with the attractive forces between the latent electrostatic image and the toner particles. Although image density may be improved by increasing the toner concentration in the developer mixture, undesirably high background toner deposition, as well as increased toner impaction and agglomeration are encountered when the toner concentration in the developer mixture is excessive.

It has been considered highly desirable and preferable to employ smooth-surfaced carrier beads which are spherical in shape. Spherical particles accept relatively uniform surface charge and are relatively uniform in their attraction of toner particles. This results in more uniform toner deposition and consequently more uniform final copies. In addition, the spherical carrier beads are more frictionless and are less likely to cause scratching of the imaging surface. However, when it is desired to produce spherical carrier beads from metals, costly procedures are required.

The size, shape, physical characteristics and chemical composition of the carrier particles influence the quality of the developed image and the ability of the carrier to retain its original properties for long periods of use.

Generally, within the average size range of about 50 to 1,000 microns, all other variables being held constant, smaller particles carry a greater amount of toner material because they have a high surface-to-mass ration, but developed images tend to be grainly in appearance. Also the smaller the carrier particles, the greater their tendency to adhere to the photoconductive plate, an effect called "blocking." Blocking interferes with the transfer process and may damage the photoconductive surfaces.

Larger carrier particles bring toner particles into closer contact with the imaged surface, thus giving less grainy developed images. However, they tend to rake the toner in the image and because of the small surface-to-mass ration, attract less toner, thus producing an inefficient developer.

Thus, keeping all other variables constant, there are disadvantages in using either small or large size carrier particles, but smooth-surfaced spherical particles are considered more advantageous than carrier particles of other known shapes. However, in view of the shortcomings of such carrier materials, there is a need for new carrier materials with superior properties as compared to carriers which are presently available.

It is accordingly an object of the present invention to provide carrier materials which overcome the above-noted deficiencies of known carrier materials.

It is a further object of the present invention to provide carrier materials which are capable of giving developed images of high density, produce images with low background development, do not damage the photoconductive surface, have low sensitivity to variations in toner concentration, and can be flexibly prepared to meet varying carrier density and electrostatic requirements.

It is a further object of the present invention to provide novel electrostatographic developer compositions containing the improved carrier materials of this invention.

It is still a further object of the present invention to provide a new and improved electrostatographic imaging process employing the novel developer compositions of this invention.

Other objects of this invention will become evident from the following detailed description thereof.

The present invention is based upon the discovery that nodular carrier beads characterized by a pebbled surface with recurring recesses and protrusions giving the particles a relatively large external surface area provide excellent developer compositions for electrostatographic use. Such nodular carrier beads have high surface-to-mass ratio as compared with substantially smooth-surfaced carrier beads of the same mass. Using the carrier materials of the present invention, one can obtain the benefits of both large and small carrier beads while avoiding their shortcomings. Nodular carrier particles present a plurality of small spherical surfaces with recesses defining pockets for toner particles. When admixed with toner material in suitable proportions, a superior developer composition for electrostatographic development processes employing carrier-toner combinations (e.g., the aforedescribed magnetic brush development and cascade development techniques), is provided.

Many noteworthy advantages follow from use of the nodular carrier of this invention. Carriers with wide ranges of density and triboelectric values can be obtained because the nodular beads can be prepared by agglomeration of widely differing and customized formulations of particulate mixtures.

Nodular beads used in accordance with this invention, not only have greater surface-to-mass ratio to hold more toner beads (as compared to spherical carrier particles), but also tend less to grind the toner particles and each other to fines during development use. Thus, in cascade development, for example, when the nodular beads impinge upon each other, the impact is mostly absorbed on the outer surface of the beads and the toner material, most of which is in the pockets defined by the recesses between the surface protrusions essentially escapes impaction. This capacity of the nodular beads to reduce impactive damage to either the beads themselves or the toner material, results in much greater developer life than has heretofore been achieved.

The nodular carrier beads are three-dimensional solids approximately 50–1,000 microns in size, of roughly cuboidal, rounded, irregular or spheroidal shape, and with surface irregularities formed by numerous nodules and recesses. Though the beads may have randomly spaced voids or a slight degree of porosity, they should have predominantly solid cores. Preferred carrier beads have generally rounded nodules and are generally spheroidal in shape thus giving an appearance reminiscent of a raspberry or cluster of grapes.

The carrier beads of the present invention can be prepared by any of several processes. For example, small particles can be agglomerated by known granulating or pelletizing procedures, preferably in the presence of a binder, and, if desired, depending on the binder, the agglomerates can then be heated to give them hardness and strength. One generally useful method involves mixing a particulate carrier material with a binder and charging the mixture to an inclined rotary mixing plate over which is sprayed a liquid which has the effect of wetting the particles. As the mixing plate rotates, the agglomerates continue to grow. The largest agglomerates come to the surface and roll off at the ascending side of the lower edge of the mixing plate. The smaller agglomerates remain on the rotary plate until they are big enough. By variation of the angle of inclination of the rotary plate, the peripheral velocity, the location of the charging area where the material is introduced to the rotary plate, and the height of the peripheral edge of the rotary plate, the size range of the resultant agglomerates can be adjusted to within close tolerances.

The "green" agglomerated particles can then be subjected to firing, fusing or sintering treatment to produce a hard compacted nodular bead of the aforementioned description.

The particles which are agglomerated to form the nodular carrier beads of this invention may be spherical or non-spherical particulate materials. In the event that they are non-spherical, after the agglomeration step, it may be desired to spheroidize the particles, as by heating, to cause surface forces to draw the particles into a spherical shape.

The constitution of the carrier is not a critical part of this invention, the criteria for selection being the same as are applicable in the case of conventional carrier materials. The carrier must be capable of inducing a triboelectric charge on the toner particles, in order to attract and carry the toner particles to the latent image. Thus, the triboelectric relationship of the toner and carrier must be such that an acceptable development of the latent electrostatic image is produced, i.e., a dense image with low background development. A material which has a relatively high triboelectric relationship with the toner, produces low-density images with clean background because of the inability of the electrostatic image to attract sufficient toner particles from a carrier. A carrier material with low triboelectric relationship to the toner will develope very low-contrast electrostatic patterns but would also produce high background density. In order to obtain a practical developer, carrier materials not falling into these extreme patterns should be avoided. In use, the average triboelectric relationship decreases with time because of cumulative physical damage to the carrier.

Additionally, the carrier material must be one which is capable of forming beads which do not tend to cake, bridge or agglomerate during handling and storage. Adherence of carrier particles to reusable electrostatic imaging surfaces causes the formation of undesirable scratches on these surfaces during image transfer and surface cleaning steps. In addition, the carrier composition must be such that it is capable of resisting the deteriorating forces normally attendant continuous development processes which require the recycling of carrier particles by bucket conveyors partially submerged in the developer supply such as disclosed in U.S. Pat. No. 3,099,943. Finally, if the carrier is to be used in a magnetic brush development process, it must also be magnetic.

Therefore, the ideal carrier material for this invention is one which exhibits a proper triboelectric relationship with the toner, is capable of being formed into nodular particles of uniform size within close tolerances, and has a high degree of resistance to physical image and impaction which can impair this critical relationship.

Any material which satisfies the foregoing requirements can be used to prepare the carrier beads of this invention. For example, metals such as steel, copper, nickel, aluminum, brass and the like, and refractory materials such as carbides, nitrides, ceramics or glasses can be advantageously employed. The ceramic or glass material can be prepared from a wide variety of magnetic or non-magnetic refractory oxides as is well known in the art, including silica, alumina, lithium oxide, berylium oxide, magnesium oxide, calcium oxide, zinc oxide, strontium oxide, cadmium oxide, barium oxide, lead oxide, magnesium ozide, iron oxide, cobalt oxide, nickel oxide, iron oxide, and the like. Representative compositions which are useful in accordance with the present invention are disclosed in U.S. Pat. Nos. 2,565,111, 2,715,109, 2,962,444 and 3,193,503.

The selected material, whether it be glass, ceramic or metal, is particulated or comminuted by conventional grinding, milling, spray-drying or spray-cooling techniques to the desired size-distribution range which is generally between 1 and 100 microns, but is preferably in the more restricted range of 5 to 40 microns. If desired, the resultant particles, if they are irregularly shaped, can be spheroidized before being agglomerated by introducing them into a high velocity stream of a hot gas such as can be produced by a plasma generator. The melted particles are spheroidized due to internal forces and then quenched in a cold liquid such as water to solidify them.

The particulate carrier material, however produced, can be agglomerated to produce the aforementioned nodular carrier beads. A convenient method for accomplishing this result involves using conventional granulating equipment to roll particulate material with a liquid and a binder on an inclined rotary mixing plate. Other types of granulating devices, e.g., drum and pan granulators, which impart a tumbling action to the particles, such as those disclosed in U.S. Pat. No. 3,192,290 may also be used.

The rotating mixing plate method of forming the nodular beads by feeding the finely-divided carrier material on to a disc at a constant rate while selectively wetting the incoming feed, causes the rolling particles to come into intimate contact with each other. The capillary attraction of the particle surfaces, as well as short range contact forces, hold the particles together in the form of a green or moist agglomerate. The size and quality of the agglomerates are functions of many variables in the operation of the rotary mixing plate, several of which are set forth below:

1. Rotating plate speed
2. Rotating plate slope

3. Slope positions
4. Position of liquid spray nozzles
5. Rate of the carrier material to the plate

It is important that the rate of feed and wetting be maintained, once the correct settings are obtained, to insure that the product has a uniform size distribution within a narrow range.

It is apparent from the foregoing, that the agglomeration effect is dependent upon the presence of liquid which gives the particulate carrier material "balling" properties. Generally, the agglomerated particles do not have a sufficiently high level of strength to be used in electrostatographic development processes without either a binder material being added during agglomeration or a hardening treatment after agglomeration. Thus, when particles are agglomerated with plain water as the wetting liquid and then dried, the agglomerates are very frangible and certainly not suitable for electrostatographic development purposes. To overcome this weakness, it is possible to add a binder during agglomeration and/or subject the agglomerates to an after-treatment which has the effect of hardening them.

Binders which can be used to impart a great strength to the agglomerates are well known in the art. A suitable binder is sodium silicate. Other materials which can be used for this purpose include synthetic resins such as epoxy or acrylic resins, waxes, polyvinyl alcohol, dextrin, esters of saturated fatty acids, natural and synthetic adhesives and the like. Other materials which act as lubricants or plasticizers for the binders may be additionally incorporated into the feed material to aid in the agglomeration process.

Depending upon the binder which is used to form the green agglomerates, it may or may not be necessary to subject the green agglomerates to a hardening treatment. If the binder is a material such as epoxy resin which is self hardening, it is not absolutely essential that the agglomerates be subjected to a hardening aftertreatment. However, it is generally more convenient and practical to use binders such as sodium silicate and waxes, which in themselves do not provide the necessary strength to the carrier particles for direct use in electrostatographic development processes. The after-treatment generally involves subjecting the green carrier agglomerates to high temperature conditions, generally in a temperature range which effects the fusing or sintering of the carrier material and a chemical change in the binder used therefor. Heating is conveniently accomplished by admixing the green carrier agglomerates with a flowing hot gas such as can be produced in a combustion furnace, a plasma generator or an electric furnace. The temperature of the hardening treatment will in the first instance depend upon the nature of the carrier material. Since refractory materials are generally employed and the heat treatment is most effective when the carrier material softens to some extent during the treatment, the temperature will be at least 1,000°F. Most usually it will be in the range of 2,000° to 2,700°F., but the temperature can be varied to take into account the residence time of the green carrier agglomerates in the hot flowing gases.

The hardening post-treatment is of importance in another respect. Under the influence of heat, the agglomerated carrier particles begin to soften and, due to internal forces, they become rounded. Thus, the heat treatment not only adds strength to the agglomerates but also smoothes out large irregularities in the surfaces of the agglomerated carrier particles.

Another way of producing nodular carrier beads is by precipitation of a salt, a metal, or a metal oxide from solution. Under controlled conditions the individual particles of the resultant precipitate are in the form of a cluster of smaller particles of generally botryoidal structure. One method of forming nodular particles in this manner is disclosed in Proceedings Thirteenth Annual Meeting, Metal Powder Association, Apr. 30 to May 1, 1957, in an article entitled "Production and Characteristics of Chemically Precipitated Nickel Powder" by K. O. Cockburn, R. J. Loree and J. B. Haworth. The authors produce nickel powder by reacting an ammoniacal nickel ammonium sulfate solution with hydrogen at elevated temperature and pressure to effect direct reduction of the nickel sulfate to elemental nickel powder. The individual particles of the powder are in the form of grape-like clusters formed of numerous sub-particles agglomerated together. Such nodular particles are generally spheroidal in shape, with an average size in the range of 30 to 200 microns, have greater than 99 percent purity, and are eminently suitable for use in the present invention, especially for developers to be used in magnetic brush development processes.

The nodular carrier beads used in the present invention can be over-coated, if desired, by conventional rolling, spraying or dipping techniques to impart triboelectric properties, strength and/or lubricity thereto. Coating materials are generally film forming polymeric materials such as homopolymers and copolymers of vinyl monomers such as styrene, acrylic acid esters, methacrylic acid esters, vinyl chloride, vinylidene chloride, fluoroethylene, vinyl acetate, polyamides, polyesters, and the like. The thickness of the coating is not critical so long as it is not so thick as to completely fill in the recesses of the nodular carrier thereby rendering the carrier surface substantially smooth. Coatings less than about 10 μ thick are generally useful, although thicker coatings can be applied to large carrier beads, e.g., those having at least one measurement greater than about 250 μ.

The carrier agglomerates produced by the present invention are surprisingly useful when combined with conventional toner materials as electrostatographic developer compositions. They are capable of giving images of high resolution with low background "noise" as compared with the standard smooth-surfaced carrier particles. They are much less sensitive to lower toner concentrations and much less subject to impaction with toner than the smooth-surfaced carrier particles heretofore conventionally used in standard electrostatographic development processes.

Any toner material of any color can be used with the carrier agglomerates of the present invention. Such toner materials are well known and fully disclosed in the literature. See for example U.S. Pat. Nos. 3,502,582; 3,345,294; 3,391,082; 2,753,308; 3,079,342; 2,659,670; 3,326,848; 3,338,991 and 3,272,644.

The proportion of carrier and toner materials in the developer compositions of the present invention is not as critical as with previously known carrier materials in view of the reduced sensitivity of the instant carrier materials to toner composition. Generally the developer composition should contain 0.5 to 2 percent of toner.

As the developer composition is used, the toner concentration decreases from its original level. However, surprisingly the density of the reproduced image shows only a slight decrease even after as much as 30 percent of the toner has been depleted.

The following examples further define and describe methods of preparing the carrier compositions and developed compositions of the present invention and of utilizing them to develop electrostatographic latent images. Parts and percentages are by weight unless otherwise indicated. The examples below should be considered to illustrate various preferred embodiments of this invention.

EXAMPLE 1

A 14 inch Dravo pelletizer equipped with a one-quarter horsepower variable drive motor and three square blades measuring 3 × 3 × 1/16 inch arranged in the 10 o'clock, 12 o'clock and 3 o'clock positions was used to pelletize various powdered materials. The pelletizing procedure was as follows. The pelletizing disc was set at an angle of 52° and driven at the rate of 53 rpm. The metal powders were fed to the disc at the rate of 15 to 20 pounds per hour. A binder solution was introduced at a specified rate over the disc so that the powder became wetted thereby. After sufficient binder had been introduced, the wetted powder was retained on the moving disc until the desired pelletization had occurred. As noted below, iron and nickel powders were pelletized with sodium silicate; a terpolymer of styrene, n-butyl acrylate and poly(vinyl butyral); and poly(vinyl chloride). The sodium silicate was in the form of a 40° Baume solution. The terpolymer binder was prepared by diluting a 30 percent solids solution of the terpolymer in toluene with methyl ethyl ketone to a 10 percent solids content. The PVC solution consisted of 10 percent solids (3 parts of polyvinyl chloride and 1 part of Luxol fast blue dye) in 9 parts of methyl ethyl ketone and 1 part of methanol. After the pelletization had been completed, in each case the pellets were dried, and in the case of those formed with sodium silicate binder the pellets were further sintered at high temperature. After drying and sintering the pellets were then classified and their density dtermined. The properties of the resultant pellets are shown in the following table.

EXAMPLE 2

Each of the nodular carrier materials produced in Example 1 was used to develop latent electrostatic images on a flat plate xerographic apparatus. The nodular carrier material was mixed with a carbon black pigmented toner consisting of a styrene-n-butyl methacrylate copolymer blended with poly(vinyl butyral) in a ratio of 200 parts of carrier to 1 part of toner. The resultant developed images were of good quality.

EXAMPLE 3

Nodular nickel particles, produced in accordance with the teachings of the aforementioned article by Cockburn et al and commercially available from Cherritt Gordon Mines Ltd. of Canada under the trade designation Grade "C" nickel powder and having a number average size of about 125 μ, were admixed with 2.2 percent of a toner composition containing 10 percent black and 90 percent of a blend of a styrene-n-butyl methacrylate copolymer and poly(vinyl butyral). The resultant developer was used in a magnetic brush developing unit to develope an imaged selenium photoconductor. Copies were made with two passes through the magnetic brush at 22 ips brush speed and 20 ips photoreceptor speed.

The copies thus produced were of superior quality.

When the same test was conducted with smooth surfaced nickel carrier beads of the same size, excellent copies were obtained, but the carrier was considered unacceptable for commercial use because of its high impaction rate.

Although specific materials and conditions are set forth in the above exemplary processes in making and using the berry-shaped carrier materials of this invention, these are merely intended as illustrations of the present invention. Various other toners, carrier materials and processes such as those listed above may be substituted 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.

TABLE I

	(1) IRON SODIUM SILICATE	(2) NICKEL SODIUM SILICATE	(3) IRON TERPOLYMER	(4) IRON PVC
Nickel (feed rate)	—	15–20 lbs/hr		
Iron (feed rate)	15–20 lbs/hr		15–20 lbs/hr	
Sodium Silicate (feed rate)	28 g/min.	18–25 g/min.		
Terpolymer (feed rate)			22 g/min.	
PVC (feed rate)				30 g/min.
Drying (°C)	125°	125°	60°	40°
Sintering (°C)	1250°–1300°	1250°–1300°		
Density	4.43 g/cc	6.30 g/cc	6.41 g/cc	—
Size Dust (%)				
+841μ	55.65	62.02	53.82	16.35
−841μ+500μ	12.21	3.26	6.43	7.26
−500μ+354μ	6.01	2.02	4.43	4.22
−354μ+210μ	6.04	4.27	4.99	5.28
−210μ+177μ	1.68	1.32	1.85	1.11
−177μ+63μ	8.64	16.47	10.28	17.34
−63μ	9.77	10.64	18.20	48.44

What is claimed is:

1. An electrostatographic imaging process comprising the steps of forming an electrostatographic latent image on a photoconductive surface and developing said electrostatographic latent image by contacting said photoconductive surface with an electrostatographic developer mixture comprising nodular carrier beads each having a generally spherical shape and a surface characterized by a plurality of small generally rounded nodular particles separated by recesses, said beads having an average size distribution in the range of 50 to 1,000 microns, and between about 95 and at least about 99.5 weight percent, based on the weight of the developer mixture, of said carrier beads relative to said finely divided toner particles electrostatically clinging to said surface of said carrier beads, whereby at least a portion of said finely divided toner particles are attracted to and held on said surface in conformance to said electrostatographic latent image.

2. An electrostatographic imaging process according to claim 1 wherein said nodular carrier beads are metal.

3. An electrostatographic imaging process according to claim 2, wherein the nodular carrier beads are nickel.

4. An electrostatographic imaging process according to claim 2 wherein the nodular carrier beads are iron.

5. An electrostatographic imaging process according to claim 1 wherein said nodular particles form into agglomerates and have an average size distribution in the range of 1 to 44 microns.

6. An electrostatographic imaging process comprising the steps of forming an electrostatographic latent image on a photoconductive surface and developing said electrostatographic latent image by contacting said photoconductive surface with a electrostatographic developer mixture comprising carrier beads and finely divided toner particles electrostatically clinging to the surface of said beads, each of said beads comprising an irregular surfaced generally spherical three dimensional solid, the irregular surface characterized by a plurality of raised generally spheroidally shaped nodular particles separated by recesses forming the junctions between adjacent ones of said nodular particles, said recesses providing traps for accummulations of said toner particles thereby increasing the toner carrying capacity of said bead, whereby at least a portion of said finely divided toner particles are attracted to and held on said photoconductive surface in conformance to said electrostatographic latent image.

7. An electrostatographic imaging process according to claim 6 wherein the nodular carrier beads are metal.

8. An electrostatographic imaging process according to claim 7 wherein the nodular carrier beads are nickel.

9. An electrostatographic imaging process according to claim 7 wherein the nodular carrier beads are iron.

10. An electrostatographic imaging process according to claim 6 wherein said nodular particles form as agglomerates and have an average size distribution in the range of 1 to 44 microns.

11. An electrostatographic imaging process comprising the steps of forming an electrostatographic latent image on a photoconducitve surface and developing said electrostatographic latent image by contacting said photoconductive surface with an electrostatographic developer mixture comprising nodular carrier beads each having a generally spherical shape and a surface characterized by a plurality of small generally rounded nodular particles separated by recesses, said beads having an average size distribution in the range of 50 to 1,000 microns, and at least about 0.5 weight percent, based on the weight of the developer mixture, of finely divided toner particles electrostatically clinging to the surface of the carrier beads, whereby at least a portion of said finely divided toner particles are attracted to and held on said photoconductive surface in conformance to said electrostatographic latent image.

12. An electrostatographic imaging process comprising the steps of forming an electrostatographic latent image on a photoconductive surface and developing said electrostatographic latent image by contacting said photoconductive surface with an electrostatographic developer mixture comprising nodular carrier beads each having a generally spherical shape and a surface characterized by a plurality of small generally rounded nodular particles, said beads having an average size distribution in the range of 50 to 1,000 microns and between about 0.5 and at least about 2.2 weight percent, based on the weight of the developer mixture, of finely divided toner particles electrostatcally clinging to the surface of the carrier beads, whereby at least a portion of said finely divided toner particles are attracted to and held on said photoconductive surface in conformance to said electrostatographic latent image.

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