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(54) **Method of preconditioning carrier particles for use in electrographic developers.**

(57) The invention provides a method of preconditioning carrier particles prior to their initial use in an electrographic developer. The method comprises forming a mixture of the carrier particles and preconditioning particles comprising a charge agent and a polymeric binder, agitating the mixture, and separating substantially all of the preconditioning particles from the carrier particles.

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METHOD OF PRECONDITIONING CARRIER PARTICLES FOR USE IN ELECTROGRAPHIC DEVELOPERS

This invention relates to treating carrier particles to render them more suitable for initial use in a dry electrographic developer comprising a mix of the carrier particles and electrographic toner particles. More particularly, the invention concerns a method of preconditioning carrier particles in order to avoid or minimize undesirable characteristics that the carrier particles would otherwise cause an electrographic developer to exhibit during the initial cycles of its use in an electrographic development process.

In electrostatography an image comprising a pattern of electrostatic potential (also referred to as an electrostatic latent image) is formed on an insulative surface by any of various methods. For example, the electrostatic latent image may be formed electrophotographically (i.e., by imagewise radiation-induced discharge of a uniform potential previously formed on a surface of an electrophotographic element comprising at least a photoconductive layer and an electrically conductive substrate), or it may be formed by dielectric recording (i.e., by direct electrical formation of a pattern of electrostatic potential on a surface of a dielectric material). Typically, the electrostatic latent image is then developed into a toner image by contacting the latent image with an electrographic developer. If desired, the latent image can be transferred to another surface before development.

One well-known, type of electrographic developer comprises a dry mixture of toner particles and carrier particles. Developers of this type are commonly employed in well-known electrographic development processes such as cascade development and magnetic brush development. The particles in, such developers are formulated such that the toner particles and carrier particles occupy different positions in the triboelectric continuum, so that when they contact each other during mixing to form the developer, they become triboelectrically charged, with the toner particles acquiring a charge of one polarity and the carrier particles acquiring a charge of the opposite polarity. These opposite charges attract each other such that the toner particles cling to the surfaces of the carrier particles. When the developer is brought into contact with the electrostatic latent image, the electrostatic forces of the latent image (sometimes in combination with an additional applied field) attract the toner particles, and the toner particles are pulled away from the carrier particles and become electrostatically attached imagewise to the latent image-bearing surface. The resultant toner image can then be fixed in place on the surface by application of heat or other known methods (depending upon the nature of the surface and of the toner image) or can be transferred to another surface, to which it then can be similarly fixed.

A number of requirements are implicit in such development schemes. Namely, the electrostatic attraction between the toner and carrier particles must be strong enough to keep the toner particles held to the surfaces of the carrier particles while the developer is being transported to and brought into contact with the latent image, but when that contact occurs, the electrostatic attraction between the toner particles and the latent image must be even stronger, so that the toner particles are thereby pulled away from the carrier particles and deposited in the desired amount on the latent image-bearing surface. In order to meet these requirements for proper development, the level of electrostatic charge on the toner and carrier particles should be maintained within an adequate range.

Toner particles in dry developers often contain material referred to as a charge agent or charge-control agent, which helps to establish and maintain toner charge within an acceptable range. Many types of charge-control agents have been used and are described in the published patent literature. However, the level of charge that will be created and maintained on the toner is still very dependent on the nature and condition of the carrier particles.

Newly formed developers, wherein neither the toner particles nor the carrier particles have been previously used in a development process, usually exhibit various disadvantages, especially during the initial cycles of their use in an electrographic development process (often referred to as the early life of the developer).

For example, during the first few minutes of use (which can involve the development of hundreds of toner images, depending upon the speed of the development process), the level of charge on the toner and carrier particles in the developer can change rapidly and drastically, resulting in a wide variation of the degree and quality of development of successive images during that period. We will refer to this problem as early life charge variation.

Also, during its early life, the developer can exhibit high levels of undesirable throw-off (also referred to as dusting), which is defined as the amount of toner and any, other particulate matter that is thrown out of the developer (i.e., that is not adequately held to the surfaces of the carrier particles) during agitation of the developer, e.g., by a typical development apparatus such as a magnetic roll applicator. High levels of dusting can involve undesirable effects such as excessive wear and damage of electrographic imaging

apparatus, contamination of toner with dirt or carrier material leading to higher charge variation, contamination of environmental air with toner powder and other particulate matter, unwanted development of background image areas, and scumming of the surface of photoconductive elements that leads to poorer electrophotographic performance and shorter useful life.

5 Both the early life charge variation problem and the early life dusting problem are thought to be caused by the physical and chemical condition of the carrier particles and alteration thereof during use in development.

For example, early life charge variation can be caused by pore packing and scumming of carrier surfaces with toner material, by abrasion of carrier surfaces that dislodges or breaks off dirt and other surface heterogeneities or irregularities, by chemical alteration of carrier core materials through reaction with chemical toner components such as colorants and charge agents, by chemical alteration of carrier coatings (e.g., polymeric materials well known to provide benefits when coated on carrier cores) through reaction with toner components or abraded carrier materials or a combination thereof, and by contamination and possible chemical reaction of the toner particles with material released from the carrier particles, all of which can change the triboelectric relationship of the carrier particles and toner particles.

Early life dusting can be both a cause (through alteration of carrier by release of portions of carrier material, carrier coating material, or carrier surface dirt, contamination of toner particles therewith, and consequent alteration of the triboelectric nature of carrier and/or toner particles) and a consequence (through less attractive force between carrier and toner due to early life lowering of developer charge level) of early life charge variation. Early life dusting, thus, can be caused by any of the same factors that cause early life charge variation, but may be mostly caused by dislodging of dirt and other extraneous matter from carrier surfaces and/or fracture and release of portions of carrier material (especially surface heterogeneities or irregularities), and subsequent contamination of toner particles therewith.

In the prior art, various methods are described for treating developers, in order to alleviate early life charge variation, among other problems. See, for example, U.S. Patents 4,678,734; 3,970,571; and 3,960,738. While these prior art methods apparently do produce a beneficial effect in regard to early life charge variation, they do not address the problem of early life dusting.

Thus, there remains a need for a relatively simple way to treat carrier particles that have not been previously used in a developer, which will simultaneously alleviate the problems of early life charge variation and early life dusting. The present invention meets that need.

The invention provides a method of preconditioning carrier particles prior to their initial use in a dry electrographic developer comprising a mixture of the carrier particles and toner particles.

The method comprises the steps of:

- A. forming a mixture of the carrier particles and preconditioning particles, wherein each of the preconditioning particles comprises a mixture of
 - (1) a polymeric binder useful in electrographic toners, and
 - (2) a charge agent, useful to control the level of triboelectric charging of electrographic toners;
- B. agitating the mixture of carrier particles and preconditioning particles to promote contact therebetween; and
- C. subsequently, separating substantially all of the preconditioning particles from the carrier particles.

The inventive method unexpectedly and beneficially alters the carrier particles in some way, such that when they are thereafter mixed with toner particles to form an electrographic developer, the developer exhibits significantly less early life charge variation and early life dusting during its use.

While the mechanistic reasons for this combination of beneficial effects are not known, it is noted that the significant reduction of early life dusting is apparently effected by the portion of the inventive method that is clearly different from the prior art methods described in the three U.S. Patents identified above. Namely, the inventive method requires substantially complete separation of the carrier particles from the preconditioning particles after agitated contact therewith, while the noted prior art methods (which do not produce the remarkable reduction in early life dusting effected by the present inventive method) involve removing none (U.S. Patents 4,678,734 and 3,970,571), or at most only a portion (U.S. Patent 3,960,738) of the "conditioning" toner particles from the mixture used in the conditioning process. It is theorized that the substantially complete separation of the preconditioning particles from the carrier particles in the present inventive method alleviates early life dusting, by reason of the dirt and other extraneous matter from the carrier surfaces, and also any carrier material fractured or abraded from the carriers during the process, becoming embedded in or otherwise associated with the preconditioning particles, such that those materials are carried away from the carrier particles along with the preconditioning particles during the separation step.

The noted prior art methods are actually methods of treating and modifying developers (comprising

toner and carrier particles), rather than just carrier particles. Those methods all involve using, as the "conditioning" particles, toner materials having the same chemical components as in the final developers produced thereby. Their intention is to produce a final developer and alter characteristics of both the toner and carrier particles in that developer, rather than just to affect the carrier particles, and there is no suggestion that the carrier particles in those developers could or should be, subsequently, substantially completely separated from the toner particles of the developer. In fact, the methods taught in that prior art intend scumming of the surfaces and packing of the pores of the carriers with the toner materials and also intend alteration of the toner particles, e.g., in regard to their particle size distribution. Any subsequent attempt to completely separate the carriers from the toner particles before mixing the carriers with other toner particles for actual development use would be contrary to the purposes of those methods, and is nowhere suggested.

Furthermore, in preferred embodiments of the method of the present invention the preconditioning particles contain substantially no colorant and can, therefore, be used to precondition carrier particles, which will then have the advantage that they can be subsequently employed in developers containing any toner particles, regardless of whether those toner particles are colorless or have any particular hue. Even though the intention in the inventive method is to separate substantially all of the preconditioning particles from the carrier particles, it would require considerable extra effort (or in some cases might be impossible) to remove every last trace amount of preconditioning material that may have adhered to surfaces of the carrier particles during the agitation step. If pigment is present in the preconditioning particles, even a trace amount of such pigment remaining on the carrier particles after the inventive method would often be enough to undesirably alter the hue in a developer formed by mixing the preconditioned carrier particles with toner particles containing a colorant having a hue different from that of the pigment in the preconditioning particles. This is the case in the methods specifically described in the three prior art U.S. patents mentioned above. I.e., in those methods a pigment is included in the conditioning process, thus rendering the carrier particles unsuitable for later use with any toner particles other than those having the same hue as the pigment included in the conditioning process.

The method of the present invention is beneficially applicable to any carrier particles known to be useful in electrographic developers. Such carrier particles can be formed from various materials and can comprise core particles or core particles overcoated with other materials such as, e.g., a thin resinous film layer.

The carrier core materials can comprise conductive, non-conductive, magnetic, or non-magnetic materials. For example, carrier cores can comprise glass beads; crystals of inorganic salts such as aluminum potassium chloride; other salts such as ammonium chloride or sodium nitrate; granular zircon; granular silicon; silicon dioxide; hard resin particles such as poly(methyl methacrylate); metallic materials such as iron, steel, nickel, carborundum, cobalt, oxidized iron; or mixtures or alloys of any of the foregoing. See, for example, U.S. Patents 3,850,663 and 3,970,571. Especially useful in magnetic brush development schemes are iron particles such as porous iron particles having oxidized surfaces, steel particles, and other "hard" or "soft" ferromagnetic materials such as gamma ferric oxides or ferrites, such as ferrites of barium, strontium, lead, magnesium, or aluminum. See, for example, U.S. Patents 4,042,518; 4,478,925; 4,546,060; and 4,764,445.

As noted above, the carrier particles can be overcoated with a thin layer of a film-forming resin for the purpose of establishing the correct triboelectric relationship and charge level with the toner employed. Examples of suitable resins are the polymers described in U.S. Patents 3,547,822; 3,632,512; 3,795,618 and 3,898,170 and Belgian Patent 797,132. Other useful resins are fluorocarbons such as polytetrafluoroethylene, poly(vinylidene fluoride), mixtures of these, and copolymers of vinylidene fluoride and tetrafluoroethylene. See, for example, U.S. Patents 4,546,060; 4,478,925; 4,076,857; and 3,970,571. Such polymeric carrier coatings can serve a number of known purposes. One such purpose can be to aid the developer to meet the electrostatic force requirements mentioned above by shifting the carrier particles to a position in the triboelectric series different from that of the uncoated carrier core material, in order to adjust the degree of triboelectric charging of both the carrier and toner particles. Another purpose can be to reduce the frictional characteristics of the carrier particles in order to improve developer flow properties. Still another purpose can be to reduce the surface hardness of the carrier particles so that they are less likely to break apart during use and less likely to abrade surfaces (e.g., photoconductive element surfaces) that they contact during use. Yet another purpose can be to reduce the tendency of toner material or other developer additives to become undesirably permanently adhered to carrier surfaces during developer use (often referred to as scumming). A further purpose can be to alter the electrical resistance of the carrier particles.

Many methods of applying such coatings in a continuous or discontinuous configuration of various uniform or non-uniform thicknesses are well known. Some useful coating methods include solvent coating, spray application, plating, tumbling, shaking, fluidized bed coating, and melt-coating, of which melt-coating

is usually preferred. See for example, U.S. Patents 4,546,060, 4,478,925, and 4,233,387. In preferred embodiments of the invention specifically illustrated in the examples below, the coatings were discontinuous and comprised poly(vinylidene fluoride) melt-coated on the carrier core materials.

The carrier particles can be spherical or irregular in shape, can have smooth or rough surfaces, and can be of any size known to be useful in developers. Conventional carrier particles usually have an average particle diameter in the range of from 2 to 1200 micrometers, preferably 2-300 micrometers.

Each of the preconditioning particles employed in the inventive method comprises a mixture of a polymeric binder and a charge agent.

The polymeric binder comprises any polymeric material that would be useful as the binder in an electrographic toner, of which many are known. Useful polymers are thermoplastic, having a glass transition temperature within the range of 40° to 150°C. The polymer can be a homopolymer or copolymer, and binders can comprise one polymer or a blend of polymers. Some useful types of polymers are polyesters (including also, polycarbonates), polyamides, phenol-formaldehyde polymers, polyesteramides, alkyd resins, and vinyl-addition polymers (typically formed from monomers such as styrenes, butadiene, acrylates, and methacrylates, among others). For further descriptions of some useful typical polymeric binders, see, for example, U.S. Patents 4,812,377; 4,446,302; 4,217,440; 4,140,644; 3,694,359; 4,601,966; 3,809,554; Re 31,072; 2,917,460; 2,788,288; 2,638,416; 2,618,552; 4,416,965; 4,691,966; and 2,659,670. Some specific examples of polymers preferred for use in preconditioning particles in the inventive method, because they are especially good at reducing early life charge variation, are poly(styrene-co-butyl acrylate), poly(styrene-co-butyl methacrylate), and poly(propylene-co-glyceryl terephthalate-co-glutarate).

Charge agents useful in the preconditioning particles comprise any materials that would be useful to establish or control the level of triboelectric charging of electrographic toner particles when incorporated therein or associated therewith. Many such charge agents are well known and include non-polymeric and polymeric materials. Some of the polymeric materials can serve a dual function as both the binder and the charge agent. Some useful types of charge agents are aromatic and aliphatic quaternary ammonium and phosphonium salts, both polymeric and non-polymeric; primary, secondary, and tertiary amines; metal complex dyes; and acidic organic molecules such as naphthalene sulfonic acid. For further descriptions of some useful typical charge agents, see, for example, U.S. Patents 3,893,935; 4,079,014; 4,323,634; 4,394,430; 4,496,643; 4,547,449; 4,684,596; 4,837,391; 4,837,392; 4,837,393; 4,837,394; 4,812,378; 4,812,382; 4,789,614; 4,812,380; 4,840,864; and 4,812,381. Preferred charge agents are non-toxic, thermally stable, and colorless. Some specific examples of charge agents preferred for use in preconditioning particles in the inventive method are benzyldimethyloctadecylammonium chloride, methyltriphenylphosphonium p-toluenesulfonate, (3-lauramidopropyl)trimethylammonium methylsulfate, and benzyldimethyloctadecylammonium 3-nitrobenzenesulfonate. Methyltriphenylphosphonium p-toluenesulfonate is especially preferred, because of superior capability in reducing early life charge variation.

The optimum proportions of binder and charge agent to be included in the preconditioning particles will vary, depending upon the nature of all materials involved and the amount of time spent in the agitation step. However, some of each must be present, and, usually, the optimum amount of charge agent will fall in the range of 1 to 4 percent by weight, based on total weight of the preconditioning particles. In some embodiments the binder and charge agent will exist as separate phases within the preconditioning particles, such that when the particles are ground to desired size, fracture occurs preferentially in the charge agent phase, with the result that the final preconditioning particles have a higher concentration of the charge agent at their surfaces than internally. This appears to produce a more pronounced effect in reducing early life charge variation. Examples of preconditioning particles exhibiting this phase separation include those wherein the charge agent is a phosphonium salt, such as methyltriphenylphosphonium p-toluenesulfonate, and the binder is a vinyl-addition polymer, such as poly(styrene-co-butyl acrylate).

The preconditioning particles are prepared by dispersing the charge agent in the polymeric binder in any convenient manner known for preparing toner particles (preferably by melt-blending as described, for example, in U.S. Patents 4,684,596 and 4,394,430). The mix is then ground to desired size to form a free-flowing powder of preconditioning particles. Size of the particles is not critical; however, extremely small particles may be more difficult to separate from the carrier particles after the agitation step of the method. In some embodiments of the practice of the inventive method the average preconditioning particle diameter is in the range of 11 to 14 micrometers, and very few particles are less than 5 to 6 micrometers.

In practicing the method of the invention, the preconditioning particles are simply mixed with the carrier particles in an amount sufficient to maximize the carrier particle surface area contacted by the preconditioning particles. This amount will vary depending upon the, relative sizes and densities of preconditioning and carrier particles. In some embodiments of the practice of the method the preconditioning particles comprise 10 to 13 percent by weight of the mixture.

The mixture is then agitated by any convenient means to promote contact between the preconditioning and carrier particles. The amount of time of agitation necessary for optimum results will depend upon the forcefulness of the agitation and the nature of the materials involved. In some embodiments optimum results are achieved by agitating for 0.1 to 6 hours.

5 After completion of the agitation step, substantially all of the preconditioning particles are separated from the carrier particles by any convenient means and discarded.

In cases where the preconditioning and carrier particles occupy significantly different positions in the triboelectric continuum, the particles will have become triboelectrically charged during the agitation step, with the preconditioning particles acquiring a charge of one polarity and the carrier particles acquiring a charge of the opposite polarity. In such cases separation can be conveniently achieved electrostatically, for example, by passing the mixture between electrode plates, one of which is grounded, and the other of which is charged with a polarity opposite that of the preconditioning particles so that those particles are attracted to it while the carrier particles are repelled by it. In some embodiments of the inventive method substantially complete separation has been achieved in this manner; i.e., from 97% to 99.9% or more of the preconditioning material by weight has been separated from the carrier particles.

15 In other cases, e.g., where the preconditioning particles are of a size significantly different from that of the carrier particles, separation can be conveniently achieved by other means, such as sieving with air agitation.

After separation, the carrier particles are then in condition for subsequent mixing with any suitable toner particles to form an electrographic developer that will exhibit significantly less early life charge variation and early life dusting, during use in any of the well known dry electroscopic development schemes such as cascade development or magnetic brush development, than it would if the carrier particles had not been subjected to the inventive preconditioning method.

20 The following examples are presented to further illustrate some preferred modes of practice of the preconditioning method of the invention and to illustrate the beneficial effects of the method on carrier particles in comparison to carrier particles that have not undergone such preconditioning or that have been conditioned other than in accordance with the present invention.

In all of the following examples the carrier particles comprised strontium ferrite carrier cores melt-coated with poly(vinylidene fluoride). They were prepared by using a formulation comprising 1-2 percent by weight poly(vinylidene fluoride) and 98-99 percent by weight strontium ferrite particles. Two kilograms of the formulation were placed in a 4-liter wide-mouth glass jar and capped. The jar was vigorously shaken by hand and then roll-milled for 15 minutes at 140 revolutions per minute. The cap was then removed, and the jar was placed in a convection oven set at a temperature of 230 °C for 4 hours. After cooling to room temperature, the coated particles were passed through a sieve having 62-micrometer openings to break up any large agglomerates.

35 In the examples the degree of early life charge variation is determined by mixing the carrier particles with typical toner particles to form a charged electrographic developer comprising 13% toner by weight, measuring the level of charge residing on the toner particles in microcoulombs per gram of toner ($\mu\text{C/g}$) before any exercise of the developer, measuring the level of charge on the toner after 5 minutes of continuous exercise of the developer, and then subtracting the latter charge level value from the former to yield the change in charge level, which is representative of the degree of early life charge variation. The continuous exercise of the developer involved placing the developer in a glass bottle held in place on top of a typical device designed to form a developer into an agitating magnetic brush for development of electrostatic images into toner images (in this case a cylindrical roll with rotating magnetic core). Thus, the continuous exercising closely approximated typical actual early life use of the developer in an electrographic development process.

45 Since the purpose in measuring toner charge level in the examples was merely to illustrate the degree of early life charge variation of developers containing carrier particles subjected to the inventive preconditioning treatment relative to the degree of early life charge variation of similar developers containing carriers not subjected to the inventive treatment, any known convenient method for measuring toner charge levels could be used. In the examples below toner charge level was measured by placing a 0.05 to 0.1 g portion of the charged developer in a sample dish situated between electrode plates and subjecting it, simultaneously for 30 seconds, to a 60 Hz magnetic field to cause developer agitation and to an electric field of about 2000 volts/cm between the plates. The toner is released from the carrier and is attracted to and collects on the plate having polarity opposite to the toner charge. The total toner charge is measured by an electrometer connected to the plate, and that value is divided by the weight of the toner on the plate to yield the charge per mass of toner in microcoulombs per gram ($\mu\text{C/g}$).

55 In the examples the degree of early life dusting (throw-off) was determined by: mixing the carrier

particles with typical toner particles to form a charged developer comprising 12% toner by weight; agitating the developer for about 10 minutes; mixing more of the same type of toner particles into the developer to form a charged developer comprising 18% toner by weight; placing the developer in an open container held in place on top of a typical device designed to form a developer into an agitating magnetic brush for development of electrostatic latent images into toner images (in this case a cylindrical roll with rotating magnetic core); placing a funnel, containing a weighed piece of fiberglass filter paper and a vacuum hose connected to its spout, in an inverted position securely over the open container; simultaneously for one minute, rotating the magnetic core to form an agitating magnetic developer brush as in a normal development process and applying vacuum to the funnel to collect on the filter paper any material thrown off of the agitating magnetic developer brush; weighing the filter paper and collected material; and then subtracting the weight of the filter paper alone from this combined weight to determine the degree of early life dusting in milligrams (mg).

Examples 1-6

In Examples 1-6 the carrier particles comprised, by weight, 98 percent strontium ferrite core material and 2 percent poly(vinylidene fluoride) resin coating. In Control A the carrier particles were not subjected to any preconditioning treatment. In Examples 1-6, the carrier particles were preconditioned in accordance with the invention by forming a mixture comprising, by weight, 87 percent carrier particles and 13 percent preconditioning particles, agitating the mixture for 30 minutes, and electrostatically separating substantially all (from 97 to 99.9 percent by weight) of the preconditioning material from the carrier particles. All of the carriers were then mixed with toner particles to form electrographic developers, and the degree of early life charge variation and early life dusting were determined as described above. In all cases the toner particles comprised a quaternary ammonium salt charge agent, a polymeric siloxane release agent, a yellow colorant, and a branched amorphous polyester binder.

In Examples 1-6 the preconditioning particles had an average particle diameter in the range of 11 to 14 micrometers and consisted of, by weight, 98 percent polymeric binder and 2 percent charge agent. In Examples 1-3 the preconditioning particles' polymeric binder was poly(styrene-co-butyl acrylate) (80:20 recurring unit weight ratio) sold by the Hercules Co., USA, under the trademark, Piccotoner 1278. In Examples 4-6 the preconditioning particles' polymeric binder was a branched amorphous polyester in which the recurring units were derived from terephthalic acid, glutaric acid, propane diol, and glycerol having a molar ratio of 87:13:95:5, respectively. In Examples 1 and 4 the preconditioning particles' charge agent was benzyldimethyloctadecylammonium chloride; in Examples 2 and 5 it was methyltriphenylphosphonium p-toluenesulfonate; and in Examples 3 and 6 it was benzyldimethyloctadecylammonium 3-nitrobenzenesulfonate.

Results are presented in Table I.

Table I

Example	Toner charge before developer exercise ($\mu\text{C/g}$)	Toner charge after 5 min. exercise ($\mu\text{C/g}$)	Early Life charge variation ($\mu\text{C/g}$)	Early life dusting (mg)
Control A	36.5	11.4	25.1	24.0
1	33.7	16.4	17.3	0.1
2	15.9	11.3	4.6	0.6
3	28.8	14.3	14.5	0.4
4	40.4	21.5	18.9	0.3
5	34.1	21.5	12.6	0.3
6	41.6	22.1	19.5	0.3

The results in Table I show that in all cases the inventive preconditioning treatment of the carrier particles significantly reduced the early life charge variation and early life dusting of the developers subsequently prepared with the treated carrier particles. The best results in reducing early life charge variation were achieved when the preconditioning particles consisted of poly(styrene-co-butyl acrylate) binder and methyltriphenylphosphonium p-toluenesulfonate charge agent (Example 2).

Examples 7 and 8

In Examples 7 and 8 the carrier preconditioning and developer testing were carried out exactly as in Examples 2 and 5, respectively. The only difference was that the carrier particles in Control B and Examples 7 and 8 comprised, by weight, 99 percent strontium ferrite core material (instead of 98 percent) and 1 percent poly(vinylidene fluoride) resin coating (instead of 2 percent). Control B underwent no preconditioning treatment. Results are presented in Table II.

Table II

Example	Toner charge before developer exercise ($\mu\text{C/g}$)	Toner charge after 5 min. exercise ($\mu\text{C/g}$)	Early Life charge variation ($\mu\text{C/g}$)	Early life dusting (mg)
Control B	35.1	8	27.1	115.8
7	11.4	7.6	3.8	0.5
8	30.9	15.2	15.7	0.5

Example 9

In Example 9 the carrier particles and inventive preconditioning were exactly the same as in Example 2. Developer testing was also the same as in Example 2, with the sole exception that the toner particles contained a magenta colorant instead of a yellow colorant. Control C underwent no preconditioning treatment. Results are shown in Table III.

Table III

Example	Toner charge before developer exercise ($\mu\text{C/g}$)	Toner charge after 5 min. exercise ($\mu\text{C/g}$)	Early Life charge variation ($\mu\text{C/g}$)	Early life dusting (mg)
Control C	73	40.3	33.0	0.3
9	29.2	24.2	5.0	0.4

Example 10

In Example 10 the carrier particles and inventive preconditioning were exactly the same as in Example 7. Developer testing was also the same as in Example 7, with the sole exception that the toner particles contained a magenta colorant instead of a yellow colorant. Control D underwent no preconditioning treatment. Results are shown in Table IV.

Table IV

Example	Toner charge before developer exercise ($\mu\text{C/g}$)	Toner charge after 5 min. exercise ($\mu\text{C/g}$)	Early Life charge variation ($\mu\text{C/g}$)	Early life dusting (mg)
Control D	67.9	32.9	35.0	3.9
10	21.2	16.1	5.1	0.7

Example 11

In Example 11, the carrier particles and inventive preconditioning were exactly the same as in Example 2. Developer testing was also the same as in Example 2, with the sole exception that the toner particles contained a cyan colorant instead of a yellow colorant. Control E underwent no preconditioning treatment. Results are shown in Table V.

Table V

Example	Toner charge before developer exercise ($\mu\text{C/g}$)	Toner charge after 5 min. exercise ($\mu\text{C/g}$)	Early Life charge variation ($\mu\text{C/g}$)	Early life dusting (mg)
Control E	41.5	14.2	27.3	36.7
11	18.4	14.1	4.3	0.8

Examples 12-15

In Examples 12-15 the carrier particles and developer testing were exactly the same as in Example 2. The inventive preconditioning treatment was the same as in Example 2, with two exceptions. The agitation step of the inventive method was carried out for 15 minutes instead of 30 minutes, and the preconditioning particles had different proportions of the binder and charge agent. In Examples 12, 13, 14, and 15 the preconditioning particles consisted of, by weight, 99, 98, 97 and 96 percent binder and 1, 2, 3, and 4 percent charge agent, respectively. Control F underwent no preconditioning treatment. Control G was subjected to a preconditioning treatment similar to that of Examples 12-15, but not in accordance with the invention, in that the preconditioning particles consisted of 100 percent binder and no charge agent. Results are shown in Table VI. Note that the treatment of Control G did produce a beneficial effect in reducing early life charge variation, but greatly worsened early life dusting.

Table VI

Example	Toner charge before developer exercise ($\mu\text{C/g}$)	Toner charge after 5 min. exercise ($\mu\text{C/g}$)	Early Life charge variation ($\mu\text{C/g}$)	Early life dusting (mg)
Control F	36.5	11.4	25.1	24.0
Control G	19.3	7.6	11.7	62.7
12	22.7	15.2	7.5	0.6
13	17.6	12.3	5.3	0.4
14	12.7	9.2	3.5	0.4
15	8.6	5.4	3.2	1.4

Claims

1. A method of preconditioning carrier particles prior to their initial use in a dry electrographic developer comprising a mix of the carrier particles and toner particles, wherein the method comprises the steps of:
 - A. forming a mixture of the carrier particles and preconditioning particles, wherein each of the preconditioning particles comprises a mixture of:
 - (1) a polymeric binder useful in electrographic toners, and
 - (2) a charge agent, useful to control the level of triboelectric charging of electrographic toners;
 - B. agitating the mixture of carrier particles and preconditioning particles to promote contact therebetween; and
 - C. subsequently, separating substantially all of the preconditioning particles from the carrier particles.
2. The method of claim 1, wherein the preconditioning particles contain substantially no colorant.
3. The method of claim 1, wherein the charge agent is methyltriphenylphosphonium p-toluenesulfonate.

4. The method of claim 1, wherein the polymeric binder comprises poly(styrene-co-butyl acrylate) or poly(propylene-co-glyceryl terephthalate-co-glutarate).
5. The method of claim 1, wherein the carrier particles comprise core particles coated with a resin.
6. The method of claim 5, wherein the core particles comprise a strontium ferrite material.
- 5 7. The method of claim 5, wherein the resin comprises poly(vinylidene fluoride).

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EUROPEAN SEARCH REPORT

Application Number

EP 90 11 4164

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	PATENT ABSTRACTS OF JAPAN vol. 13, no. 245 (P-881)(3593) 08 June 1989, & JP-A-1 46767 (MINOLTA CAMERA CO., LTD.) 21 February 1989, * the whole document * -- -- --	1	G 03 G 9/10 G 03 G 9/113
A	PATENT ABSTRACTS OF JAPAN vol. 12, no. 19 (P-657)(2866) 21 January 1988, & JP-A-62 174774 (FUJITSU LTD.) 31 July 1987, * the whole document * -- -- --	1	
A	CHEMICAL ABSTRACTS, vol. 78, no. 10, 12 March 1973 Columbus, Ohio, USA page 487; ref. no. 65267X * abstract & SU-A-347726(SUNDUKOV A.K.)(10.08.1972) * -- -- -- --	1	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			G 03 G 9
The present search report has been drawn up for all claims			
Place of search The Hague		Date of completion of search 16 November 90	Examiner HINDIAS E.
CATEGORY OF CITED DOCUMENTS X: particularly relevant if taken alone Y: particularly relevant if combined with another document of the same category A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention E: earlier patent document, but published on, or after the filing date D: document cited in the application L: document cited for other reasons ----- &: member of the same patent family, corresponding document			