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EUROPEAN PATENT APPLICATION

21 Application number: 81300373.8

51 Int. Cl.³: **G 03 G 9/10**

22 Date of filing: 28.01.81

30 Priority: 28.01.80 US 116067

43 Date of publication of application:
26.08.81 Bulletin 81/34

84 Designated Contracting States:
BE FR GB NL

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54 A method of making coated carrier particles for electrostatographic developer mixtures; coated carrier particles made thereby; developer mixtures comprising the coated particles, and an imaging process employing the developer mixtures.

57 Electrostatographic carrier particles possessing all the desirable characteristics for development of negatively charged photoreceptor surfaces are provided by coating carrier cores with polyvinylidene fluoride. After coating, the carrier particles are thermally treated as to provide them with lower negative triboelectric charging values compared with untreated carrier particles.

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A METHOD OF MAKING COATED CARRIER PARTICLES FOR ELECTROSTATOGRAPHIC DEVELOPER MIXTURES; COATED CARRIER PARTICLES MADE THEREBY; DEVELOPER MIXTURES COMPRISING THE COATED PARTICLES, AND AN IMAGING PROCESS EMPLOYING THE DEVELOPER MIXTURES.

This invention is concerned with carrier particles for electrostatographic toner.

It is well known to form and develop images on the surface of photoconductive materials by electrostatic methods such as described, for example, in U.S. Patents 2,297,691; 2,277,013; 2,551,582; 3,220,324; and 3,220,833. In summary, these processes as described in the aforementioned patents involve the formation of an electrostatic latent charged image on an insulating electrophotographic element, and rendering the latent image visible by bringing the charged surface of the photoconductive element into contact with a developer mixture. As described in U.S. Patent 2,297,691, for example, the resulting electrostatic latent image is developed by depositing thereon a finely-divided electroscopic material referred to in the art as toner, the toner being generally attracted to the areas of the layer which retain a charge, thus forming a toner image corresponding to the electrostatic latent image. Subsequently, the toner image can be transferred to a support surface such as paper and this transferred image can be permanently affixed to the support surface using a variety of techniques including pressure fixing, heat fixing, solvent fixing, and the like.

Many methods are known for applying the electroscopic particles to the latent image including cascade development, touchdown and magnetic brush as illustrated in U.S. Patents 2,618,552; 2,895,847 and 3,245,823. One of the most widely used methods is cascade development, wherein the developer material, comprising relatively-large carrier particles having finely-divided toner particles electrostatically clinging to them, is conveyed to and rolled or cascaded across the electrostatic latent image-bearing surface. Magnetic brush development is also known, and involves the use of a developer material comprising toner and magnetic carrier particles which are carried by a magnet so that the magnetic field produced by the magnet causes alignment of the magnetic carriers in a brush-like configuration. Subsequently, this brush is brought into contact with the electrostatic latent image-bearing surface causing the toner particles to be attracted from the brush to the electrostatic latent image by electrostatic attraction, as more

specifically disclosed in U.S. Patent 2,874,063.

Carrier materials used in the development of electrostatic latent images are described in many patents including, for example, U.S. Patent 3,590,000. The type of carrier material to be used depends on many factors such as the type of development used, the quality of the development desired, the type of photoconductive material employed and the like. Generally, however, the materials used as carrier surfaces or carrier particles or the coating thereon should have a triboelectric value commensurate with the triboelectric value of the toner in order to generate electrostatic adhesion of the toner to the carrier. Carriers should be selected that are not brittle so as to cause flaking of the surface or particle break-up under the forces exerted on the carrier during recycle, as such causes undesirable effects and could, for example, be transferred to the copy surface thereby reducing the quality of the final image.

There have been recent efforts to develop carriers and particularly coatings for carrier particles in order to obtain better development quality and also to obtain a material that can be recycled and does not cause any adverse effects to the photoconductor. Some of the coatings commercially utilized deteriorate rapidly especially when employed in a continuous process whereby the entire coating may separate from the carrier core in the form of chips or flakes as a result of poorly-adhering coated material and fail upon impact and abrasive contact with machine parts and other carrier particles. Such carrier particles generally cannot be reclaimed and reused and usually provide poor print quality results. Further, the triboelectric values of some carrier coatings have been found to fluctuate when changes in relative humidity occur and thus these carriers are not desirable for use in electrostatographic systems, as they can adversely affect the quality of the developed image.

In addition, in particular electrostatographic reproduction systems in order to develop a latent image comprised of negative electrostatic charges, an electrostatic carrier and toner powder combination must be selected in which the toner is triboelectrically charged positively relative to the granular carrier. Likewise, in order to develop a latent image comprised of positive electrostatic charges such as where a selenium photoreceptor is employed, an electroscopic toner powder and carrier mixture must be selected in which the toner is triboelectrically charged negatively relative to the carrier. Thus, where the latent image is formed of negative electrostatic charges such as

when employing an organic electrophotosensitive material as the photoreceptor, it is highly desirable to develop the latent image with a positively-charged electroscopic powder and a negatively-charged carrier material.

Further, for a given toner-carrier pair, the magnitude of the triboelectric charge is important in that, if the charge is too low, the developed copy will be characterized by high print density but resolution will be poor and background areas will be overdeveloped. By the same token, if the triboelectric charge is too high, background areas will not contain unwanted deposits and resolution will be good, but the developed image print density will be too low. Therefore, for a toner-carrier pair to be satisfactory, the carrier material must be one wherein its coating has a high resistance to abrasion and good adhesion properties, it must be capable of triboelectrically charging the toner to the desired polarity, and charge the toner to a level within a range of triboelectric values whereby developed copies of high quality are obtained.

The development of electrostatographic coated carrier materials has been to a main extent on a trial and error basis. Since certain desirable functional characteristics of carrier materials having coatings are known, it has been somewhat possible to select coating materials for the purpose of determining their potential usefulness as carrier coatings. However, it has not been possible to reliably predict whether any particular coating material is viable or possesses any advantage over another coating material for use as an electrostatographic carrier coating. The only effective means of determining whether any coating material will satisfy the functional characteristics of a carrier material is to actually prepare carrier particles with the coating material and evaluate the product. Thus, even if a coating material is a member of a broad class of generally desirable materials, it may be that the particular coating material is difficult or impossible to coat by normal means or requires a complicated or expensive preparation process.

One such class of generally desirable carrier coating materials is the class of fluoropolymers as disclosed in U S Patent No 3 798 167. In said patent, carrier particle cores are coated with a substantially-insoluble fluoropolymer or a mixture of a fluoropolymer and a modifying resin in which the fluoropolymer is essentially insoluble. As the fluoropolymer therein, that is, polytetrafluoroethylene or a copolymer thereof, is substantially insoluble, it is applied to the carrier cores by first preparing a suspension or dispersion of

the coating material. After coating the carrier cores, the coating material is heated to a temperature sufficiently high, that is, about 400° C., so that the coating will be cured and fused as to adhere to the cores. As will be appreciated, such a coating procedure is multi-step, time-consuming and more expensive than standard coating processes such as dipping or spray-drying a coating solution. Further, after treatment at the temperature required to fuse the fluoropolymer coating to the carrier cores, it is found that the carrier particles possess stronger and more negative triboelectric charging characteristics than the untreated coated particles. Also, inasmuch as it would be desirable to provide a carrier particle coated with a fluoropolymer, but simultaneously provide such a coated carrier particle by a single-step coating operation, such a need exists.

The present invention is intended to provide a coated carrier material manufacturing technique and product by a single-step coating operation.

The present invention provides coated carrier core particles as claimed in the appended claims.

The solution of polyvinylidene fluoride may comprise copolymers of polyvinylidene fluoride, or polyblends of polyvinylidene fluoride and another coating material. The other coating material is preferably one which possesses strong adhesive properties with respect to metallic carrier core particles and is selected from soluble acrylics such as styrene and alkyl acrylates and methacrylates, for example, copolymers of styrene and methyl methacrylate, terpolymers of styrene, methyl methacrylate and an organo-silane; methyl methacrylate and methacrylic acid copolymers, styrene and methacrylic acid copolymers; polymethacrylonitrile and copolymers thereof; acrylonitrile copolymers such as those containing vinylidene chloride; polyvinyl chloride-maleate copolymers; copolymers containing methacrylic acid and salts thereof; polysulfones; polycarbonates; polyesters such as polycaprolactone, polyhexamethylene terephthalate; polyamides such as Trogamid (trademark) T (poly-2,2,4-trimethylhexamethylene terephthalamide available from Dynamit Nobel of America); and other polyamides such as Amidel (trademark) (a transparent Nylon (trademark) available from Union Carbide Corp., New York, N.Y.).

Any suitable ratio of polyvinylidene fluoride may be employed with respect to the ratio of the second polymer in the polyblends for the

electrostatographic carrier coatings of this invention. Typical ratios of the polyvinylidene fluoride to the second polymer include from 5 parts to 95 parts by weight of the polyvinylidene fluoride to from 95 to 5 parts by weight of the second polymer. However, it is preferred to employ from 20 parts to 80 parts of the polyvinylidene fluoride to from 80 parts of the second polymer, all parts given being by weight, because coated carrier particles possessing more satisfactory physical and electrostatographic properties are obtained.

In the preparation of the carrier materials of this invention, the coating solution is applied to the carrier core particles to provide them with a thin, substantially continuous coating of polyvinylidene fluoride. To improve adhesion of the polyvinylidene fluoride coating to the carrier core particles, it is preferred that the coating material comprise a copolymer or polyblend of polyvinylidene fluoride. In addition, multi-layer coatings may be employed such as coating a primer material on the carrier core particles and then applying the polyvinylidene fluoride coating. The polyvinylidene fluoride coating is applied to the carrier core particles by dissolving the coating material in a suitable solvent such as methyl ethyl ketone and dipping, tumbling or spraying the core particles with the coating solution. Preferably, a fluidized bed coating process is employed as typically a more uniform coating is provided to the carrier core particles. In such a coating process, the core particles are suspended and circulated in an upwardly flowing stream of heated air so that the particles are sprayed by the coating material in a first zone. Then, in a second zone, the particles settle through an air stream of lower air velocity where the solvent evaporates to form a thin solid coating on the particles. Successive layers of coating on the particles are obtained by recirculating them through the first and second zones of the fluid bed coating apparatus.

Any suitable coating weight or thickness of polyvinylidene fluoride, copolymer or polyblend thereof, may be employed to coat the carrier core particles. However, a coating having a thickness at least sufficient to form a substantially continuous film on the core particles is preferred because the carrier coating will then possess sufficient thickness to resist abrasion and minimize pinholes which may adversely affect the triboelectric properties of the coated carrier particles, and also in order that the desired triboelectric effect to the carrier is obtained and to maintain a sufficient negative charge

on the carrier, the toner being charged positively in such an embodiment so as to allow development of negatively-charged images to occur. Generally, for cascade and magnetic brush development, the carrier coating may comprise from 0.05 microns to 3.0 microns in thickness on the carrier particle. Preferably, the coating should comprise from 0.2 microns to 0.7 microns in thickness on the carrier particle because maximum coating durability, toner impactation resistance, and copy quality are achieved. To achieve further variation in the properties of the final coated product, other additives such as plasticizers, reactive or non-reactive resins, dyes, pigments, conductive fillers such as carbon black, wetting agents and mixtures thereof may be mixed with the coating material. In addition, where the carrier core is a magnetizable material, it is possible to provide carrier particles having magnetic properties.

Following application of the coating to the carrier particles of this invention, it has been found that, when the carrier particles are mixed with a conventional toner material, such as one comprising a styrene/n-butyl methacrylate copolymer and carbon black, the triboelectric charge generated on the carrier particles is in the range of between -35 to -60 microcoulombs per gram of toner particles. Since such a triboelectric charge is too high to provide satisfactory developed image print density with conventional toner materials, it has been found that thermal treatment of the coated carrier particles at a temperature of up to about 200° C provides coated carrier particles which generate much lower negative triboelectric charging values. That is, the thermal treated coated carrier particles of this invention unexpectedly obtain triboelectric charging values in the range of between -11 to -24 microcoulombs per gram of toner material after having been treated at the aforementioned temperature range for between 30 minutes and up to 60 minutes. It was found that the triboelectric charging values of the thus heat-treated coated carrier particles are excellent to provide developed copies having high image print density, high resolution and low background. In addition, the triboelectric charging values of the carrier particles remain stable over extended periods of milling. Further, the magnitude of the change in the triboelectric charging values of the thus-treated coated carrier particles of this invention being on the order of 40 to 70% is unexpected in view of the prior art. Although there is substantial commercial interest in fluoropolymer coated carrier particles, no method of

accomplishing this degree of control of triboelectric charging values of such coated carrier particles was previously known. In addition, it was also found that powder coatings and dispersion coatings of polyvinylidene fluoride normally require a higher temperature treatment, that is, of at least 225° C, to fuse the polymer and form a continuous film on metallic carrier cores. Otherwise, the polymer has poor adhesion and does not yield a useful carrier particle coating. The same is true of polytetrafluoroethylene coatings which require a fusion temperature of about 400° C. Thus, the thermal treatment conditions employed in modifying the triboelectric charging values of solution coated polyvinylidene fluoride carrier particles are much less stringent. In addition, the effect on the triboelectric charging values of the coated carrier particles of this invention appears to be independent of the second polymer material or primer used either as a multi-layer or polyblend since they have markedly different triboelectric charging properties.

Any suitable well-known coated or uncoated carrier material may be employed as the core or substrate for the carrier particles of this invention. Typical carrier core materials are methyl methacrylate, glass, silicon dioxide, flintshot, ferromagnetic materials such as iron, steel, ferrite, nickel, and mixtures thereof. An ultimate coated carrier particle having an average diameter in the range substantially 30 microns to substantially 1,000 microns is preferred because the carrier particle then possesses sufficient density and inertia to avoid adherence to the electrostatic images during the development process. Adherence of carrier particles to an electrostatographic drum is undesirable because of the formation of deep scratches on the drum surface during the image transfer and drum cleaning steps, particularly where cleaning is accomplished by a web cleaner such as the web disclosed in U S Patent No. 3 186 838.

Any suitable pigmented or dyed toner material may be employed with the carrier particles of this invention. Typical toner materials are gum copal, gum sandarac, resin, cumarone-indene resin, asphaltum, gilsonite, phenolformaldehyde resins, resin -modified phenolformaldehyde resins, methacrylic resins, polystyrene resins, epoxy resins, polyester resins, polyethylene resins, vinyl chloride resins, and copolymers or mixtures thereof. The particular toner material to be employed depends upon the separation of the toner particles from the carrier particles in the triboelectric series. Among the patents describing toner compositions are U.S. Patents Nos. 2 659 670,

2 753 308, 2 788 288 and 3 070 342 and U.S. Reissue 25 136. These toners generally have an average particle diameter in the range substantially 5 to 30 microns.

Any suitable pigment or dye may be employed as the colorant for the toner particles. Colorants for toners are well known and are, for example, carbon black, nigrosine dye, aniline blue, Caleo Oil Blue, chrome yellow, ultramarine blue, Quinoline Yellow, methylene blue chloride, Monastral Blue, Malachite Green Oxalate, lampblack, Rose Bengal, Monastral Red, Sudan Black BN, and mixtures thereof. The pigment or dye should be present in the toner in a sufficient quantity to render it highly colored so that it will form a clearly visible image on a recording member.

Any suitable conventional toner concentration may be employed with the carrier particles of this invention. Typical toner concentrations are 1 part toner with 10 to 200 parts by weight of carrier.

Any suitable well-known electrophotosensitive material may be employed as the photoreceptor with the carrier particles of this invention. Well-known photoconductive materials are vitreous selenium, organic or inorganic photoconductors embedded in a non-photoconductive matrix, organic or inorganic photoconductors embedded in a photoconductive matrix, or the like. Representative patents in which photoconductive materials are disclosed include U.S. Patents 2 803 542, 2 970 906, 3 121 006, 3 121 007 and 3 151 982.

In the following examples, the relative triboelectric values generated by contact of carrier particles with toner particles are measured by means of a Faraday cage. This device comprises a stainless steel cylinder having a diameter of about 1 inch and a length of about 1 inch. A screen is positioned at each end of the cylinder; the screen openings are of such a size as to permit the toner particles to pass through the openings but prevent the carrier particles from making such passage. The Faraday cage is weighed, charged with about 0.5 gram of the carrier particles and toner particles, reweighed, and connected to the input of a coulomb meter. Dry compressed air is then blown through the cylinder to drive all the toner particles from the carrier particles. As the electrostatically charged toner particles leave the Faraday cage, the oppositely-charged carrier particles cause an equal amount of

electronic charge to flow from the cage, through the coulomb meter, to ground. The coulomb meter measures this charge which is then taken to be the charge on the toner which was removed. Next, the cylinder is reweighed to determine the weight of the toner removed. The resulting data are used to calculate the toner concentration and the average charge-to-mass ratio of the toner. Since the triboelectric measurements are relative, the measurements should for comparative purposes be conducted under substantially-identical conditions. Other suitable toners may be substituted for the toner composition used in the examples.

The following examples, other than the control example, further illustrate and compare methods of preparing and utilizing the carrier particles of the present invention in electrostatographic applications. Parts and percentages are by weight unless otherwise indicated.

EXAMPLE I

A developer mixture was prepared by applying to steel carrier particles having an average diameter of 100 microns a primer material comprising a polyvinyl chloride-maleate copolymer commercially available as Exon 470 from Firestone Plastics Company, Pottstown, Pa. The primer material was dissolved to about 5.0% solids by weight in methyl ethyl ketone and applied to the carrier cores in a fluidized bed coating apparatus wherein the bed temperature was limited to between about 40° C and 50° C. The primer solution is applied to provide a net coating weight, by weight of solids, of about 0.3% to the carrier cores.

The primed carrier particles were then overcoated with a coating solution comprising polyvinylidene fluoride, commercially available as Kynar 201 from Pennwalt Corp., Philadelphia, Pa. The coating solution was prepared with methyl ethyl ketone and applied to the carrier particles in the aforementioned coating apparatus maintained at a temperature of between about 40° C and 50° C to provide a net coating weight, by weight of solids, of about 0.3% polyvinylidene fluoride to the primed carrier particles.

The coated carrier particles are cooled to room temperature and screened to remove agglomerated particles. About 100 parts of the screened carrier particles are mixed with about 1 part of finely-divided toner particles to form a developer mixture. The composition of the toner particles comprises a styrene-n-butyl methacrylate copolymer and carbon black. The resultant developer mixture was roll-mill mixed for various times and samples taken

therefrom after 0.5 and 2.0 hours for measurement of the triboelectric charge generated on the carrier particles as previously indicated. The triboelectric values were found to be about -37 and -60 microcoulombs per gram of toner particles, respectively.

A fresh sample of the coated carrier particles was then placed in an air circulating oven at about 200° C for about 1 hour. Due to the heat-up time for the glass trays and the carrier particles, the actual treatment time is about 45 minutes. After cooling in air and screening for agglomerates, 100 parts of the treated carrier particles were mixed with 1 part of the toner particles as above. The resultant developer mixture was roll-mill mixed and samples taken therefrom after 0.5 and 2.0 hours for measurement of the triboelectric charge generated on the carrier particles as previously indicated. The triboelectric values were found to be -12 and -12 microcoulombs per gram of toner particles, respectively.

Further, upon examination of the carrier particles, it was found that carrier coating adhesion is excellent and toner impaction on the carrier coating is insignificant.

EXAMPLE II

A developer mixture was prepared by applying to steel carrier particles as in Example I a primer material comprising an acrylic primer, commercially available as BFG 1104 from B. F. Goodrich Company, Akron, Ohio. The primer material was diluted with methyl ethyl ketone to about 26.0% solids by weight and applied to the carrier cores in a fluidized bed coating apparatus wherein the bed temperature was limited to between about 40° C and 50° C. The primer solution was applied to provide a net coating weight, by weight of solids, of about 0.3% to the carrier cores.

The primed carrier particles were then overcoated with a coating solution comprising polyvinylidene fluoride. The coating solution was prepared with methyl ethyl ketone and applied to the carrier particles in the aforementioned coating apparatus maintained at a temperature of between about 40° C and 50° C to provide a net coating weight, by weight of solids, of about 0.6% polyvinylidene fluoride to the primed carrier particles.

After screening to remove any agglomerates, about 100 parts of the coated carrier particles were mixed with about 1 part of the toner particles of Example I. The resultant developer mixture was roll-mill mixed for various

times and samples taken therefrom after 0.5 and 2.0 hours for measurement of the triboelectric charge generated on the carrier particles as previously indicated. The triboelectric values were found to be -29 and -36 microcoulombs per gram of toner particles, respectively.

A fresh sample of the coated carrier particles was then placed in an air circulating oven at about 200° C for about 1 hour. Due to the heat-up time for the glass trays and the carrier particles, the actual treatment time is about 45 minutes. After cooling in air and screening for agglomerates, about 100 parts of the treated carrier particles were mixed with about 1 part of the toner particles of Example I. The resultant developer mixture was roll-mill mixed and samples taken therefrom after 0.5 and 2.0 hours for measurement of the triboelectric charge generated on the carrier particles as previously indicated. The triboelectric values were found to be -16 and -20 microcoulombs per gram of toner particles, respectively.

Further, upon examination of the carrier particles, it was found that carrier coating adhesion is excellent and toner impaction on the carrier coating is insignificant.

EXAMPLE III

A developer mixture was prepared by applying to steel carrier particles as in Example I a coating composition comprising a blend of a polyvinyl chloride-maleate copolymer mixed with polyvinylidene fluoride. The coating composition was dissolved in methyl ethyl ketone and blended as to provide a net coating weight, by weight of solids, of the polyvinyl chloride-maleate copolymer and of the polyvinylidene fluoride, of 0.5% and 0.3%, respectively.

After application of the polyblend coating composition in a fluidized bed coating apparatus wherein the bed temperature was limited to between 40° C and 50° C, about 100 parts of the dry coated carrier particles were mixed with about 1 part of the toner particles of Example I. The resultant developer mixture was roll-mill mixed and samples taken therefrom after 0.5 and 2.0 hours for measurement of the triboelectric charge generated on the carrier particles as previously indicated. The triboelectric values were found to be -33 and -55 microcoulombs per gram of toner particles respectively.

A fresh sample of the coated carrier particles was then placed in

an air circulating oven at about 200° C for about 1 hour. Due to the heatup time for the glass trays and the carrier particles, the actual treatment time is about 45 minutes. After cooling in air and screening for agglomerates, about 100 parts of the treated carrier particles were mixed with about 1 part of the toner particles of Example I. The resultant developer mixture was roll-mill mixed and samples taken therefrom after about 0.5 and 2.0 hours for measurement of the triboelectric charge generated on the carrier particles as previously indicated. The triboelectric values were found to be -10 and -9 microcoulombs per gram of toner particles, respectively.

Further, upon examination of the carrier particles, it was found that carrier coating adhesion is excellent and toner impaction on the carrier coating is insignificant.

EXAMPLE IV

A developer mixture was prepared by applying to steel carrier particles as in Example I a coating composition comprising a blend of a polyvinyl chloride-maleate copolymer mixed with polyvinylidene fluoride. The coating composition was dissolved in methyl ethyl ketone and blended as to provide a net coating weight, by weight of solids, of the polyvinyl chloride-maleate copolymer and of the polyvinylidene fluoride, of 0.4% and 0.4%, respectively.

After application of the polyblend coating composition in a fluidized bed coating apparatus wherein the bed temperature was limited to between 40° C and 50° C, about 100 parts of the dry coated carrier particles were mixed with about 1 part of the toner particles of Example I. The resultant developer mixture was roll-mill mixed and samples taken therefrom after about 0.5 and 2.0 hours for measurement of the triboelectric charge generated on the carrier particles as previously indicated. The triboelectric values were found to be -52 and -55 microcoulombs per gram of toner particles, respectively.

A fresh sample of the coated carrier particles was then placed in an air circulating oven at about 200° C for about 1 hour. Due to the heat-up time for the glass trays and the carrier particles, the actual treatment time is about 45 minutes. After cooling in air and screening for agglomerates, about 100 parts of the treated carrier particles were mixed with about 1 part of the toner particles of Example I. The resultant developer mixture was roll-mill

mixed and samples taken therefrom after about 0.5 and 2.0 hours for measurement of the triboelectric charge generated on the carrier particles as previously indicated. The triboelectric values were found to be -16 and -19 microcoulombs per gram of toner particles, respectively.

Further, upon examination of the carrier particles, it was found that carrier coating adhesion is excellent and toner impaction in the carrier coating is insignificant.

EXAMPLE V

A developer mixture was prepared by applying to steel carrier particles as in Example I a coating composition comprising a blend of a polyvinyl chloride-maleate copolymer mixed with polyvinylidene fluoride. The coating composition was dissolved in methyl ethyl ketone and blended as to provide a net coating weight, by weight of solids, of the polyvinyl chloride-maleate copolymer and of the polyvinylidene fluoride, of 0.2% and 0.6%, respectively.

After application of the polyblend coating composition in a fluidized bed coating apparatus wherein the bed temperature was limited to between 40°C and 50°C, about 100 parts of the dry coated carrier particles were mixed with about 1 part of the toner particles of Example I. The resultant developer mixture was roll-mill mixed and samples taken therefrom after about 0.5 and 2.0 hours for measurement of the triboelectric charge generated on the carrier particles as previously indicated. The triboelectric values were found to be about -33 and -47 microcoulombs per gram of toner particles, respectively.

A fresh sample of the coated carrier particles was then placed in an air circulating oven at about 200°C for about 1 hour. Due to the heat-up time for the glass trays and the carrier particles, the actual treatment time is about 45 minutes. After cooling in air and screening for agglomerates, about 100 parts of the treated carrier particles were mixed with about 1 part of the toner particles of Example I. The resultant developer mixture was roll-mill mixed and samples taken therefrom after about 0.5 and 2.0 hours for measurement of the triboelectric charge generated on the carrier particles as previously indicated. The triboelectric values were found to be about -21 and -23 microcoulombs per gram of toner particles, respectively.

Further, upon examination of the carrier particles, it was found

that carrier coating adhesion is excellent and toner impaction on the carrier coating is insignificant.

In summary, it has been shown that the adhesion properties of electrostatographic carrier particles coated with polyvinylidene fluoride may be substantially improved by employing a priming material in multi-layer or polyblend fashion. Further, the triboelectric properties of polyvinylidene fluoride coated carrier particles may be modified by a modest post-treatment step as to lower the unacceptably high range of triboelectric values obtained therewith of from between -35 to -60 microcoulombs per gram of toner material to a lower and satisfactory range of between -11 and -24 microcoulombs per gram of toner material as to provide maximum copy quality. In addition, the polyvinylidene fluoride coatings may be applied as a solution compared to a solid particle fusion procedure for other fluoropolymers such as polytetrafluoroethylene and copolymers thereof.

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CLAIMS:

1. A method of making a coated carrier particle for electrostatographic developer mixtures, including the steps of:

choosing a core having an average size between 30 and 1000 microns, characterised by

contacting the core with a solution of polyvinylidene fluoride in a suitable solvent;

evaporating the solvent to form an integral thin film of polyvinylidene fluoride, and

thermally treating the coated core by heating it up to 200⁰C for between 30 and 60 minutes.

2. A method as claimed in claim 1, characterised in that the core is coated in a fluidised bed, with the core being suspended in an upward stream of heated air while it is sprayed with the solution.

3. A method as claimed in claim 1 or 2, characterised in that the solution comprises a copolymer of polyvinylidene fluoride.

4. A method as claimed in claim 1 or 2, characterised in that said coating solution includes a second coating material which possesses strong adhesive properties with respect to the core.

5. A method as claimed in claim 4, characterised in that said second coating material is styrene, alkyl acrylate, alkyl methacrylate, organosilane, or polyvinyl chloride-maleate.

6. A method as claimed in claim 4 or 5, characterised in that said polyvinylidene fluoride is present in an amount of from 5 to 95 parts by weight with respect to said second coating material.

7. A method as claimed in any preceding claim, characterised in that the thickness of said thin film on said core is between 0.05 and 3.0 microns.

8. A method as claimed in any preceding claim, characterised in that said core comprises a ferromagnetic material of iron, steel, ferrite, nickel, or mixtures thereof.

9. A coated carrier particle characterised by being made by the method claimed in any preceding claim.

10. An electrostatographic developer mixture comprising finely-divided toner particles electrostatically clinging to the surface of carrier particles as claimed in claim 9.

11. An electrostatographic developer mixture as claimed in claim 10, characterised in that said toner particles comprise a styrene/n-butyl methacrylate copolymer and carbon black.

12. An electrostatographic imaging process comprising the steps of providing an electrostatographic imaging member having a recording surface, forming a negatively-charged electrostatic latent image on said recording surface, characterised by contacting said electrostatic latent image with a developer mixture as claimed in claim 10 or 11, whereby at least a portion of said finely-divided toner composition is attracted to and deposited on said recording surface in conformance with said electrostatic latent image.



European Patent
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EUROPEAN SEARCH REPORT

0034423

Application number
EP 81 30 0373

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl.)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
	<u>GB - A - 1 438 973 (XEROX)</u> * The claims; page 4, lines 79-105; page 5, lines 73-98; page 6, lines 22-58; page 7, lines 83-106 * --- <u>GB - A - 2 014 876 (XEROX)</u> * The claims; page 4, lines 13-93* --- RESEARCH DISCLOSURE, June 1974, no. 122, art. no. 12243 HAMPSHIRE (GB) A.E. FIELDS: "Carrier particles for use in electrographic developer composition" pages 35-36 * The whole article * --- PRODUCT LICENSING INDEX, August 1972, no. 100, art. no. 10029 HAMPSHIRE (GB) "Method of and apparatus for fluidized bed coating of electrophotographic toner carrier particles" pages 69-71 * Page 69, column 2, paragraphs 2-4; page 71, the examples * --- RESEARCH DISCLOSURE, April 1974, no. 120, art. no. 12050 HAMPSHIRE (GB) G. NEUNER: "Treating iron carrier particles for electrography" page 28 * Entire article * --- . / .	1-3,8-12 1-12 1,3,8-12 1-3,8-12 1,2,8-12	G 03 G 9/10 TECHNICAL FIELDS SEARCHED (Int. Cl.) G 03 G 9/10 CATEGORY OF CITED DOCUMENTS X: particularly relevant A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention E: conflicting application D: document cited in the application L: citation for other reasons &: member of the same patent family, corresponding document
The present search report has been drawn up for all claims			
Place of search The Hague	Date of completion of the search 18-05-1981	Examiner VANHECKE	

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