

[54] COATED CARRIER PARTICLES
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[56] References Cited

UNITED STATES PATENTS

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3,507,686	4/1970	Hagenbach	117/168
3,533,835	10/1970	Hagenbach	117/16
3,558,492	1/1971	Proskow	96/1.5
3,725,118	4/1973	Fuller	117/100 M
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[57] ABSTRACT

An electrophotographic development carrier comprises core particles coated with a mixture of a fluoropolymer and a modifying material. When utilized with appropriate electroscopic toner materials, the carrier is effective in producing a relatively negative triboelectric charging of the toner particles while it obtains a relatively positive charge. The relatively positive triboelectric characteristic is obtained by curing the coated particles through heating at a temperature less than about 700°F.

6 Claims, No Drawings

COATED CARRIER PARTICLES

This is a division of copending application Ser. No. 110,756 filed Jan. 28, 1971 now U.S. Pat. No. 2,778,262.

In electrophotography, a photoconductor is charged and then exposed imagewise to light. In the area of the photoconductor exposed to light, the charge dissipates or decays while the dark areas retain the electrostatic charge.

The difference in the charges between the areas exposed to light and dark areas produces electrical fields therebetween. Accordingly, the resultant latent electrostatic image on the photoconductor is developed by depositing small colored particles, which are known as toner particles, over the surface of the photoconductor with the toner particles having a charge so as to be directed by the electrical fields to the image areas of the photoconductor to develop the electrostatic image.

A number of means are known for developing the latent electrostatic image by the application of the toner particles. One of these is known as cascade development and is described in U.S. Pat. No. 2,618,552 to Wise.

Another means is known as the magnetic brush development process. This method is described in U.S. Pat. No. 2,874,063 to Greig.

In each of the cascade and magnetic brush development processes, a two component developer material is utilized. The developer material comprises a mixture of small toner particles and relatively large carrier particles. The toner particles are held on the surfaces of the relatively large carrier particles by electrostatic forces, which develop from the contact between the toner and carrier particles producing triboelectric charging of the toner and the carrier to opposite polarities. When the developer material is moved into contact with the latent electrostatic image of the photoconductor, the toner particles are attracted to the latent image.

The toner and carrier particles of the developer material are specially made and processed so that the toner obtains the correct charge polarity and magnitude of charge to insure that the toner particles are preferentially attracted to the desired image areas of the photoconductor. For a given developer-hardware system, the magnitude of the triboelectric charge is important in that if such charge is too low, the copy will be characterized by high print density but heavy background; if the charge is too high, the background is good but the print density will tend to be low. Thus, there is an optimum range of toner charge for best overall results.

Prior art dry developer materials, which are employed in an automatic copy machine, have carrier filming problems due to the recycling of the carrier particles through many cycles producing many collisions between the carrier particles and between the carrier particles and parts of the machine. The attendant mechanical friction causes some toner material to form a physically adherent film on the surfaces of the coatings of the carrier particles.

When this occurs, there is a gradual accumulation of permanently attached film of toner material on the surfaces of the carrier particles. This filmed layer of toner tends to impair the normal triboelectric charging of the toner particles in the developer mix because the normal toner-carrier triboelectric charging is partly replaced

by a toner-toner relationship. As a result, the toner, which is available for developing the latent electrostatic image, is less highly charged on the average. If this occurs to a sufficient degree, the improperly charged toner particles can be deposited on the non-image areas whereby the quality of the copies is impaired since the non-image areas possess an unacceptable level of background toner.

When toner filming occurs to a sufficient degree, the entire developer material must be replaced thereby increasing the cost of operation of the copy machine. Furthermore, it is time consuming. This problem is especially significant in high speed copy machines in which thousands of copy cycles occur in a relatively short period of time or in copy machines in which the developer is continuously agitated.

Furthermore, because of the contact between the carrier particles and between the carrier particles and parts of the machine, there is abrasion of the coating of the carrier particles. This abrasion of the coating also may reduce the effectiveness of the triboelectric charging between the carrier and the toner by exposing the toner to the core material of the carrier.

Thus, if the coating is not sufficiently resistant to abrasion, early replacement of the entire developer material is required. Again, this replacement of the entire developer material is costly and time consuming, especially in high speed copy machines.

Furthermore, even if the coating of the carrier particle resists abrasion, the coating also must have good adhesion to the core of the carrier particle. Otherwise, the coating can chip, flake, or spall, even if the coating is of a material that is not subject to abrasion, due to the rubbing or contact between the various carrier particles and between the carrier particles and parts of the machine. This also requires early replacement of the developer material.

Therefore, in addition to having the proper triboelectric characteristics, the coating of a carrier particle must have good anti-stick (low surface energy) properties to prevent filming of the carrier particle by the toner. The coating also must have good adherence to the core and be resistant to abrasion. Fluoropolymers such as fluorocarbons and fluorosilicones, for example, are materials having good anti-stick properties to prevent or greatly inhibit toner filming thereon as well as being capable of adhering to a core and having resistance to abrasion.

It has previously been suggested in U.S. Pat. No. 3,533,835 to Hagenbach et al. to employ fluorocarbons such as polytetrafluoroethylene, for example, as a coating for a carrier particle if finely-divided conductive particles are impacted into the coating. However, polytetrafluoroethylene, which is sold under the trademark Teflon by du Pont, has always been described as being at or near the bottom of any published triboelectric series. In fact, the trademark Teflon has been used in some published triboelectric series as the identification of the material rather than polytetrafluoroethylene or fluorocarbon. The trademark Teflon is employed by du Pont to identify various non-stick finishes including both polymers and/or copolymers of fluorocarbons and mixtures of polymers and/or copolymers of a fluorocarbon and a modifying resin or material.

Accordingly, materials sold under the trademark Teflon, particularly polytetrafluoroethylene, have not been considered applicable for use as carrier coatings

in any electrophotographic system in which it is desired to employ toner particles having a negative triboelectric charge because of the location of Teflon, particularly polytetrafluoroethylene, in the various published triboelectric series.

The present invention satisfactorily solves the foregoing problem by providing a coating of a mixture of fluorocarbon and a modifying material on a core so that the carrier particle has the characteristic of being triboelectrically positive with respect to many toners. Because of the fluorocarbon in the mixture, which is sold as Teflon, the coating of the carrier particle has all the desired properties of resistance to abrasion, adherence to the core, and an anti-stick surface so that the filmed layer of toner cannot form thereon while still having the characteristic of being triboelectrically positive with respect to various toners.

The present invention achieves this unexpected result by heating the coating carrier particles at a temperature at which the coating adheres to the core and becomes triboelectrically positive with respect to various toners. While it is known that the various materials, which are sold by du Pont under the trademark Teflon, require a curing temperature to produce a desired finish, there is no suggestion that controlling the curing conditions through selecting a curing temperature can produce a coating by the material on a core that results in the coated core being positioned substantially high in a triboelectric series so as to be positive with respect to various materials which may be readily employed as toners in an electrophotographic system whereby the toners may have a triboelectrically negative charge.

The mechanism by which an overall triboelectrically electropositive carrier is obtained has not been elucidated. It may be conjectured that the inherent electronegativity of the fluorocarbon is simply overridden by the electropositive modifying material. Possibly such an effect might be accentuated by having a heavier concentration of the modifying material at or near the surface of the coating.

By using the coated carrier particles of the present invention, an improved electrophotographic process is provided. In this improved process, a latent electrostatic image is contacted with a developer mixture utilizing the coated carrier particles of this invention.

An object of this invention is to provide a method of forming an electrophotographic development carrier having a long life while being triboelectrically positive with respect to various toners.

Another object of this invention is to provide an electrophotographic development carrier having a long life while being triboelectrically positive with respect to various toners.

A further object of this invention is to provide an improved electrophotographic process.

The foregoing and other objects, features, and advantages of the invention will be more apparent from the following more particular description of a preferred embodiment of the invention.

The core of the carrier particle formed by the present invention may be any material to which the coating can adhere and can withstand the curing temperature. Thus, the material of the core of the carrier particle may be sand, glass beads, or metallic beads, for example.

When the carrier particles of the present invention are employed in a developer utilized in the magnetic

brush process, the material of the core is a ferromagnetic material such as iron or steel, for example. Other suitable ferromagnetic materials such as magnetic oxides and alloys (copper-nickel-iron), for example, may be employed.

The size of the core particles generally may be between 50 and 1,000 microns. The preferred size range is between 100 and 600 microns.

The material of the coating of the core of the carrier particle of the present invention is formed of a mixture of a fluoropolymer and a modifying material. While the fluoropolymer may be a fluorosilicone, for example, it is preferably a fluorocarbon. Furthermore, the fluorocarbon is preferably a copolymer of tetrafluoroethylene and hexafluoropropylene having thermal properties very close to the 1:1 copolymer.

Mixtures of the copolymer of tetrafluoroethylene and hexafluoropropylene having thermal properties very close to the 1:1 copolymer and a modifying material are sold by du Pont as Teflon. The particular mixture is identified by numerals as a description thereof.

The coating may be applied to the core by any suitable means such as dipping, spraying, tumbling the cores with a coating solution in a barrel, or through a controlled fluidized bed. The fluidized bed process is preferred since it enables a uniform coating to be applied to the cores of the particles. The fluidized bed process is described in U.S. Pat. Nos. 2,648,609, 2,799,241, and 3,253,944 to Wurster and 3,196,827 and 3,241,520 to Wurster et al.

In the Wurster fluidized bed process, for example, the cores are suspended and circulated in an upwardly flowing stream of heated gas such as air, for example, in a tower in a manner such that the particles move upwardly and are sprayed by the coating material in a first zone. Then, in a second zone, the particles settle through the air stream in a zone of lower air velocity and the liquid, which is a solvent and/or a dispersant, of the sprayed coating evaporates to leave a thin solid coating on the particles. The particles recirculate to the first zone so that successive layers of the coating material are built up on the core in a uniform manner.

After the core has been coated to form the carrier particle, the coating is cured. After the coating has been appropriately cured, it possesses the desired triboelectric properties.

Curing of the coating occurs by heating the carrier particles at a temperature below about 700°F and preferably above 300°F. The particular temperature would be dependent upon the coating.

The minimum temperature of 300°F insures that the coating adheres to the core. The curing time is preferably about 15 minutes.

The carrier particles are then cooled to a low temperature, preferably by ambient air cooling. By maintaining the temperature at which the carrier particles are heated after their cores have been coated to below 700°F, the carrier particles have an electropositive characteristic even though they include a fluoropolymer whereby they would be expected to have an electronegative characteristic.

The thickness of the carrier coating may vary from 1 to 25 microns. However, it is preferably about 2 to 5 microns. The coating thickness must be sufficient to impart the desired triboelectric effect to the carrier with the upper limit of the thickness being determined by physical integrity of the coating.

Various suitable pigmented or dyed electroscopic toner materials may be utilized with the carrier, which have the cores of their particles coated by the coatings of the present invention. The suitability of a toner material to be used in conjunction with these carriers depends on its triboelectric behavior with such carriers.

Examples of materials which are potentially viable as candidate toners includes: rosin, gilsonite, phenolformaldehyde resins, rosin modified phenolformaldehyde resins, methacrylic resins, polystyrene resins, polyethylene resins, polypropylene resins, epoxy resins, cumarone indene resin, asphaltum, polyamides, polyurethanes, polyesters, carboxylated polyethylene ionomer resins, and mixtures of any of the foregoing.

The following are examples of the present invention in detail. The examples are included merely to aid in the understanding of the invention, and variations may be made by one skilled in the art without departing from the spirit and scope of this invention.

EXAMPLE I

A coating formulation containing a fluoropolymer and a modifying resin, which is sold by du Pont as 954-101 light green Teflon-S, is diluted about three volumes to one volume with methyl ethyl ketone by stirring at room temperature and sprayed onto steel beads having an average diameter of about 450 microns and a surface suitably clean for adhesion. The fluoropolymer is a copolymer of tetrafluoroethylene and hexafluoropropylene which has thermal properties very close to the 1:1 copolymer. The modifying resin is epoxy.

The coating formulation of 954-101 light green Teflon-S is a solution including solvents and a pigment in addition to the fluoropolymer and the modifying resin. The modifying resin is substantially dissolved in the solvents, which comprise a mixture of methyl isobutyl ketone and xylenes in ratios of 2:3 by weight. The pigment, which is chromic oxide, and the fluoropolymer are cosuspended in the solution of the solvents and the modifying resin. By weight, the fluoropolymer comprises approximately 36% of the total solution, the modifying resin approximately 18.5% of the total solution, the solvents approximately 41.5% of the total solution, and the pigment approximately 4% of the total solution.

About 50 milliliters of the diluted material is applied per pound of steel beads. The material is sprayed onto the beads in a Wurster cyclic fluidized bed tower at a coating temperature of about 100° F.

The coated cores are then placed in an oven, and the temperature of the beads is brought to about 575° F. The beads are left at 575° F for about 15 minutes and then removed from the oven. The beads are cooled to room temperature via ambient air cooling. The coated particles are then screened through a U.S. standard 30 mesh screen to remove agglomerates.

Quantities of this material are now thoroughly mixed with each of three different toners. These are Hunt Graph-O-Print toner sold by Philip A. Hunt Chemical Corporation, Palisades Park, New Jersey, IBM Part No. 1162057 toner, and IBM Part No. 1162051 toner. The resulting developer mixes contain by weight about 1% toner and 99% carrier.

The Hunt Graph-O-Print toner comprises a copolymer of styrene/n-butyl methacrylate resin, polyvinyl butyral plasticizer, and carbon black pigment. The IBM

Part No. 1162057 toner comprises approximately 63.4% by weight of a 70/30 copolymer of styrene/n-butyl methacrylate resin, approximately 29.1% by weight Amberol 800 (Rhom and Haas) maleic anhydride modified polyester, approximately 1.5% by weight polyvinyl stearate plasticizer (Allaco), and approximately 6.0% by weight carbon black pigment. The IBM Part No. 1162051 toner comprises a copolymer of n-butyl methacrylate/methylmethacrylate resin, maleic anhydride modified polyester, polyvinyl butyral plasticizer, carbon black pigment, and a fumed silica physically mixed in the toner after compounding.

The charge generated between the toner and the carrier of each of the mixtures is measured by cascading portions of the mixture across an inclined slide upon which is imposed an electrostatic voltage pattern forming an image and observing the toner weight deposited and the charge that is displaced by the toner.

The basic component of the charge measuring system is a phenolic circuit board wherein the copper has been etched so that a center electrode area is isolated from the outer electrode area by a fine etched lined about 0.005 inch wide. After making arrangements for electrical contacts to the electrodes, a ½ mil Mylar sheet is laminated over the copper electrodes.

The slide is then charged by an AC cut-off corona which has the characteristic of supplying current to the test slide only as long as a potential difference exists between the corona screen and the slide. During charging, the center electrode is biased positive or negative depending on the toner charge polarity being measured.

Since the slide surface potential becomes equal to the screen potential, this serves as a means of repeatedly controlling the charge on the slide. After the Mylar is charged, the two electrodes are returned to ground.

The surface potential is then due to the charge trapped on the Mylar surface and a charge image remains which is quite similar to the charge image on a photoconductor. A proximity voltmeter is used to measure the voltage to which the slide is charged. In these tests, ± 350 volts was used depending on the toner charge polarity. It should be understood that the Mylar acts as a capacitor so that there is a charge stored on the test electrode which is of equal magnitude and opposite polarity to the charge on the Mylar surface.

When the toner-carrier mixture is cascaded over the slide, toner deposits over the center electrode and discharges the slide. The resulting current is fed to an integrating amplifier where the output voltage is proportional to the integral of the input current. A 10^{-8} farad feedback capacitor is used giving a calibration factor of 10^{-8} coulombs charge per volt output. With the observed voltage output, the charge displaced by the toner is easily calculated. The toner weight deposited is easily measured by weighing the slide before and after cascading the toner-carrier mixture. The charge is calculated by dividing the charge displaced by the toner weight deposited and converting to electrons per gram.

The calculated charges are found to be 3.0 to 6.0×10^{13} electrons/gram of toner and the toner charge is negative. Since the toners are negatively charged to a desired magnitude, the carrier, which has been coated as described above, has served as a functional electro-positive carrier with these toners.

EXAMPLE II

A coating formulation containing a fluoropolymer and a modifying resin, which is sold by du Pont as 959-205 dark chocolate one coat Teflon enamel, is diluted about one volume to one volume with du Pont T-8741 thinner by stirring at room temperature and sprayed onto steel beads having an average diameter of about 450 microns and a surface suitably clean for adhesion. The fluoropolymer is a copolymer of tetrafluoroethylene and hexafluoropropylene which has thermal properties very close to the 1:1 copolymer. The modifying resin is urethane.

The coating formulation of 959-205 dark chocolate one coat Teflon enamel is a solution including solvents and a pigment in addition to the fluoropolymer and the modifying resin. The modifying resin is substantially dissolved in the solvents, which comprise a mixture of methyl isobutyl ketone and n-methyl-2-pyrrolidone in ratios of 2:3 by weight with a small amount of water (approximately 5% of the solvents). The pigment, which is iron oxide, and the fluoropolymer are cosuspended in the solution of the solvents and the modifying resin. By weight, the fluoropolymer comprises approximately 20% of the total solution, the modifying resin approximately 6% of the total solution, the solvents approximately 71% of the total solution, and the pigment approximately 3% of the total solution. The du Pont T-8741 thinner is a diluent having the same basic solvent make-up as the solvents in the coating formulation of the 959-205 dark chocolate one coat Teflon enamel.

About 50 milliliters of the diluted material is applied per pound of steel beads. The material is sprayed onto the beads in a Wurster cyclic fluidized bed tower at a coating temperature of about 150°F.

The coated cores are then placed in an oven and the temperature of the beads is brought to about 575°F. The beads are left at 575°F for about 15 minutes and then removed from the oven. The beads are cooled to room temperature via ambient air cooling. The coated particles are then screened through a U.S. standard 30 mesh screen to remove agglomerates.

Quantities of this material are now thoroughly mixed with each of three different toners, which are the same as in Example I. The resulting developer mixes contain by weight about 1% toner and 99% carrier.

The calculated charges, which are determined in the same manner as in Example I, are found to be 3.0 to 6.0 $\times 10^{13}$ electrons/gram of toner. With Hunt Graph-O-Print and IBM Part No. 1162057, the toner charge is negative, and with IBM Part No. 1162051, the toner charge is positive. Since the Hunt Graph-O-Print and IBM Part No. 1162057 toners are negatively charged to a desired magnitude, the carrier, which has been coated as described above, has served as a functional electropositive carrier with these toners. Since the IBM Part No. 1162051 toner has positively charged to a desired magnitude, the carrier, which has been coated as described above, has served as a functional electronegative carrier with this toner.

EXAMPLE III

A coating formulation containing a fluoropolymer and a modifying resin, which is sold by du Pont as 958-202 steel blue Teflon-S, is diluted about one volume to one volume with du Pont T-8595 thinner by

stirring at room temperature and sprayed onto steel beads having an average diameter of about 450 microns and a surface suitably clean for adhesion. The fluoropolymer is a copolymer of tetrafluoroethylene and hexafluoropropylene which has thermal properties very close to the 1:1 copolymer. The modifying resin is urethane.

The coating formulation of 958-202 steel blue Teflon-S is a solution including solvents and a pigment in addition to the fluoropolymer and the modifying resin. The modifying resin is substantially dissolved in the solvents, which comprise a mixture of methyl isobutyl ketone and n-methyl-2-pyrrolidone in ratios of 1:3 by weight. The pigment, which is cobalt aluminate, and the fluoropolymer are cosuspended in the solution of the solvents and the modifying resin. By weight, the fluoropolymer comprises approximately 16% of the total solution, the modifying resin approximately 5% of the total solution, the solvents approximately 75% of the total solution, and the pigment approximately 4% of the total solution. The du Pont T-8595 thinner is a diluent having the same basic solvent make-up as the solvents in the coating formulation of 958-202 steel blue Teflon-S and contains, by weight, 75% n-methyl-2-pyrrolidone and 25% methyl isobutyl ketone.

About 50 milliliters of the diluted material is applied per pound of steel beads. The material is sprayed onto the beads in a Wurster cyclic fluidized bed tower at a coating temperature of about 150°F.

The coated cores are then placed in an oven and the temperature of the beads is brought to about 500°F. The beads are left at 500°F for about 15 minutes and then removed from the oven. The beads are cooled to room temperature via ambient air cooling. The coated particles are then screened through a U.S. standard 30 mesh screen to remove agglomerates.

Quantities of this material are now thoroughly mixed with each of two different toners. These toners are Hunt Graph-O-Print toner sold by Philip A. Hunt Chemical Corporation, Palisades Park, New Jersey and IBM Part No. 1162057 toner. The resulting developer mixes contain by weight about 1% toner and 99% carrier.

The calculated charges, which are determined in the same manner as in Example I, are found to be 3.0 to 6.0 $\times 10^{13}$ electrons/gram of toner and the toner charge is negative. Since the toners are negatively charged to a desired magnitude, the carrier, which has been coated as described above, has served as a functional electropositive carrier with these toners.

EXAMPLE IV

A coating formulation containing a fluoropolymer and a modifying resin, which is sold by du Pont as 955-105 dark chocolate one coat Teflon enamel, is diluted about one volume to two volumes with a mixture of 60% methyl isobutyl ketone and 40% xylene by weight by stirring at room temperature and sprayed onto steel beads having an average diameter of about 450 microns and a surface suitably clean for adhesion. The fluoropolymer is a copolymer of tetrafluoroethylene and hexafluoropropylene which has thermal properties very close to the 1:1 copolymer. The modifying resin is methyl phenyl silicone.

The coating formulation of 955-105 dark chocolate one coat Teflon enamel is a solution including solvents and a pigment in addition to the fluoropolymer and the

modifying resin. The modifying resin is substantially dissolved in the solvents, which comprise a mixture of n-butyl carbitol, methyl isobutyl ketone, and Panasol RX-4 (xylenes-technical grade) in the ratio of 4.5:4.5:1 by weight. The pigment, which is red iron (III) oxide, and the fluoropolymer are cosuspended in the solution of the solvents and the modifying resin. By weight, the fluoropolymer comprises approximately 17% of the total solution, the modifying resin approximately 17% of the total solution, the solvents approximately 62% of the total solution, and the pigment approximately 4% of the total solution.

About 13 milliliters of the diluted material is applied per pound of steel beads. The material is sprayed onto the beads in a Wurster cyclic fluidized bed tower at a coating temperature of about 130°F.

The coated cores are then placed in an oven, and the temperature of the beads is brought to about 500°F. The beads are left at 500°F for about 15 minutes and then removed from the oven. The beads are cooled to room temperature via ambient air cooling. The coated particles are then screened through a U.S. standard 30 mesh screen to remove agglomerates.

Quantities of this material are now thoroughly mixed with each of three different toners, which are the same as in Example I. The resulting developer mixes contain by weight about 0.9% toner and 99.1% carrier.

The calculated charges, which are determined in the same manner as in Example I, are found to be 3.0 to 6.0×10^{13} electrons/gram of toner and the toner charge is negative. Since the toners are negatively charged to a desired magnitude, the carrier, which has been coated as described above, has served as a functional electro-positive carrier with these toners.

While Examples I to IV show that the use with particular toners and correct heat treatment of the mixture of the fluoropolymer and the modifying material can produce a coating for a carrier particle of a developer in which the carrier particles are triboelectrically positive with respect to the toners, further examples will be given to show that the coatings of Examples I and II have a long life when used in a developer simulator.

In the developer simulator in which the developer mixtures of Examples V to VII were tested, the developer simulator was a conventional bucket elevator cascade developer. The developer mixture was scooped from a reservoir by buckets, elevated to a point above a drum used to simulate a photoconductor drum, cascaded across the drum surface, and then returned to the sump by gravity. This cycle, which is continuously repeated, simulates the environment to which a developer mixture is subjected in an operating copy machine.

The following examples were prepared and tested in the developer simulator:

EXAMPLE V

A coating formulation containing about 0.6% by weight Orasol red "B" dye, sold by Ciba Chemical and Dye Company, Route 208, Fairlawn, New Jersey, and about 4.4% by weight N-type ethyl cellulose, sold by Hercules, Inc., Wilmington, Del., dissolved in methyl ethyl ketone by stirring at room temperature is sprayed onto steel beads having an average diameter of about 450 microns and a surface suitably clean for adhesion.

About 100 milliliters of the solution is applied per pound of steel beads. The material is sprayed onto the

beads in a Wurster cyclic fluidized bed tower at a coating temperature of about 80°F.

The coated cores are then placed in an oven and the temperature of the beads is brought to about 190°F and left there for about 24 hours, at which time the temperature is raised to about 270°F for about an additional one hour. The cured beads are now removed from the oven, cooled to room temperature via ambient air cooling, and screened through a U.S. standard 30 mesh screen to remove agglomerates.

A developer mixture, which forms the control sample, is now prepared by thoroughly mixing 0.5% by weight of Hunt Graph-O-Print toner, sold by Philip A. Hunt Chemical Corporation, Palisades Park, N.J., with the carrier particles. The resultant developer mixture is now exercised in the cascade developer simulator.

After 273 hours of such simulation, the carrier is examined. Substantial amounts of coating are missing, and the carrier surface is heavily filmed or impacted with toner. Charge imparted to the Hunt Graph-O-Print toner is measured by the method outlined in Examples I to IV on two samples. One sample is removed from the developer mixture at the beginning of the simulation and the second sample is removed from the developer mixture at the end of the simulation. The charge of the toner has degraded by about 30% during the simulation.

In addition, electrostatic images developed with the final material in a copy making robot are characterized by high background and poor character definition. Much toner dusting in the operating developer also is noted.

EXAMPLE VI

The same developer simulator experiment, as performed in Example V, is performed except 954-101 light green Teflon-S carrier, prepared as per Example I, is substituted for the red dyed ethyl cellulose carrier. Hunt Graph-O-Print toner at 0.5% by weight is used, and the same developer simulator unit is used.

The carrier is exercised for about 360 hours and then examined. There is no significant filmed-on or impacted toner, and the amount of coating missing from the carrier is minimal.

The charge imparted to the Hunt Graph-O-Print toner is measured by the method outlined in Examples I to IV on two samples. One sample is removed from the developer mixture at the beginning of the simulation and the second sample is removed from the developer mixture at the end of the simulation. No significant difference is found in the charge.

Copy made with this material in the same copy making robot as referred to in Example VIII has low background, good print quality, and there is less dusting in the developer unit than in Example V.

EXAMPLE VII

The same developer simulator experiment, as performed in Example V, is performed except 959-205 dark chocolate one coat Teflon enamel carrier, prepared as per Example II, is substituted for the red dyed ethyl cellulose carrier. Hunt Graph-O-Print toner at 0.5% by weight is used, and the same developer simulator unit is used.

The carrier is exercised for about 340 hours and then examined. There is no significant filmed-on or im-

pacted toner, and the amount of coating missing from the carrier is minimal.

The charge imparted to the Hunt Graph-O-Print toner is measured by the method outlined in Examples I to IV on two samples. One sample is removed from the developer mixture at the beginning of the simulation and the second sample is removed from the developer mixture at the end of the simulation. A significant but not limiting degradation difference is found in the charge.

Copy made with this material in the same copy making robot as referred to in Example VIII has low background, good print quality, and there is less dusting in the developer unit than in Example V.

To ascertain the type of copy produced from a developer mixture having the carriers prepared in accordance with the presence invention, carrier particles formed in accordance with Examples I and II were tested in a copy making robot and then compared with a control sample. The copy making robot is equipped with charging, imaging, developing, transferring, and cleaning stations. The developing station has a conventional bucket cascade developer. The copy making robot uses a photoconductor of the type employed in the copying machine sold by IBM, the assignee of this application, and described in U.S. Pat. No. 3,484,237 to Shattuck et al.

The following examples show the results:

EXAMPLE VIII

The carrier particles were prepared in the same way as described in Example V. The only difference being that the Hunt Graph-O-Print toner was 0.8% by weight rather than 0.5% by weight.

The resultant developer mixture was placed in the copy making robot and one million copies were made. The carrier performance was monitored throughout by observing coating loss, filmed-on or impacted toner, and the toner concentration required for equivalent print densities at essentially constant photoconductor electrostatics.

After 300,000 copies, the carrier has lost 10% to 15% of its coating, exhibits some filmed-on toner, and must operate at 0.6% to 0.7% by weight toner to give print densities equivalent to those obtained at 0.8% to 0.9% toner at the beginning of the test. After one million copies, the carrier has lost about 20% to 25% of its coating, is heavily filmed with toner, and must operate at 0.3% to 0.4% by weight toner to give print densities equivalent to those obtained at 0.8% to 0.9% toner at the beginning of the test. This demonstrates that the carrier's ability to charge toner has been seriously degraded and that operating considerations (toner concentration) has had to have been changed to accommodate the degradation.

EXAMPLE IX

The same copy making robot experiment, as performed in Example VIII, is performed except 954-101 light green Teflon-S carrier, prepared as per Example I, is substituted for the red dyed ethyl cellulose carrier. The Hunt Graph-O-Print toner of 0.8% by weight is used, a sister robot with equivalent hardware is used, and the test is run to one million copies. Again, carrier performance is monitored throughout by observing coating loss, filmed-on or impacted toner, and toner

concentration required for equivalent print densities at essentially constant photoconductor electrostatics.

After 300,000 copies, the carrier has lost only about 5% of its coating, has essentially no filmed-on toner, and the toner concentration for equivalent print density has not changed significantly since the beginning of the test. After one million copies, the carrier has lost only 10% to 15% of its coating, still has no significant filmed-on toner, and the toner concentration for equivalent print density has not changed significantly since the beginning of the test.

EXAMPLE X

The same copy making robot experiment, as performed in Example VIII, is performed except 959-205 dark chocolate one coat Teflon enamel carrier, prepared as per Example II, is substituted for the red dyed ethyl cellulose carrier. Hunt Graph-O-Print toner of 0.8% by weight is used, and the same copy making robot is used as in Example IX. Again, carrier performance is monitored throughout by observing coating loss, filmed-on or impacted toner, and toner concentration required for equivalent print densities at essentially constant photoconductor electrostatics.

After 300,000 copies, the carrier has lost only about 5% of its coating, has essentially no filmed-on toner, and the toner concentration for equivalent print density is lower by only 0.1% toner since the beginning of the test. The test was not run to 1,000,000 copies.

The carrier was in better condition at 300,000 copies than the red dyed ethyl cellulose of Example VIII — less coating loss and no filmed-on toner — but not as good as the 954-101 light green Teflon-S of Example IX as the toner charge (as indicated by the need to run at slightly lower toner concentration) had degraded slightly.

An advantage of this invention is that an electropositive carrier is produced having a long life. Another advantage of this invention is that toner filming of a carrier is reduced.

While the invention has been particularly shown and described with reference to a preferred embodiment thereof, it will be understood by those skilled in the art that various changes in form and details may be made therein without departing from the spirit and scope of the invention.

What is claimed is:

1. Electrophotographic development carrier particles for use with toner particles including:

a plurality of core particles;
a substantially continuous film coating surrounding each of said core particles and firmly adhered thereto;

said coating being formed of an inherently triboelectrically negative fluoropolymer and a modifying resin in which said fluoropolymer is essentially insoluble, said fluoropolymer and said modifying resin being physically mixed with each other;

said carrier particles having a positive triboelectric charge characteristic with respect to toner particles formed of IBM part number 1162057 and with respect to the toner particles with which said carrier particles are used.

2. The carrier particles according to claim 1 in which said fluoropolymer is a fluorocarbon.

3. The carrier particles to claim 2 in which said fluorocarbon is a copolymer of tetrafluoroethylene and

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hexafluoropropylene having thermal properties very close to the 1:1 copolymer.

4. The carrier particles according to claim 3 in which said modifying material is epoxy resin.

5. The carrier particles according to claim 3 in which

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said modifying material is urethane resin.

6. The carrier particles according to claim 3 in which said modifying material is methyl phenyl silicone resin.

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