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Kukla et al.

[11] **3,922,382**
[45] **Nov. 25, 1975**

[54] METHOD OF MANUFACTURING CARRIER PARTICLES

[75] Inventors: **William J. Kukla,** Boulder; **Howard E. Munzel,** Lafayette, both of Colo.

[73] Assignee: **International Business Machines Corporation,** Armonk, N.Y.

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[21] Appl. No.: **402,509**

Related U.S. Application Data

[62] Division of Ser. No. 110,725, Jan. 28, 1971, Pat. No. 3,798,167.

[52] **U.S. Cl.** **427/58;** 427/127; 427/14; 427/221; 427/216; 427/388; 252/62.1

[51] **Int. Cl.**^{2} **G03G 9/00**

[58] **Field of Search** .... 117/17.5, 100 S, 100 M, 117/100 C, 100 B, 100 A, DIG. 6, 138.8 UF, 132 CF, 132 BE, 132 BS, 161 UF, 161 UG, 161 UH, 161 P, 161 UT, 161 UN, 161 ZA, 161 ZB; 96/1 R; 427/127, 14, 221, 216, 388

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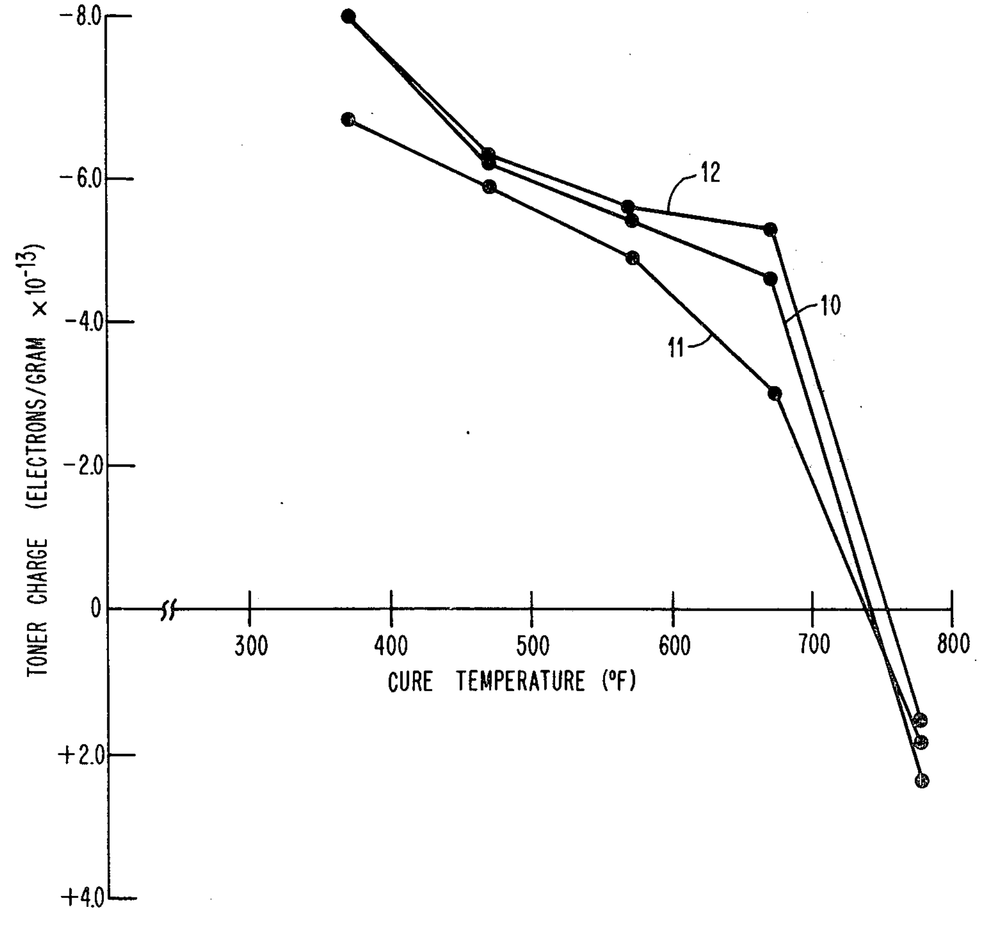
3,062,793	11/1962	Eleuterio	117/161 UH
3,194,428	7/1965	Dereich	117/132 CF
3,344,064	9/1967	Brady et al.	117/132 CF
3,533,835	10/1970	Hagenbach et al.	117/16
3,787,382	1/1974	Wright et al.	117/132 CF
3,873,356	3/1975	Queener et al.	117/201

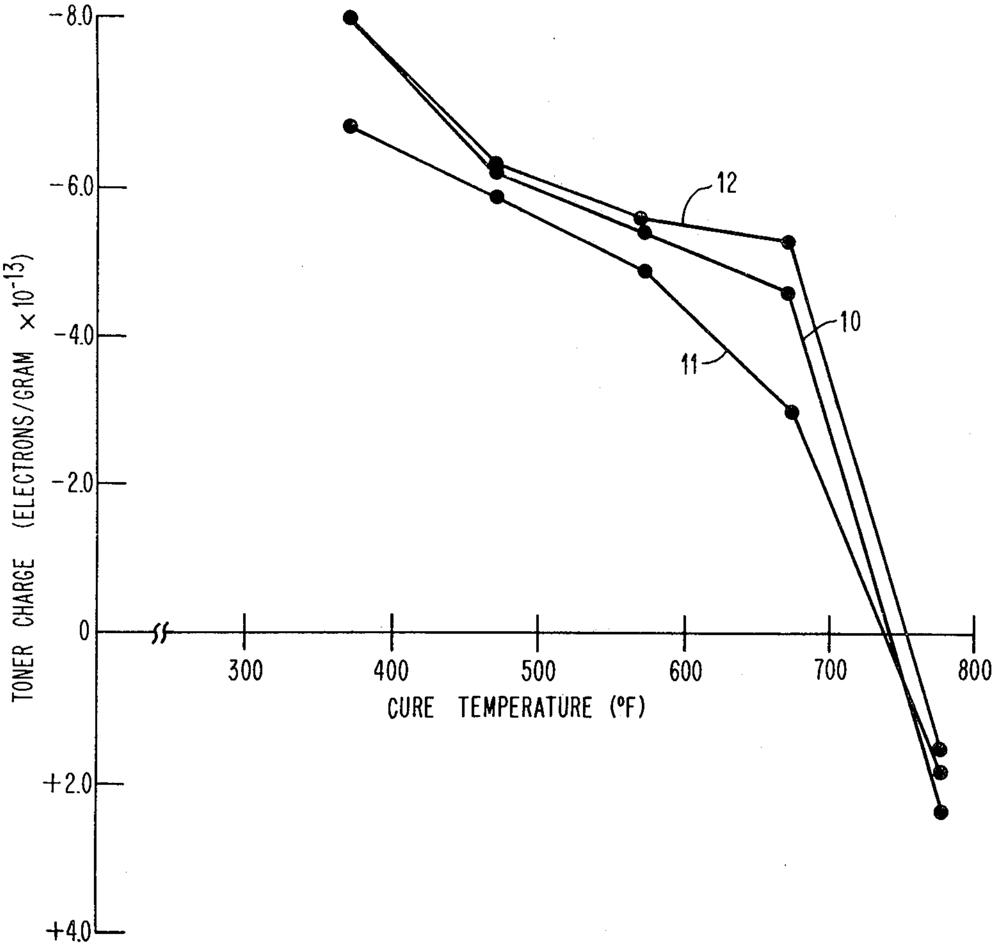
Primary Examiner—Cameron K. Weiffenbach
Assistant Examiner—Charles R. Wolfe, Jr.
Attorney, Agent, or Firm—John W. Girvin, Jr.

[57] **ABSTRACT**

An electrophotographic development carrier comprises core particles coated with a fluoropolymer or a mixture of a fluoropolymer and a modifying material. When utilized with appropriate electroscopic toner materials, the carrier, which is coated with the mixture of the fluoropolymer and the modifying material, is effective in producing a desired polarity and magnitude of the triboelectric charge on the toner particles, and the carrier, which is coated with the fluoropolymer, is effective in producing a triboelectric charge of a desired magnitude on the toner particles. Control of the polarity and magnitude of the triboelectric charge characteristic of the carrier, which has its particles coated with the mixture of the fluoropolymer and the modifying material, is obtained by heating the coated particles to a selected temperature depending upon the desired polarity and magnitude and the particular toner with which the carrier is used. Control of the magnitude of the triboelectric charge characteristic of the carrier, which is coated with the fluoropolymer, is obtained by controlling the curing conditions.

15 Claims, 4 Drawing Figures

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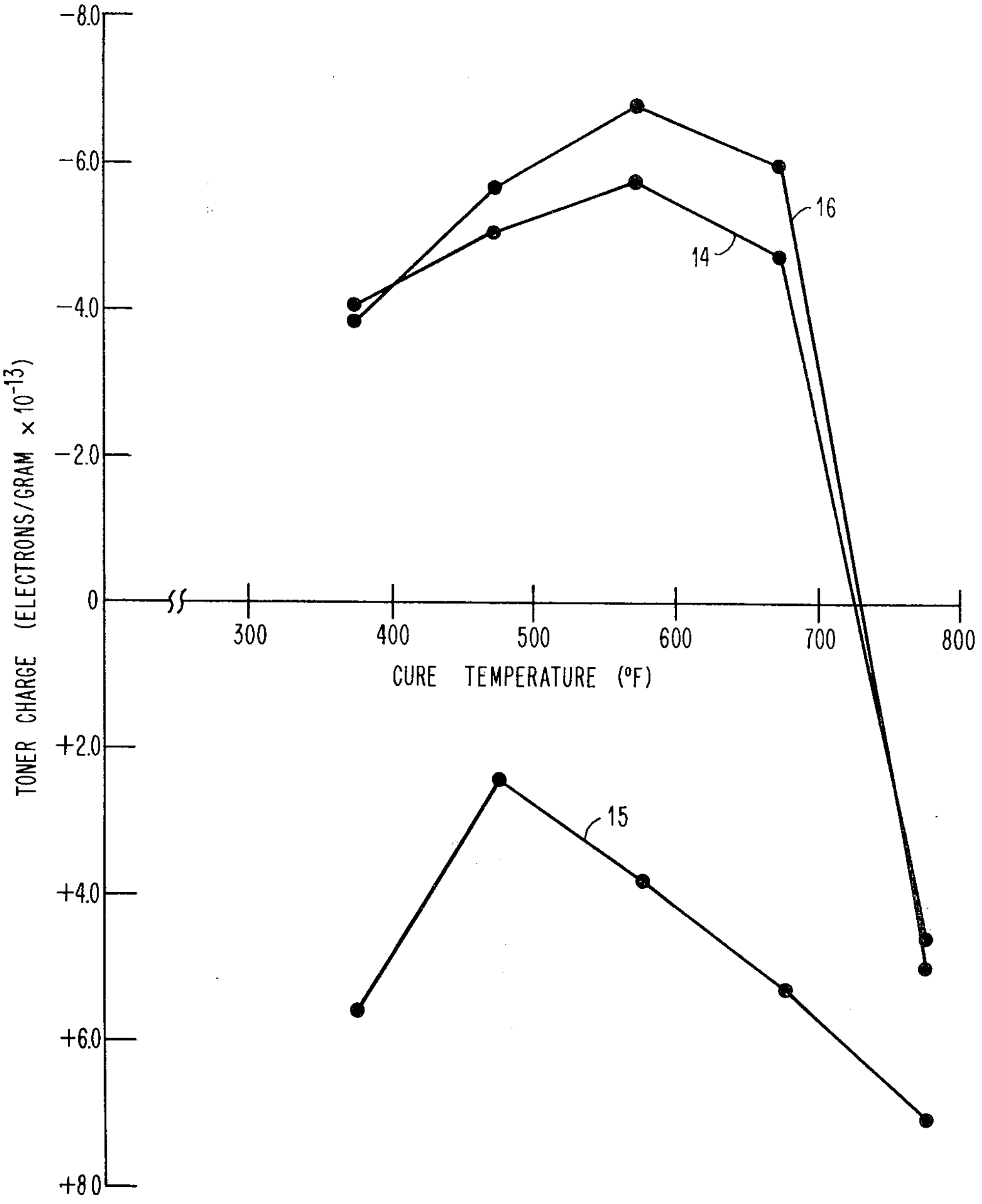
+2.0
+4.0
TONER CHARGE (ELECTRONS/GRAM $\times 10^{-13}$)
300
400
500
600
700
800
CURE TEMPERATURE (°F)
12
10
11

FIG. 1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TONER CHARGE (ELECTRONS/GRAM × 10^{-13})
300
400
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600
700
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CURE TEMPERATURE (°F)
16
14
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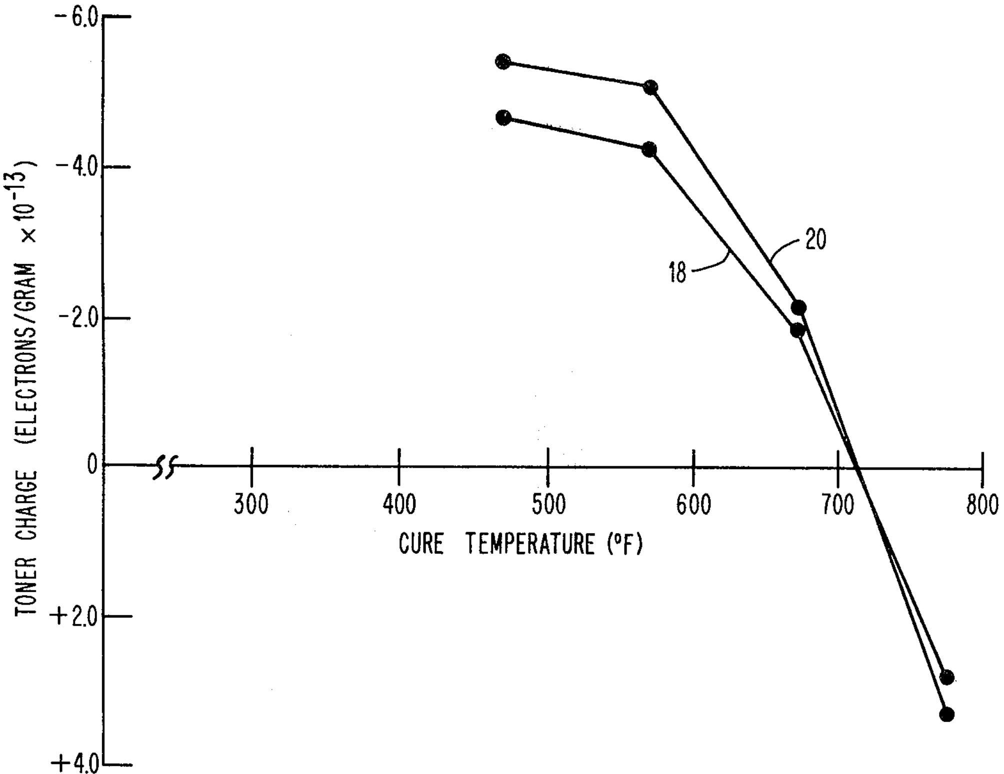
FIG. 2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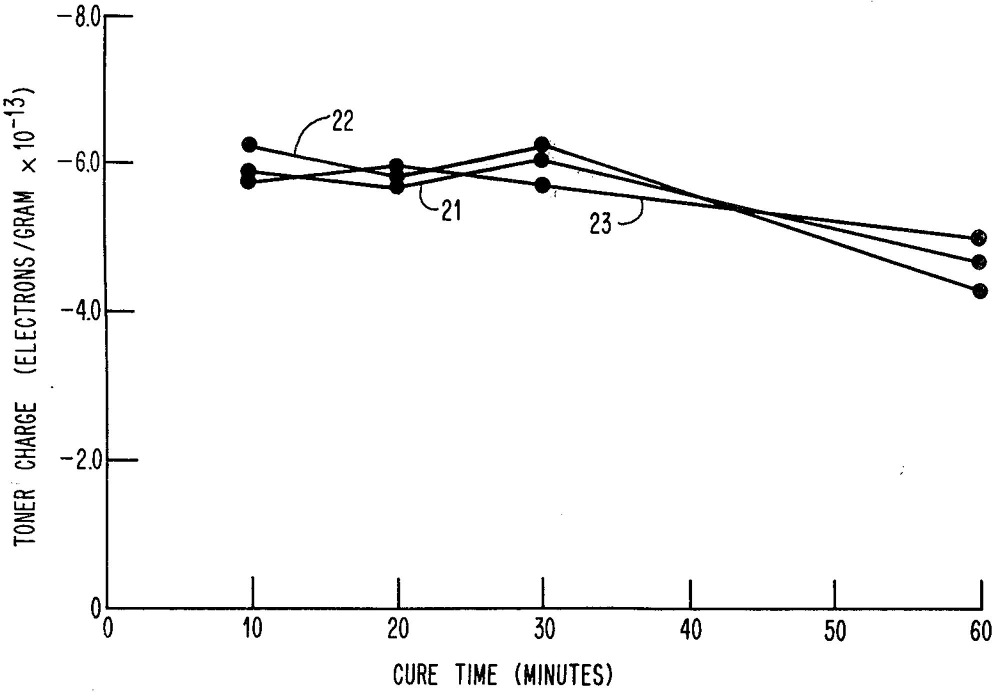
500
600
700
800
CURE TEMPERATURE (°F)
18
20

FIG. 3


-8.0
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0
TONER CHARGE (ELECTRONS/GRAM × 10⁻¹³)
0
10
20
30
40
50
60
CURE TIME (MINUTES)
22
21
23

FIG. 4

METHOD OF MANUFACTURING CARRIER PARTICLES

This is a division of copending application Ser. No. 110,725 filed Jan. 28, 1971, now U.S. Pat. No. 3,798,167.

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 the 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 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 (loro 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.

In addition to having the foregoing desired properties, the carrier particles must have the characteristic of having a triboelectric charge of a desired magnitude and polarity when used with a particular electroscopic toner. This is because the magnitude of the triboelectric charge of the toner is controlled by the magnitude and polarity of the carrier charge when the toner and the carrier are mixed.

The magnitude of the charge of the toner is important for the electrophotographic system to produce copies of a high quality. If the magnitude of the charge of the toner is too low, the copies have poor edge definition and lack contrast since the non-image or background areas possess an unacceptable level of toner as previously mentioned. If the magnitude of the charge of the toner is too high, then there is poor image fill since the toner would tend to stay with the carrier. Accordingly, the magnitude of the charge of the toner must be within a range above that in which poor edge definition is produced and below that in which poor image fill occurs.

Thus, if the coating of the carrier particle has the characteristic of imparting a triboelectric charge to the toner when mixed therewith so that the toner charge does not fall within the range in which copies of high quality can be obtained, the coating cannot be employed for a carrier for the toner even though it meets the abrasion, anti-stick, and adhesion requirements. Accordingly, for a carrier coating to be satisfactory, it not only must meet the abrasion, anti-stick, and adhesion requirements but also must be capable of causing the carrier to have the characteristic of triboelectrically charging the toner when mixed with the toner so that the charge of the toner is within the desired range that enables copies of high quality to be produced.

Fluoropolymers such as fluorocarbons and fluorosilicones, for example, have 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 so that these would seem to make good carrier coatings. In fact, 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, because of the location of Teflon, particularly polytetrafluoroethylene, in the various published triboelectric series, materials sold under the trademark Teflon, particularly polytetrafluoroethylene, have not been considered applicable for use as carrier coatings in electrophotographic systems other than those in which the triboelectric charge imparted to the toner particles by mixing with the coated carrier particles has produced a toner having a charge of a specific magnitude that is compatible with the particular electrophotographic system. Because of this position in the various published triboelectric series, one would expect the magnitude of the charge imparted to the toner particles by mixing with the carrier particles coated with Teflon to be fixed so that it could not be varied.

The present invention satisfactorily solves the foregoing problems by providing a method for coating carrier particles of an electrophotographic developer with a material having the desired antistick, abrasion, and adhesion properties while being able to control the magnitude of the triboelectric charge of the carrier coating in accordance with the toner with which the carrier is used whereby the magnitude of the charge of the toner is controlled. Thus, the present invention enables the charge of a toner to be selectively controlled so that the magnitude of the charge of the toner falls within the desired range in which the charge is not so low as to produce poor edge definition and/or high background or so high as to produce poor image fill. Therefore, the electrophotographic process utilizing the developer material of the present invention is substantially improved due to the high quality copy produced thereby.

In addition to being able to control the magnitude of the charge of carrier particles coated with polytetrafluoroethylene, the present invention also is capable of controlling the magnitude of the charge of carrier particles coated with a mixture of a fluoropolymer and a modifying material or resin, for example. Suitable examples of these mixtures in which the fluoropolymer is a fluorocarbon or a copolymer thereof also are sold by du Pont as Teflon.

Furthermore, when utilizing the mixture of the fluoropolymer and the modifying material, the present invention is not only capable of controlling the magnitude of the charge but also its polarity. While the broad concept of changing the triboelectric charge polarity of a mixture of a fluoropolymer and a modifying material with respect to various toners from electronegative to electropositive is disclosed in the copending application of Carl A. Queener, et al. for "Improved Electrophotographic Process" Ser. No. 110,756 filed Jan. 28, 1971, now U.S. Pat. No. 3,778,262, and assigned to the same assignee as the assignee of this application, the present invention is able to selectively control both the polarity and the magnitude of the charge of the coated carrier particles in accordance with the toner with which the carrier is used.

The present invention achieves this unexpected result by controlling the curing of the coated particles. With polytetrafluoroethylene, curing is controlled by quenching the coated carrier prticles after they have been heated. With carrier particles coated with a mixture of a fluoropolymer and a modifying material, curing is controlled through regulating the temperature to which the particles are heated. 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 of the material on a core that results in the coated core being selectively positioned in a triboelectric series with respect to various materials which may be readily employed as toners in electrophotographic systems so that the triboelectric charge of the toners may have a desired magnitude and polarity. With either coating, the temperature must be sufficient to cause the coating to adhere to the core of the carrier particle.

With the mixture of the fluoropolymer and the modifying material, the triboelectric characteristic of the carrier material can be varied over a wide range while that of polytetrafluoroethylene can be changed to a lesser extent. Thus, a wider control of the magnitude of the triboelectric characteristic of the carrier particles is obtained when using the mixture of the fluoropolymer and the modifying material than when using only the fluoropolymer thereby making it compatible with a greater number of toner materials of differing triboelectric characteristics.

Additionally, the mixture of the fluoropolymer and the modifying material can be treated so as to be capable of being used as a carrier coating with a variety of toners, irrespective of whether they need to have an electronegative or electropositive charge, in various types of electrophotographic systems. This allows the polarity and the magnitude of the toner charge to be controlled so that the toner can be readily usable with any electrophotographic system.

Accordingly, even if the potential of the image areas in an electrophotographic system were changed significantly so that the charge and/or polarity of the toner must be changed for the toner to continue to be employed in the electrophotographic system, this invention allows the particular toner to still be used. Additionally, this invention permits the selection of any one of a plurality of toner for use with a particular electrophotographic system.

At the same time that this flexibility of the toner charge through controlling the triboelectric characteristic of the carrier material is available by employing the method of the present invention, the present invention also insures that the carrier particles have a relatively long life. This is because the coating of the carrier particles has the required anti-stick, abrasion, and adhesion properties necessary for a long life coating for a carrier.

An object of this invention is to provide a method for controlling the magnitude and/or polarity of the triboelectric charge of a coated carrier particle in accordance with the toner and the electrophotographic system with which it is used.

Another object of this invention is to provide a coated carrier particle having the magnitude and/or polarity of its triboelectric charge controlled in accordance with the toner and the electrophotographic system with which it is used.

A further object of this invention is to provide an electrophotographic development carrier having a relatively long life.

Still another 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 the preferred embodiments of the invention as illustrated in the accompanying drawings.

In the drawings:

FIGS. **1** to **3** are graphs having curves showing the relationship between the toner charge and the curing temperature for different toners and different coatings on the carrier particles.

FIG. **4** is a graph having curves showing the relationship of the charge of various toners relative to different cure times of a single carrier coating at a constant cure temperature.

The core of the carrier particle formed by the present invention may be any material to which the coating can adhere and which 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 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 fluoropolymer or 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 polytetrafluoroethylene when no modifying material is used and is a copolymer of tetrafluoroethylene and hexafluoropropylene having thermal properties very close to the 1:1 copolymer when a modifying material is used.

Polytetrafluoroethylene is sold as pure Teflon by du Pont. The copolymer of tetrafluoroethylene and hexafluoropropylene having thermal properties very close to the 1:1 copolymer and mixed with a modifying material is sold by du Pont as Teflon with a modifying description including a number.

In applying the coating to the core, the coating may be applied 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 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 so as to possess the desired triboelectric properties. The curing process depends upon the material of the coating and the composition of the toner with which the carrier particles of the present invention are to be employed.

Thus, if the coating is a fluoropolymer such as polytetrafluoroethylene, for example, then curing of the coating occurs by heating the carrier particles at a selected temperature for a selected period of time. After the carrier particles have been heated at the selected temperature for the selected period of time, the carrier particles are quenched in a suitable fluid such as water, for example, thereby affecting the magnitude of the triboelectric charge of the carrier particle when mixed with a particular toner. Thus, for a particular toner, quenching of the carrier particles having a coating of polytetrafluoroethylene produces an increase in the magnitude of the triboelectric charge of about 5 to 40 percent depending upon the core material, the core size, and the toner being used. This enables the triboelectric charge of the toner to fall within a desired range in which high quality copies are produced.

When the material of the coating is a mixture of a fluoropolymer and a modifying material, the curing process is different. In this curing process, the carrier particles are heated at a selected temperature for a selected period of time and then cooled to a low temperature such as by ambient air cooling. By selecting the temperature at which the carrier particles are heated after their cores have been coated, the magnitude and polarity of the triboelectric charge of the toner, which is mixed with the carrier particles, is controlled.

It should be understood that the temperature must be sufficiently high so that the coating will adhere to the core. The desired magnitude and polarity of the toner charge for the particular toner determines the actual temperature selected.

The thickness of the coating may vary from 1 to 20 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 carriers, which have the cores of their particles formed 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 include: rosin, gilsonite, phenol-formaldehyde 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 3 volumes to 1 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 percent of the total solution, the modifying resin approximately 18.5 percent of the total solution, the solvents approximately 41.5 percent of the total solution, and the pigment approximately 4 percent 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.

five portions of the material so prepared are now cured in ovens at five different temperatures with one portion at 375°F, one portion at 475°F, one portion at 575°F, one portion at 675°F, and one portion at 775°F. For each portion, the coated beads are brought to their designated temperature, left there for about 15 minutes, then 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.

Aliquots of these five portions, which have been cured at the different temperatures, are now mixed with each of three different toners to a level by weight of about 0.8% toner and 99.2% carrier. The three toners are Hunt Graph-O-Print toner sold by Philip A. Hunt Chemical Corporation, Palisades Park, New Jersey, IBM Part No. 1162057, and IBM Part No. 1162051.

The Hunt Graph-O-Print toner comprises a copolymer of styrene/n-butyl metharcrylate resin, polyvinyl butyral plasticizer, and carbon black pigment. The IBM Part No. 1162057 toner comprises a copolymer of styrene/n-butyl methacrylate resin, maleic anhydride modified polyester, polyvinyl stearate plasticizer, and 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 each of these **15** toner-carrier mixtures is now measured by cascading a portion of each 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 line about 0.005 inch wide. After making arrangements for electrical contacts to the electrodes, a ½ mill 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 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 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 charges calculated are plotted graphically versus curing temperatures in FIG. **1** wherein curve **10** represents the charges for the Hunt toner, curve **11** illustrates the charges for IBM part No. 1162051 toner, and curve **12** shows the charges for IBM Part No. 1162057 toner. The curing temperature has controlled at will the magnitude and polarity of the charge imparted to the three toners by the 954–101 light green Teflon-S coated carrier.

EXAMPLE II

A coating formulation containing a fluoropolymer and a modifying resin, which is sold du Pont as 959–205 dark chocolate one-coat Teflon enamel, is diluted about 1 volume to 1 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 comprises 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 dilutent having the same basic solvent make-up as the solvents in the coating formulation of 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.

Five portions of the material so prepared are now curved in ovens at five different temperatures with one portion at 375°F, one portion at 475°F, one portion at 575°F, one portion at 675°F, and one portion at 775°F. For each portion, the coated beads are brought to their designated temperature, left there for about 15 minutes, then 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.

Aliquots of these five portions, which have been cured at the different temperatures, are now mixed with each of three different toners to a level by weight of about 0.7% toner and 99.3% carrier. The three toners are the same as in Example I. The charge generated between each of these 15 toner-carrier mixtures is now measured in the same manner as in Example I. The charges calculates are plotted graphically versus curing temperatures in FIG. **2** wherein curve **14** represents the charges for the Hunt toner, curve **15** illustrates the charges for IBM Part No. 1162051 toner, and curve **16** shows the charges for IBM Part No. 1162057 toner. The curing temperature has greatly controlled the charge imparted to the three toners by the 959–205 dark chocolate one-coat Teflon enamel coated carrier.

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 1 volume to 1 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 dilutent 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 cyclie fluidized bed tower at a coating temperature of about 150°F.

Five portions of the material so prepared are now cured in ovens at five different temperatures with one portion at 375°F, one portion at 475°F, one portion at 575°F, one portion at 675°F, and one portion at 775°F. For each portion, the coated beads are brought to their designated temperature, left there for about 15 minutes, then removed from the oven, cooled at room temperature via ambient air cooling, and screened through a U.S. standard 30 mesh screen to remove agglomerates.

Aliquots of these five portions, which have been cured at the different temperatures, are now mixed with each of two different toners to a level by weight of about 1% toner and 99% carrier. The two toners are Hunt Graph-O-Print toner sold by Philip A. Hunt Chemical Corporation, Palisades Park, New Jersey and IBM Part No. 1162057. The charge generated between each of these 10 toner-carrier mixtures is now measured in the same manner as in Example I. The charges calculated are plotted graphically versus curing temperature in FIG. **3** wherein curve **18** represents the charges for the Hunt toner and curve **20** shows the charges for IBM Part No. 1162057 toner. The curing temperature has controlled at will the magnitude and polarity of the charge imparted to the two toners by the 958–202 steel blue Teflon-S coated carrier.

EXAMPLE IV

Carrier particles are prepared in the same manner as in Example I. Four separate portions of the material are now placed in an oven, and the temperature of the beads in each portion is now brought to about 575°F. One portion is removed after 10 minutes at 575°F, one portion after 20 minutes at 575°F, one portion after 30 minutes at 575°F, and one portion after 60 minutes at 575°F. All are cooled to room temperature via ambient air cooling and all are screened through a U.S. standard 30 mesh screen to remove agglomerates.

Aliquots of these four portions, which have been cured at 575°F for different times, are now mixed with each of three different toners to a level by weight of about 0.7% toner and 99.3% carrier. The three toners are the same as in Example I.

The charge on each of the **12** toner-carrier mixtures is measured by the method described in Example I. The charges so measured are plotted versus curing time in FIG. **4** wherein curve **21** represents the charges for the Hunt toner, curve **22** illustrates the charges for IBM Part No. 1162051 toner, and curve **23** shows the charges for IBM Part No. 1162057 toner. The curing time does not have a major effect on charge between 954–101 green Teflon-S carrier and these three toners.

While Examples I to III 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 can have their triboelectric charge magnitude and polarity controlled 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, Delaware, 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, New Jersey, 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 coated carrier, prepared as per Example I, is substituted for the red dyed ethyl cellulose coated 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 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. 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 present 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 substitued 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 7% 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.

The following is an example of controlling the magnitude of the charge in which the coating is formed of polytetrafluoroethylene through controlling the curing by quenching:

EXAMPLE XI

A coating formulation consisting of 850–201 Teflon primer for steel, which is sold by du Pont, is diluted about 2 volumes to 1 volume with water 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 coating formulation of 850–201 Teflon primer for steel is a solution comprising, by weight, approximately 35% polytetrafluoroethylene, approximately 12% chromic acid and phosphoric acid, and approximately 53% water.

The material is applied to the beads in a Wurster cyclic fluidized bed tower at a temperature of about 190°F. About 12 milliliters of the diluted material is applied per pound of beads.

The primed beads are now removed from the tower, placed in an oven, and the temperature of the beads is brought to about 780°F and left there for about 11 minutes. The beads are now removed from the oven, cooled to room temperature via ambient air cooling, and then placed back into the fluidized bed tower.

A coating formulation of du Pont 852–201 clear Teflon enamel diluted about 2 volumes of 1 volume with water by stirring at room temperature is now sprayed onto the beads in the Wurster cyclic fluidized bed tower at a coating temperature of about 190°F. The coating formulation of 852–201 clear Teflon enamel contains, by weight, approximately 48% polytetrafluoroethylene, approximately 3% Triton type surface active agent (blend of alkyl aryl polyether alcohol with organic sulfonate), and approximately 49% water and toluene in the ratio of 95 to 5. About 30 milliliters of the diluted material is applied per pound of beads.

The beads are then removed from the tower, placed in an oven, and the temperature of the beads is brought to about 780°F and left there for about 11 minutes. The material is now immediately divided into two equal portions. One half is allowed to cool to room temperature via ambient air cooling and the other half is rapidly quenched in water whose temperature is about 50°F to 70°F.

The air cooled material is screened through a U.S. standard 30 mesh screen to remove agglomerates. The quenched material is broken up to reduce the agglomerates, then dried off in the fluidized bed tower with warm (approximately 250°F) air for about 20 minutes, and then cooled to room temperature. The triboelectric charges between the quenched material and IBM Part No. 1162051 toner and between the air cooled material and IBM Part No. 1162051 toner are now measured by the technique described in Example I. The triboelectric charge between the carrier having the quenched material as the coating and this toner is higher than the triboelectric charge between the carrier having the air cooled material as the coating and this toner by on the order of 10%. All charge data at about 0.7% toner by weight is between 3.0 to 6.0 × 10^{13} electrons/gram of toner and the toner is triboelectrically positive. Quenching in water has increased the triboelectric charge between the carrier having the coating of polytetrafluoroethylene and IBM Part. No. 1162051 toner by affecting the cooling rate after curing.

While Example XI shows that the use with a particular toner and quenching of the polytetrafluoroethylene produces a coating for carrier particles of a developer in which the carrier particles have their triboelectric charge magnitude controlled and increased with respect to the toner, an example will be given to show that the coating of Example XI has a long life when used in a developer simulator.

Example XII

A sample of a carrier having a coating of quenched polytetrafluoroethylene prepared as per Example XI is life simulated for 650 hours in the developer simulator. The developer simulator is the conventional bucket elevator cascade developer as described with respect to Examples V to VII. No toner is used in the simulator; however, the carrier's ability to triboelectrically charge toner is checked periodically by removing the carrier from the simulator, mixing with about 0.8% by weight IBM Part No. 1162051 toner, and making copy in an operating cascade development copy robot. The carrier is also monitored for coating damage and loss.

After 650 hours, the carrier has lost less than 10% of its coating and makes excellent copy in a copy making robot. The 650 hour developer simulation has not significantly degraded the performance of the coating of polytetrafluoroethylene.

EXAMPLE XIII

A coating formulation containing about 11% by weight Exon 497 resin, which is sold by Firestone Plastics Company, Pottstown, Pennsylvania, and about 1% by weight Orasol red "B" dye, which is sold by Ciba Chemical and Dye Company, Fairlawn, New Jersey, 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. The material is sprayed onto the beads in a Wurster cyclic fluidized bed coating tower at a temperature of about 90°F and about 45 milliliters per pound is applied.

The coated beads are then placed in an oven, and the temperature of the beads is brought to about 190°F for about 6 hours. The temperature is then raised to about 210°F for about 1 hour; then the beads are removed from the oven and cooled to room temperature via ambient air cooling. The material is next screened through a U.S. standard 30 mesh screen to remove agglomerates.

A sample of the material so prepared is now life simulated for 50 hours in the developer simulator as per Example XII. After only 50 hours simulation, the coating is at least 50% gone, and the carrier is badly deteriorated as an electronegative carrier.

To ascertain the type of copy produced from a developer mixture having the carrier with the coating prepared in accordance with Example XI, carrier particles formed in accordance with Example XI were tested in a copy making robot as described for Examples VIII to X. Because of the damage to the coating of Example XIII, this carrier could not be tested in a copy making robot.

EXAMPLE XIV

A sample of a carrier having a coating of quenched polytetrafluoroethylene prepared as per Example XI is life tested in an operating copy machine for 380,000 copies. The machine has conventional charging, imaging, cascade developing, transferring, fusing, and cleaning stations. Carrier performance is monitored by observing coating loss, filmed-on or impacted toner, and copy quality.

After 380,000 copies, there is no significant filmed-on toner, only about 10% coating loss, and the copy is excellent. There has been no significant degradation in the ability of the carrier to triboelectrically charge toner. Based on these recognized parameters for carrier degradation, the life of this carrier is significantly greater than 380,000 copies.

Examples I to IV show that the magnitude of the triboelectric charge and its polarity is not affected by the curing time but only by the temperature at which the particles are heated. Therefore, it is not necessary to heat the carrier particles at the selected temperature for over 15 minutes.

Example XI discloses that control of the magnitude of the triboelectric charge of the carrier particles, dependent upon the toner composition, can be effectively increased. Thus, this enables more flexibility for the use of the particles coated with pure Teflon.

From the foregoing, it is readily observed that the coating of the carrier particles comprises at least essentially a fluoropolymer irrespective of whether the coating is a fluoropolymer or a mixture of a fluoropolymer and a modifying material. Thus, when used in the claims, the term "at least essentially a fluoropolymer" includes a fluoropolymer or a mixture of a fluoropolymer and a modifying material.

An advantage of this invention is that carrier particles having a fluoropolymer coating can have the magnitude of the triboelectric charge and its polarity controlled precisely for various toners whereby flexible selection of the toner is obtained. Another advantage of this invention is that high quality copies are obtained from a copying machine. A further advantage of this invention is that toner filming is reduced. Still another advantage of this invention is that good adhesion of the coating on the core is obtained with the carrier having the desired triboelectric properties.

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

What is claimed is:

1. A method of selectively controlling the magnitude of the triboelectric charge characteristic of an electrophotographic development carrier for use with toner particles in an electrophotographic system including:

coating a plurality of core particles which will withstand a selected curing with a substantially continuous film of a material comprising at least essentially a substantially insoluble fluoropolymer;

and selecting the curing of the coating to firmly adhere the coating to each of the core particles and to control the magnitude of the triboelectric charge characteristic of the electrophotographic development carrier with respect to toner particles of a given composition and a given percent by weight of said toner particles relative to said carrier and a given electrophotographic system with which the carrier and toner particles are to be used, said magnitude being within a range to produce good quality copy when used in said electrophotographic system, said copy exhibiting good edge definition and image fill characteristics.

2. The method according to claim 1 in which the material is a fluoropolymer.

3. The method according to claim 2 in which the material is a fluorocarbon.

4. The method according to claim 3 in which the material is polytetrafluoroethylene.

5. The method according to claim 1 in which the material is a mixture of a fluoropolymer and a modifying resin in which the fluoropolymer is essentially insoluble.

6. The method according to claim 5 in which curing is obtained by heating the carrier particles to a selected temperature within a range between 300°F and 800°F for a sufficient period of time to adhere the coating to each of the carrier particles, the temperature being selected in accordance with the controlled magnitude of the triboelectric charge characteristic.

7. The method according to claim 6 in which the fluoropolymer is a fluorocarbon and the modifying resin is selected from the group consisting of epoxy and urethane resins.

8. The method according to claim 1 in which curing is obtained by heating the material of said film to a temperature in a range between the glass transition temperature of the fluoropolymer and 800°F and then quenching the material.

9. The method according to claim 8 in which the fluoropolymer is a fluorocarbon.

10. The method according to claim 9 in which the fluorocarbon is polytetrafluoroethylene.

11. The method according to claim 1 in which the coating is applied by a fluidized bed coating process.

12. A method of controlling the polarity and magnitude of the triboelectric charge characteristic of an electrophotographic development carrier for use with toner particles including:

coating a plurality of core particles which will withstand a selected curing temperature with a mixture of a fluoropolymer and a modifying resing:

selecting the temperature at which the coating is to be cured with the selected temperature being in the range between 300°F and 800°F to adhere the coating to each of the core particles and to produce a selected polarity and magnitude of the triboelectric charge on the carrier with respect to toner particles of a selected composition of material and a selected percent by weight of toner particles relative to said carrier and a given electrophotographic system with which the carrier and toner particles are to be used, said magnitude being within a range to produce good quality copy when used with said toner particles in an electrophotographic process, said copy exhibiting good edge definition and image fill characteristics;

and curing the coating at the selected temperature for a time period sufficient to adhere the coating to each of the core particles.

13. The method according to claim 12 in which the fluoropolymer is a fluorocarbon and the modifying resin is selected from the group consisting of epoxy and urethane resins.

14. The method according to claim 12 in which the coating is applied by a fluidized bed coating process.

15. The method according to claim 12 in which the core particles are a ferromagnetic material.

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