

- [54] **CELLULOSE COATED CARRIERS**
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References Cited

UNITED STATES PATENTS

- 2,857,290 9/1958 Bolton 117/17.5

2,874,063	5/1959	Greig	117/17.5
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[57]

ABSTRACT

An electrostatographic developer mixture comprising finely-divided toner particles electrostatically clinging to the surface of carrier beads, each of the carrier beads comprising a core having a uniform coating thereon comprising a polymeric cellulose ester wherein said coating exhibits a volume resistivity of between about 10^{10} and about 10^{14} ohm-centimeters at 23°C. The process for employing the developer mixture in developing an electrostatic latent image is also disclosed.

6 Claims, No Drawings

CELLULOSE COATED CARRIERS

This application is a continuation application of Ser. No. 18,316 filed on Feb. 5, 1970 which is now abandoned.

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

The formation and development of latent electrostatic images on an electrostatographic imaging surface is well known. The basic electrostatographic process as taught by C. F. Carlson in U.S. Pat. No. 2,297,691, involves placing a uniform electrostatic charge on a photoconductive insulating layer, exposing the layer to a light and shadow image to dissipate the charge on the areas of the layer exposed to the light and developing the resulting latent electrostatic image by depositing on the image a finely divided electroscopic material referred to in the art as "toner." The toner will normally be attracted to those areas of the layer which retain a charge, thereby forming a toner image corresponding to the latent electroscopic image. This powder image may then be transferred, usually electrostatically, to a support surface such as paper. The transferred image may subsequently be permanently affixed to the support surface by heat. Other suitable fixing means such as solvent or overcoating treatment may be substituted for the foregoing heat fixing steps.

Many methods are known for applying the electroscopic particles to the latent electrostatic image to be developed. One development method as disclosed by E. N. Wise in U.S. Pat. No. 2,618,552, is known as "cascade" development. In this method, developer material, comprising relatively large carrier particles having finely divided toner particles electrostatically clinging to the surface of the carrier particles, is conveyed to and rolled or cascaded across the latent electrostatic imagebearing surface. The composition of the toner particles is so chosen as to have a triboelectric polarity opposite that of the carrier particles. In order to develop a negatively charged latent electrostatic image, an electroscopic powder and carrier combination should be selected in which the powder is triboelectrically positive in relation to the carrier. Conversely, to develop a positively charged latent electrostatic image, the electroscopic powder and carrier should be selected in which the powder is triboelectrically negative in relation to the carrier. This triboelectric relationship between the powder and carrier depends on their relative positions in a triboelectric series in which the materials are arranged so that each material is charged with a positive electrical charge when contacted with any material below it in the series and with a negative electrical charge when contacted with any material above it in the series. As the mixture cascades or rolls across the image-bearing surface, the toner particles are electrostatically deposited on and secured to the charged portions of the latent image and are not secured to the uncharged or background portions of the image. The "cascade" development process has the distinct advantage that most of the toner particles accidentally deposited on the background portion are removed by the rolling carrier, due apparently to the greater electrostatic attraction between the toner and the carrier than between the toner and the discharged background. The carrier particles and unused toner particles are then recycled. The cascade development process is extremely good for the development of line copy images, and is

the most widely used commercial electrostatographic development technique. A general purpose office copying machine incorporating this technique is described in U.S. Pat. No. 3,099,943.

Another technique for developing electrostatic images is the "magnetic brush" process as disclosed, for example, in U.S. Pat. No. 2,874,063. In this process, a developer material containing toner and magnetic carrier particles is attracted to and is carried by a magnet. The magnetic field of the magnet causes alignment of the magnetic carriers in a brush-like configuration. This "magnetic brush" is engaged with an electrostatic image-bearing surface and the toner particles are drawn from the brush to the electrostatic image by electrostatic attraction. Many other methods such as "touchdown" development as disclosed by C. R. Mayo in U.S. Pat. No. 2,895,847 are known for applying electroscopic particles to the latent electrostatic image to be developed. The development processes as mentioned above together with numerous variations are well known to the art through various patents and publications and through the widespread availability and utilization of electrostatographic imaging equipment.

In automatic electrostatographic reproducing equipment, it is conventional to employ an electrostatographic imaging surface in the form of a cylindrical drum which is continuously rotated through a cycle of sequential operations including charging, exposure, developing, transfer and cleaning. The imaging surface is usually charged with corona with positive polarity by means of a corona generating device of the type disclosed by L. E. Walkup in U.S. Pat. No. 2,777,957 which is connected to a suitable source of high potential. After forming a powder image on the electrostatic image during the development step, the powder image is electrostatically transferred to a support surface by means of a corona generating device such as the corona device mentioned above. In automatic equipment employing a rotating drum, a support surface to which a powdered image is to be transferred from the drum is moved through the equipment at the same rate as the periphery of the drum and contacts the drum in the transfer position interposed between the drum surface and the corona generating device. Transfer is effected by the corona generating device which imparts an electrostatic charge to attract the powder image from the drum to the support surface. The polarity of charge required to effect image transfer is dependent upon the visual form of the original copy relative to the reproduction and the electroscopic characteristics of a developing material employed to effect development. For example, where a positive reproduction is to be made of a positive original, it is conventional to employ a positive polarity corona to effect transfer of a negatively charged toner image to the support surface. When a positive reproduction from a negative original is desired, it is conventional to employ a positively charged developing material which is repelled by the charged areas on the plate to the discharge areas thereon to form a positive image which may be transferred by negative polarity corona. In either case, a residual powder image and occasionally carrier particles remain on the plate after transfer. Before the plate may be reused for a subsequent cycle, it is necessary that the residual image and carrier particles, if any, be removed to prevent ghost images from forming on subsequent copies. In the positive-to-positive reproduction process de-

scribed above, the residual developer powder as well as any carrier particles present are tightly retained on the plate surface by a phenomenon that is not fully understood but believed caused by an electric charge. The charge is substantially neutralized by means of a corona generating device prior to contact of the residual powder with a cleaning device to enhance the cleaning efficiency of the cleaning device.

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

While ordinarily capable of producing good quality image, conventional developing systems suffer serious deficiencies in certain areas. In the reproduction of high contrast copies such as letters, tracings and the like, it is desirable to select the electroscopic powder and carrier materials so that their mutual electrification is relatively large; the degree of such electrification being governed in most cases by the distance between their relative positions in the triboelectric series. However, when otherwise compatible electroscopic powder and carrier materials are removed from each other in the triboelectric series by too great a distance, the resulting images are very faint because the attractive forces between the carrier and toner particles compete with the attractive forces between the latent electrostatic image and the toner particles. Although the image density described in the immediately preceding sentence may be improved by increasing the toner concentration in the developer mixture, undesirably high background toner deposition as well as increased toner impaction and agglomeration is encountered when the toner concentration in the developer mixture is excessive. It has been proposed to increase the initial charge on the electrostatographic imaging surface to improve the density of the deposited powder image, but this would necessitate an excessively high charge on the imaging surface to attract the electroscopic powder away from the carrier particle. Excessively high electrostatographic imaging surface charges are not only undesirable because of the high power consumption necessary to maintain the imaging surface at high potentials, but also because the high potential causes the carrier particles to adhere to the electrostatographic imaging surface rather than merely roll across and off said electrostatographic surface. When carrier particles adhere to reusable electrostatographic imaging surfaces, undesirable print deletion and massive carry-over of carrier particles often occur. Massive carrier carry-over problems are particularly acute when the developer is employed in solid area coverage machines where excessive quantities of toner particles are removed from carrier particles thereby leaving many carrier particles substantially bare of toner particles. Further, adherence of carrier particles to reusable electrostatographic imaging surface promotes the formation of undesirable

scratches on the surfaces during image transfer and surface cleaning operations.

Carrier particles must be made from or coated with materials having appropriate triboelectric properties as well as certain other physical characteristics. Thus, the materials employed in the carrier particles should have a triboelectric value commensurate with the triboelectric values of the toner and the imaging surface to afford electrostatic transfer of the toner to the carrier particle and subsequent transfer of the toner from the carrier particle to the image on the imaging surface without excessive power requirements. Furthermore, the triboelectric properties of all the carrier particles should be relatively uniform to permit uniform pick-up and subsequent deposition of toner. The materials employed in the carrier particles also should have an intermediate hardness so as not to scratch the imaging surface upon which the electrostatic image is initially placed while being sufficiently hard to withstand the forces to which they are subjected during recycle. The carrier particles as well as the surface thereof also should not be comprised of materials which are so brittle as to cause either flaking of the surface or particle break-up under the forces exerted on the particles during recycle. The flaking causes undesirable effects in that the relatively small flaked particles will eventually be transferred to the copy surface thereby interfering with the deposited toner and causing imperfections in the copy image. Furthermore, flaking of the carrier particle surface will cause the resultant carrier particles to have nonuniform triboelectric properties when the carrier particle is composed of a core material different than the surface coating thereon. This results in undesirable nonuniform pick-up of toner by the carrier particles and nonuniform deposition of toner on the image. In addition, when the carrier particle size is reduced, the removal of the resultant small particles from the imaging surface becomes increasingly difficult. Thus, the type of materials useful for making carrier particles or for coating carrier particles, although having the appropriate triboelectric properties, are limited because other physical properties which they possess may cause the undesirable results discussed above.

It is highly desirable to alter triboelectric properties of the carrier particles to accommodate the use of desirable toner compositions while retaining the other desirable physical characteristics of the carrier particle. The alteration of the triboelectric properties of carrier particles by applying a surface coating thereon is a particularly desirable technique. With this technique, not only is it possible to alter the triboelectric properties of carrier particles made from materials having desirable physical characteristics, it is also possible to employ materials previously not suitable as carrier particles. Thus, for example, carrier particles having desirable physical properties with the exception of hardness, can be coated with a material having desirable hardness as well as other physical properties, rendering the resultant product useful as carrier particles. Coating the carrier particles with the additive to alter the triboelectric properties thereof rather than blending the additive into the carrier material during initial formation of the carrier particles is preferred since less additive need be employed to effect the desired change in the triboelectric value. Furthermore, the addition of high concentrations of additive to the original carrier material to alter the triboelectric value thereof requires a major

manufacturing operation and often undesirably alters the original physical characteristics of the carrier material. Thus, there is a present need for providing improved electrostatographic carrier particles which can have their triboelectric value varied over a wide range while retaining desirable physical characteristics of hardness, durability and the like. This is especially true in view of the constant development of new and improved toner compositions.

It is, therefore, an object of this invention to provide carrier materials which overcome the above-noted deficiencies.

It is another object of the present invention to provide novel electrostatographic developer compositions.

It is a further object of the present invention to provide a method for forming carrier particles of varying triboelectric values while retaining desirable physical and chemical properties of the original carrier particles.

It is a still further object of the present invention to provide carrier particles and development compositions useful in presently known electrostatographic techniques. Further objects of the present invention will become evident in view of the following detailed discussion.

The present invention provides carrier particles comprising a core material and a surface coating thereon comprising a polymeric cellulose ester.

It has been found that polymeric cellulose esters possess suitable physical properties of durability, hardness, triboelectric value and the like, to afford their use as coatings for carrier particles useful in electrostatography. The use of polymeric cellulose esters is advantageous in that they can easily be applied as durable coatings to carrier particles which are resistant to the forces normally encountered in electrostatographic reproduction. Furthermore, it has been found that the triboelectric values of the cellulose esters can be varied over a wide range without adversely affecting the properties thereof which render them useful in carrier particles.

The polymeric cellulose esters which are useful in the present invention include cellulose esters which have good hardness, stiffness, tensile strength, impact strength, dimensional stability, hydrophobicity and triboelectric values rendering them suitable in carrier particles. Representative cellulose esters which can be employed include: Cellulose acetate, cellulose acetate butyrate, cellulose acetate propionate, cellulose propionate, cellulose triacetate and the like. The polymeric cellulose esters employed herein have a volume resistivity of between about 10^{10} and about 10^{14} ohm-centimeters at 23°C.

The polymeric cellulose esters can be applied to coat any of the well-known carrier particle materials. Typical carrier core materials include: Sodium chloride, ammonium chloride, aluminum potassium chloride, Rochelle salt, sodium nitrate, potassium chlorate, granular zircon, granular silicon, methylmethacrylate, glass, silicon dioxide, flintshot, iron, steel, nickel, carborundum, and mixtures thereof. Many of the foregoing and other typical carriers are described by L. E. Walkup in U.S. Pat. No. 2,618,511; L. E. Walkup, et al. in U.S. Pat. No. 2,638,416 and E. M. Wise in U.S. Pat. No. 2,618,552. An ultimate coated carrier particle diameter between about 30 microns to about 1,000 microns is preferred for electrostatographic use because the

treated carrier particle then possesses sufficient density and inertia to avoid adherence to the latent electrostatic images during the development.

In order to apply the polymeric cellulose ester coatings to the carrier particles, any conventional solvent coating process can be employed. Thus, the polymeric cellulose derivative can be reduced to a liquid or semi-liquid state by dissolving the polymer in a suitable solvent.

The uncoated carrier particles are intimately contacted with the dissolved polymeric cellulose ester in order to completely coat the particles. The conditions of contact, including temperature, polymer concentration and carrier particle concentration, are regulated so that a uniform coating is applied to the carrier particles thereby forming coated particles exhibiting a uniform triboelectric value. Similarly, these conditions are maintained so that the coating thickness does not become excessive and promote formation of carrier particle agglomerates. After contact of the particles and the coating material and/or during contact thereof, the mixture can be treated to solidify the coating material on the particles as, for example, by evaporating the solvent. A particularly suitable method for evaporating the solvent is by contacting the mixture with a stream of inert gas, for example, air. The resultant carrier particles having the coating solidified thereon are then screened to separate the particles of the desired size, which are then ready for use in electrostatographic processes.

The choice of solvent depends upon the particular polymeric cellulose ester employed. Thus, for example, when polymeric cellulose esters such as cellulose triacetate or cellulose acetate are employed, suitable solvents which can be employed are: ketones, such as acetone, methyl ethyl ketone, isophorone, cyclohexanone and the like; esters such as methyl acetate, ethyl acetate, ethyl lactate, ethylene glycol monomethyl ether acetate and the like; halogenated solvents such as methylene dichloride, ethylene dichloride and the like; nitroparaffins such as nitroethane, nitromethane and the like, as well as other solvents such as 1,4-dioxane, diacetone alcohol and the like. Mixtures of the above solvents with alcohols, especially the lower alkanols containing from one to about six carbon atoms, are also useful. Such mixtures generally contain from about 10 to about 50 percent by volume of the alcohol. Illustrative of such mixtures are: acetone:methanol (80:20), acetone:ethanol (90:10), methylene dichloride:methanol (80:20), nitroethane:ethanol (50:50), nitroethane:ethanol (80:20), ethyl acetate:ethanol (80:20), ethylene dichloride:methanol (80:20), and the like.

When employing polymeric cellulose esters such as cellulose acetate butyrate, cellulose acetate propionate and the like, solvents such as ketones, for example, acetone, methyl ethyl ketone, cyclohexanone and the like; esters such as methyl acetate, ethyl acetate, methyl Cellosolve acetate and the like; halogenated solvents such as methylene chloride, ethylene chloride and the like; nitroparaffins such as nitroethane, 1-nitropropane and the like, can be suitably employed.

Helpful guidance in selection of a suitable solvent for a particular cellulose ester can be found in *Modern Plastics Encyclopedia*, Vol. 46; No. 10A, pages 1006-1007 (October, 1969).

Generally, the polymeric cellulose ester can be dissolved in a suitable solvent to form a coating solution

containing from about 5 to about 20 percent by weight solids. Preferably, the solids content is about 10 percent by weight.

It is most convenient to remove the solvent from the polymer-carrier particle mixture by contact with an inert gas stream from which it can be condensed and recycled for further use.

One distinct advantage of the present invention is that the triboelectric value of the polymeric cellulose esters employed herein can be varied over a wide range by incorporating additives into the polymer composition to be coated on the carrier particle. Thus, in one specific aspect of the present invention it is contemplated to use additives having suitable triboelectric values for incorporation in the coating composition. The additives which can be employed can be discrete particulate material or they can be dissolved or dispersed in the polymeric cellulose ester to form homogeneous compositions. When it is desired to employ cellulose esters having an additive which is to be homogeneously dispersed or dissolved therein, it is preferred to employ a coating process utilizing a solvent which is effective for both the polymeric cellulose ester and the additive.

The polymeric cellulose esters employed as coatings in the present invention can contain the conventional additives normally employed therewith including plasticizers, antioxidants and the like. Suitable plasticizers which can be employed are diesters of adipic acid including diethyl adipate, dibutyl adipate, diisobutyl adipate, dicapryl adipate, di-(2-ethylhexyl)adipate; azelaic acid derivatives such as di-(2-ethylhexyl)azelate, di-n-hexyl azelate and diisooctyl azelate; benzoic acid derivatives such as diethylene glycol dibenzoate and dipropylene glycol dibenzoate; citric acid derivatives such as triethyl citrate, tricyclohexyl citrate and acetyl tri-n-butyl citrate; glycerol derivatives such as glycerol monoacetate, glycerol diacetate, glycerol triacetate, glycerol tripropionate, glycerol tributyrate, glycerol ether acetate; glycol derivatives such as ethylene glycol dipropionate, ethylene glycol dibutyrate, diethylene glycol dipropionate, triethylene glycol diacetate, triethylene glycol dipropionate, methyl phthalyl ethyl glycolate, ethyl phthalyl ethyl glycolate, butyl phthalyl ethyl glycolate; phosphoric acid derivatives such as triethylphosphate, tributylphosphate, and triphenylphosphate; phthalic acid derivatives such as dimethyl phthalate, diethyl phthalate, dipropyl phthalate, dibutyl phthalate, ditridecyl phthalate, diallyl phthalate; succinic acid derivatives such as diethyl succinate and dibutyl succinate; and tartaric acid derivatives such as diethyl tartarate and dibutyl tartarate and the like.

Any suitable pigmented or dyed electroscopic toner material may be employed with the treated carriers of this invention. Typical toner materials include: gum copal, gum sandarac, rosin, cumaroneindene resin, asphaltum, gilsonite, phenol-formaldehyde resins, rosin-modified phenol-formaldehyde resins, methacrylic resins, polystyrene resins, polypropylene resins, epoxy resins, polyethylene resins and mixtures thereof. The particular toner material to be employed obviously depends upon the separation of the toner particles from the treated carrier beads in the triboelectric series. Among the patents describing electroscopic toner compositions are U.S. Pat. No. 2,659,670 to Copley; U.S. Pat. No. 2,753,308 to Landrigan; U.S. Pat. No. 3,079,342 to Insalaco; U.S. Pat. No. Re 25,136 to Carl-

son and U.S. Pat. No. 2,788,288 to Rheinfrank et al. These toners generally have an average particle diameter between about 1 and about 30 microns.

The following examples further define, describe and compare methods of preparing the preferred carrier and developer materials of the present invention and of utilizing them to develop electrostatic latent images. Parts and percentages are by weight unless otherwise indicated.

In the following examples, the relative triboelectric values generated by contact of carrier beads with toner particles are measured by means of a Faraday Cage. The device comprises a brass cylinder having a diameter of 1 inch and a length of 1 inch. A 100-mesh screen is positioned at each end of the cylinder. The cylinder is weighed, charged with 0.5 gram of a mixture of carrier and toner particles and connected to ground through a capacitor and an electrometer connected in parallel. Dry compressed air is then blown through the brass cylinder to drive all the toner from the carrier. The charge on the capacitor is then read on the electrometer. Next, the chamber is reweighed to determine the weight loss. The resulting data is used to calculate the toner concentration and the charge in micro-coulombs per gram of toner. Since triboelectric measurements are relative, the measurements should, for comparative purposes, be conducted under substantially identical conditions. Thus, a toner comprising styrene-n-butyl-methacrylate copolymer, polyvinyl butyral and carbon black by the method disclosed by M. A. Insalaco in U.S. Pat. No. 3,079,342 is used as a contact triboelectrification standard in all the examples. Obviously, other suitable toners such as those listed above may be substituted for the toner used in the examples.

EXAMPLE 1

Coated glass carrier particles were made and tested as follows: 800 grams of Potters No. 6 glass beads were placed in a tumbling barrel type mixer. 72 grams of a 10 percent cellulose acetate butyrate solution (EA-B-171-2 manufactured by Eastman Kodak Co., Rochester, N.Y., approximate butyryl content 17 percent) in ethylene dichloride solvent was charged to the tumbling barrel mixer. The resultant mixture was mixed for about 1 hour at a temperature of about 50°C. During mixing, hot air was directed into the barrel at a temperature of about 80°C. for 15 minutes to evaporate the solvent. Thereafter, cold air at a temperature of about 25°C. was directed into the barrel to solidify the cellulose acetate butyrate coating on the beads. The coated beads dried very well with only a small percentage of agglomerates. The beads were then screened through a No. 25 mesh screen and onto a 35 mesh screen to obtain glass carrier beads uniformly coated with cellulose acetate butyrate.

The triboelectric value of the carrier beads was determined in accordance with the method described above and were found to have a value of about 13.8 micro-coulombs per gram of toner. The coated beads were mixed with a toner comprising styrene-n-butyl methacrylate copolymer, polyvinyl butyral and carbon black to form a developing composition in a weight ratio of 100 parts carrier beads to 1 part toner for evaluation. The test was conducted in a "Model D" electrostatographic apparatus (manufactured by Xerox Corporation, Rochester, N.Y.) and the qualities of the cop-

ies produced therefrom were evaluated. In every respect, the electrostatographic prints showed excellent copy quality as to density, resolution and background levels.

EXAMPLE 2

Coated flintshot carrier particles are made and tested as follows: 5 pounds of 20-35 mesh flintshot was placed in a tumbling barrel type mixer. 204 grams of a 10 percent cellulose acetate butyrate solution (EAB 171-2) in ethylene dichloride solvent were charged to the tumbling barrel mixer. The resultant mixture was mixed for about 1 1/4 hours at a temperature of about 50°C. During mixing, hot air was directed into the barrel at a temperature of about 70°C. for about 10 minutes to evaporate the solvent. Thereafter, cold air at a temperature of about 24°C. was directed into the barrel to solidify the cellulose acetate butyrate coating on the beads. The coated beads dried very well with only a small percentage of agglomerates. The beads were then screened through a 25 mesh screen and onto a 35 mesh screen to obtain flintshot carrier beads uniformly coated with cellulose acetate butyrate.

The triboelectric value of the carrier beads was determined in accordance with the method described above and were found to have a value of about 10.4 microcoulombs per gram of toner. The coated beads were mixed with the toner composition described in Example 1 to form a developing composition in a weight ratio of 100 parts carrier beads to 1 part toner for evaluation. The test was conducted in a "Model D" electrostatographic apparatus and the qualities of the copies produced therefrom were evaluated. In every respect, including toner pick-up, resolution and overall quality, the copies so obtained were rated "good."

EXAMPLE 3

Coated flintshot carrier particles were made and tested as follows: 5 pounds of 20-35 mesh flintshot were placed in a tumbling barrel type mixer. 204 grams of a 10 percent solution of cellulose acetate butyrate (EAB-171-2) containing 2 grams of Hansa Yellow in ethylene dichloride solvent were charged to the tumbling barrel mixer. The resultant mixture was mixed for about 1.5 hours at a temperature of about 50°C. During mixing, hot air was directed into the barrel at a temperature of about 60°C. for 15 minutes to evaporate the solvent. Thereafter, cold air at a temperature of about 25°C. was directed into the barrel to solidify the cellulose acetate butyrate coating on the beads. The coated beads dried very well with only a small percentage of agglomerates. The beads were then screened through a 25 mesh screen and onto a 35 mesh screen to obtain carrier beads uniformly coated with cellulose acetate butyrate.

The triboelectric value of the carrier beads was determined in accordance with the method described above and found to have a value of about 11.6 microcoulombs per gram of toner. The coated beads were mixed with the toner described in Example 1 to form a developing composition in a weight ratio of 100 parts carrier beads to 1 part toner for evaluation. The test was conducted in a "Model D" electrostatographic apparatus and the qualities of the copies produced therefrom were evaluated. In every respect, including toner pick-up, background resolution and overall quality, the copies so obtained were rated "good."

EXAMPLE 4

Coated flintshot carrier particles were made and tested as follows: 5 pounds of 20-35 mesh flintshot were placed in a tumbling barrel mixer. 204 grams of a 10 percent cellulose acetate butyrate solution (EAB - 500-1 manufactured by Eastman Kodak Company, Rochester, N.Y., approximate butyryl content 50 percent) in ethylene dichloride solvent as well as 2 grams Luxol blue dye were charged to the tumbling barrel mixer. The resultant mixture was mixed for about 1.5 hours at a temperature of about 55°C. During mixing, hot air was directed into the barrel at a temperature of about 70°C. for about 15 minutes to evaporate the solvent. Thereafter, cold air at a temperature of about 22°C. was directed into the barrel to solidify the cellulose acetate butyrate coating beads. The coated beads dry very well with only a small percentage of agglomerates. The beads were then screened through a 25 mesh screen and onto a 35 mesh screen to obtain flintshot carrier beads uniformly coated with cellulose acetate butyrate.

The triboelectric value of the carrier beads was determined in accordance with the method described above and were found to have a value of 3.9 microcoulombs per gram of toner. The coated beads were mixed with the toner composition described in Example 1 to form a developing composition in a weight ratio of 100 parts carrier beads to 1 part toner for evaluation. The test was conducted in a "Model D" electrostatographic apparatus and the qualities of the copies produced therefrom were evaluated. In every respect, including toner pick-up, resolution and overall quality, the copies so obtained were rated "fair" with a slight background.

Although specific materials and conditions were set forth in the above exemplary processes in making and using the carrier materials of this invention, these are merely intended as illustrations of the present invention. Various other toners, carrier cores, substituents and processes such as those listed above may be substituted in the examples with similar results.

Other modifications of the present invention will occur to those skilled in the art upon a reading of the present disclosure. These are intended to be included within the scope of this invention.

What is claimed is:

1. An electrostatographic developer mixture comprising finely divided toner particles electrostatically clinging to the surface of carrier beads, each of said carrier beads comprising a core having a uniform coating thereon comprising a polymeric cellulose ester wherein said coating exhibits a volume resistivity of between about 10^{10} and about 10^{14} ohm-centimeters at 23°C.
2. An electrostatographic developer mixture according to claim 1 wherein said polymeric cellulose ester is cellulose acetate butyrate.
3. An electrostatographic developer mixture according to claim 1 wherein the carrier bead core is glass.
4. An electrostatographic developer mixture according to claim 1 wherein the carrier bead core is flintshot.
5. An electrostatographic imaging process comprising the steps of forming an electrostatic latent image on a surface and developing said electrostatic latent image by contacting said electrostatic latent image with an

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electrostatographic developer mixture comprising finely divided toner particles electrostatically clinging to the surface of carrier beads, each of said carrier beads comprising a core having a uniform coating thereon comprising a polymeric cellulose ester wherein said coating exhibits a volume resistivity of between about 10^{10} and about 10^{14} ohm-centimeters at $23^{\circ}\text{C}.$, whereby at least a portion of said finely divided toner particles are attracted to and held on said surface in conformance with said electrostatic latent image.

6. An electrostatographic imaging process comprising the steps of forming an electrostatic latent image on a surface and developing said electrostatic latent image

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by contacting said electrostatic latent image with an electrostatographic developer mixture comprising finely divided toner particles electrostatically clinging to the surface of carrier beads, each of said carrier beads comprising a core having a uniform coating thereon comprising cellulose acetate butyrate wherein said coating exhibits a volume resistivity of between about 10^{10} and about 10^{14} ohm-centimeters at $23^{\circ}\text{C}.$, whereby at least a portion of said finely divided toner particles are attracted to and held on said surface in conformance with said electrostatic latent image.

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