

Aug. 14, 1973

R. J. HAGENBACH ET AL

3,752,666

ELECTROSTATIC IMAGING PROCESS USING CARRIER BEADS CONTAINING
CONDUCTIVE PARTICLES

Original Filed Oct. 11, 1966

2 Sheets-Sheet 1

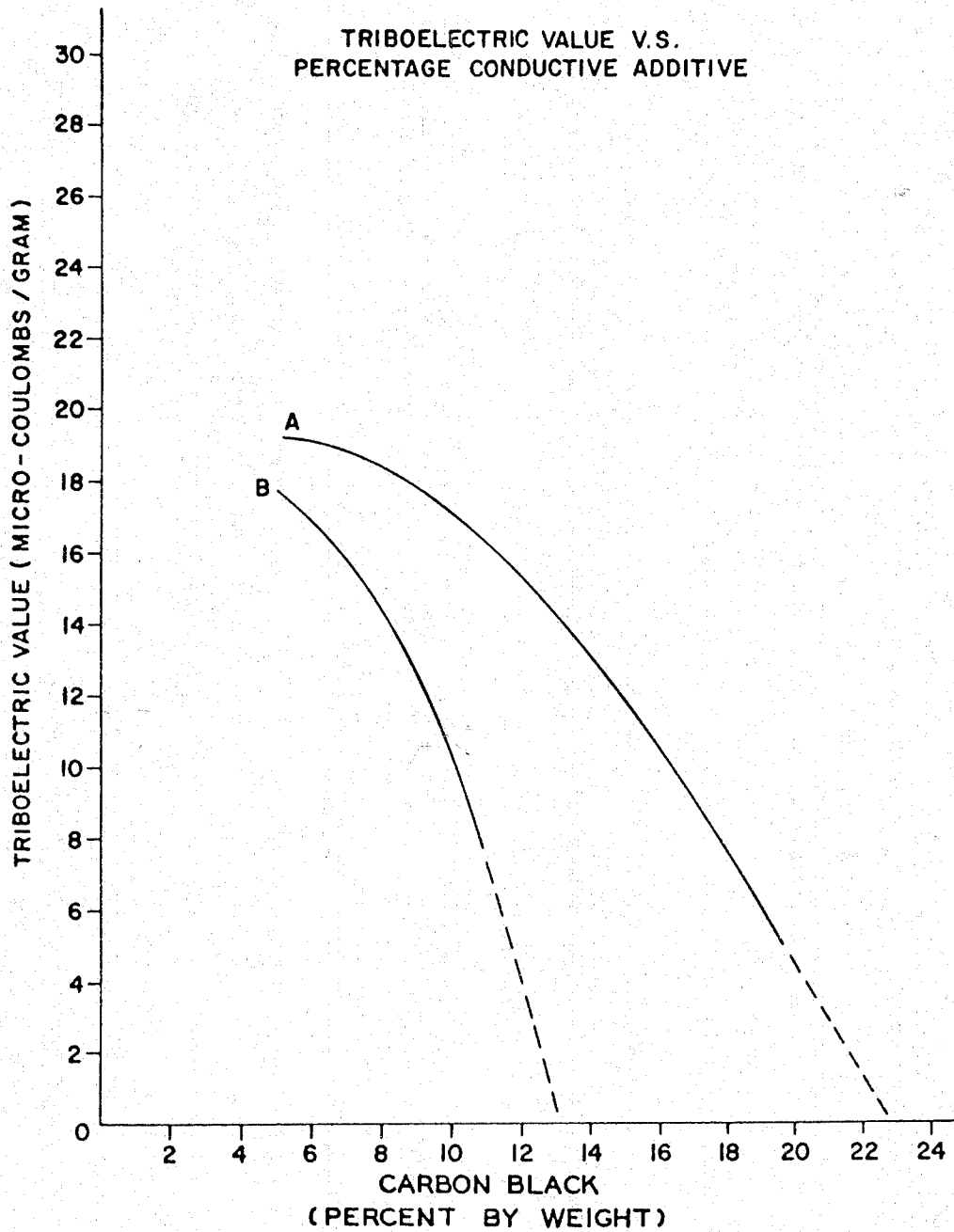


FIG. 1

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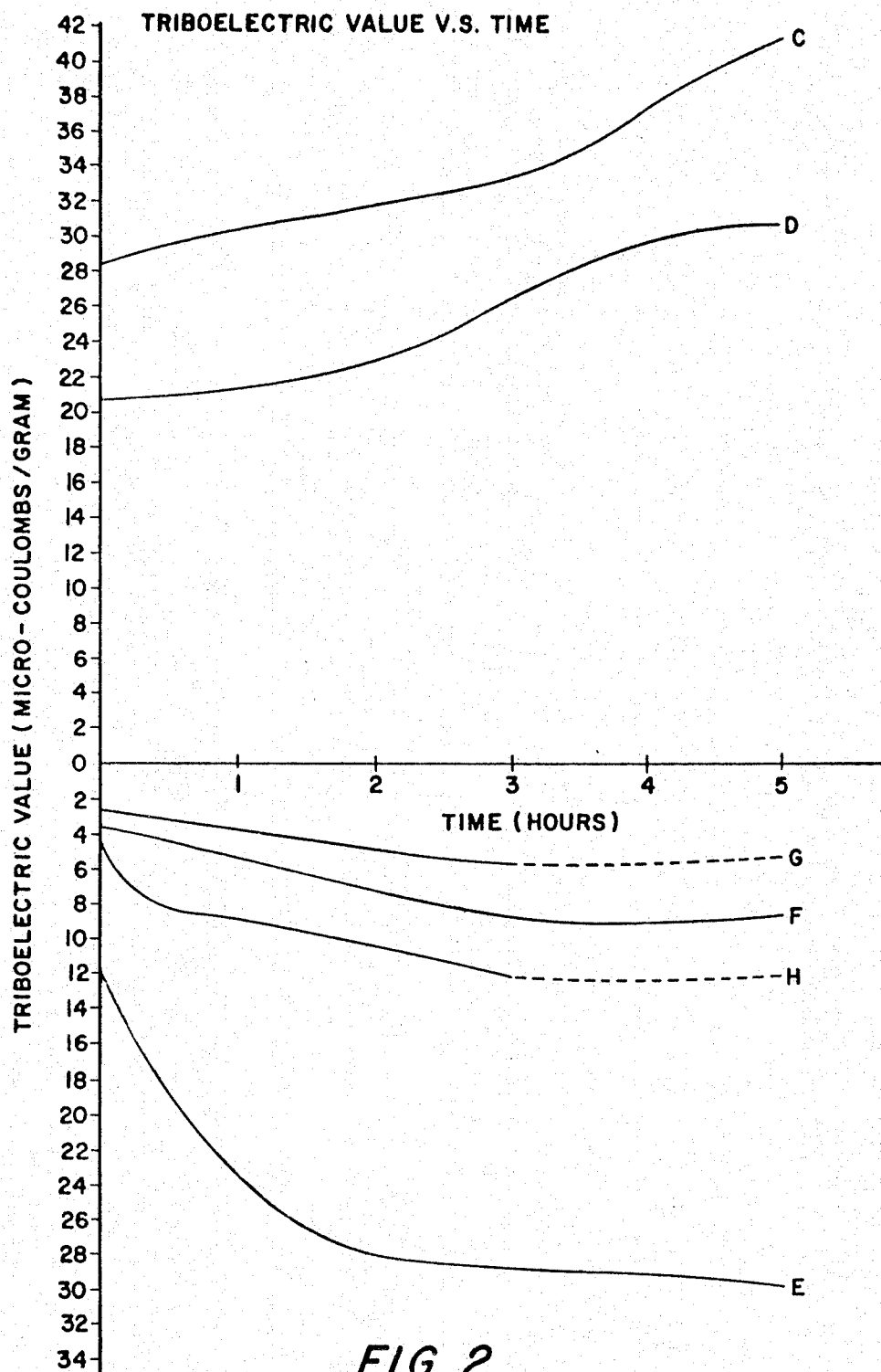


FIG. 2

1

2

3,752,666
**ELECTROSTATIC IMAGING PROCESS USING
CARRIER BEADS CONTAINING CONDUCTIVE PARTICLES**

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Original application Oct. 11, 1966, Ser. No. 585,817, now Patent No. 3,533,835, dated Oct. 13, 1970. Divided and this application June 9, 1970, Ser. No. 44,676 Int. Cl. G03g 5/02, 13/08

U.S. Cl. 96—1

14 Claims

ABSTRACT OF THE DISCLOSURE

Electrostatic latent images are developed with an electrostatic developer mixture comprising finely-divided toner particles electrostatically clinging to the surface of grossly larger carrier particles, each of the carrier particles comprising a matrix material adjacent to at least the external surface of the carrier particle, the matrix containing solid finely-divided electrically conductive particulate material.

This is a divisional of application Ser. No. 585,817, filed Oct. 11, 1966 and now U.S. Pat. 3,533,835.

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

The formation and development of images on the surface of photoconductive materials by electrostatic means is well known. The basic xerographic process as taught by C. F. Carlson in U.S. Pat. 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 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. 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 image-bearing 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 which the materials are arranged in such a way 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 in the series. As the mixture cascades or rolls across the image-bearing surface, the toner particles are electrostatically deposited and secured to the charged portions of the latent image and are not deposited on the uncharged or background portions of the image. Most of toner particles accidentally deposited in the background 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. This technique is extremely good for the development of line copy images. The cascade development process is the most widely used commercial xerographic development technique. A general purpose office copying machine incorporating this technique is described in U.S. Pat. 3,099,943.

Another technique for developing electrostatic images is the "magnetic brush" process as disclosed, for example, in U.S. Pat. 2,874,063. In this method, a developer material containing toner and magnetic carrier particles 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. 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 electrostatic imaging equipment.

In automatic xerographic equipment, it is conventional to employ a xerographic plate 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 plate 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. 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 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 described 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. The neutralization of a charge enhances 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. 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 developer mixture is over toned. The initial electrostatographic plate charge may be increased to improve the density of the deposited powder image, but the plate charge would ordinarily have to be excessively high in order to attract the electroscopic powder away from the carrier particle. Excessively high electrostatographic plate charges are not only undesirable because of the high power consumption necessary to maintain the electrostatographic plate at high potentials, but also because the high potential causes the carrier particles to adhere to the electrostatographic plate surface rather than merely roll across and off the electrostatographic plate surface. Print deletion and massive carry-over of carrier particles often occur when carrier particles adhere to reusable electrostatographic imaging surfaces. 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 surfaces promotes the formation of undesirable scratches on the surfaces during image transfer and surface cleaning operations. It is therefore apparent that many materials which otherwise have suitable properties for employment as carrier particles are unsuitable because they possess too high a triboelectric value. In addition, uniform triboelectric surface characteristics of many carrier surfaces are difficult to achieve with mass production techniques. Quality images are, in some instances, almost impossible to obtain in high speed automatic

machines when carriers having non-uniform triboelectric properties are employed. Although it may be possible to alter the triboelectric value of an insulating carrier material by blending the carrier material with another insulating material having a triboelectric value remote from the triboelectric value of the original carrier material, relatively larger quantities of additional material is necessary to alter the triboelectric value of the original carrier material. The addition of large quantities of material to the original carrier material to change the triboelectric properties thereof requires a major manufacturing operation and often undesirably alters the original physical characteristics of the carrier material. Thus, there is a continuing need for a better electrostatographic carrier and an improved method for forming same.

It is therefore an object of this invention to provide a carrier manufacturing technique and a resulting product which overcome the above-noted deficiencies.

It is another object of this invention to provide carrier beads which do not tend to stick to electrostatographic imaging surfaces.

It is still another object of this invention to provide a method for rapidly altering triboelectric values of a carrier material without markedly changing the physical and chemical properties of the original carrier material.

It is a further object of this invention to provide a carrier manufacturing technique for producing carriers having uniform triboelectric properties.

It is a still further object of this invention to render suitable many materials which were heretofore unsuitable as carrier materials.

It is another object of this invention to provide carrier beads having physical and chemical properties superior to known carrier beads.

The foregoing objects and others are accomplished, generally speaking, by incorporating finely-divided electrically conductive particulate material in at least the surface of carrier substrates. The electrically conductive particulate material employed should preferably have a volume resistivity less than about 10^{10} ohm centimeters and a maximum average particle size of less than about 15 microns because less particulate material is necessary to reduce the triboelectric value of the original carrier material, less difficulty is encountered in incorporating the conductive particles into a carrier substrate and many important physical properties of the original carrier material such as adhesion is substantially unaffected by the additional material. Although the actual mechanism is not entirely clear, the relative position of a specific carrier material in the triboelectric series is changed when electrically conductive materials are incorporated in at least the surface of the carrier substrate.

Any suitable organic or inorganic finely-divided particulate material having a volume resistivity of less than about 10^{10} ohm centimeters at 23° C. may be employed to alter the triboelectric properties of carrier substrates. Optimum results are achieved with particulate materials having a volume resistivity of less than about 1 ohm centimeters at 23° C. because maximum reduction of triboelectric value occurs with a minimum amount of alteration of the original carrier material characteristics. Preferably, the conductivity of the particulate additives should be independent of ambient relative humidity conditions. Typical materials having volume resistivity less than about 10^{10} ohm centimeters at 23° C. include: boron, aluminum bronze, antimony, arsenic, bismuth, bronze, beryllium, lithium, manganese, cadmium, thallium, cesium, molybdenum, rhodium, titanium, tungsten, chromium, tantalum, steel, cobalt, calcium, rubidium, thorium, calcium chloride, potassium bromide, silver nitrate, sodium chloride, lithium chloride, silver iodide, lithium bromide, cesium bromide, sodium iodide, nickel oxide, ferric oxide, aurin tricarboxylic acid ammonium salts, isoviolanthone, indanthrone black, cyananthrone, perylene-iodine complexes, tetracyanoquinodimethane complexes, isoviolan-

throne-iodine chloride complex, isoviolanthrene-aluminum, chloride complex, isoviolanthrene-titanium chloride complex, isoviolanthrene-iodine complex, isoviolanthrene-potassium complex, isoviolanthrene-sodium complex, sodium-anthracene complex, chloranil - N,N,N',N' - tetramethyl-p-phenylene diamine complex, bromanil-N,N,N',N'-tetramethyl-p-phenylene diamine complex, iodanil-N,N,N',N'-tetramethyl-p-phenylene diamine complex, chlorinal-3,8-diaminopyrene complex, chlorinal-3,10-diaminopyrene complex, bromanil-3,8-diaminopyrene complex, iodanil-3,8-diaminopyrene complex, tetracyanoquinodimethane-N,N'-dimethyl-p-phenylenediamine complex, tetracyanoquinodimethane - 2 - methyl p-phenylenediamine complex, tetracyanoquinodimethane - N,N,N',N' - tetramethyl-p-phenylenediamine complex, lithium-tetracyanoquinodimethane complex salt, cesium-tetracyanoquinodimethane complex salt, sodium-tetracyanoquinodimethane complex salt, potassium-tetracyanoquinodimethane complex salt, copper-tetracyanoquinodimethane complex salt, barium-tetracyanoquinodimethane complex salt, silver-tetracyanoquinodimethane complex salt, ammonium-tetracyanoquinodimethane complex salt, N - methylquinolinium-tetracyanoquinodimethane complex salt, 4-hydroxy-N-benzylanilinium complex salt, 4 - amino-N,N-diethylanilinium, 4-amino - 2,3,5,6 - tetramethylanilinium pyridium complex salt, quinolinium complex salt, N-(N-propyl)quinolinium complex salt, 2,2'-bipyridinium complex salt, aluminum phthalocyanine, aluminum polychlorophthalocyanine, antimony phthalocyanine, barium phthalocyanine, beryllium phthalocyanine, cadmium hexadecachlorophthalocyanine, cadmium phthalocyanine, calcium phthalocyanine, cerium phthalocyanine, chromium phthalocyanine, cobalt phthalocyanine, cobalt chlorophthalocyanine, copper 4-aminophthalocyanine, copper bromochlorophthalocyanine, copper 4-chlorophthalocyanine, copper 4-nitrophthalocyanine, copper phthalocyanine, copper phthalocyanine sulfonate, copper polychlorophthalocyanine, deutero-phthalocyanine, dysprosium phthalocyanine, erbium phthalocyanine, europium phthalocyanine, gadolinium phthalocyanine, gallium phthalocyanine, germanium phthalocyanine, hafnium phthalocyanine, halogen substituted phthalocyanine, holmium phthalocyanine, indium phthalocyanine, iron phthalocyanine, iron polyhalophthalocyanine, lanthanum phthalocyanine, lead phthalocyanine, lead polychlorophthalocyanine, cobalt hexaphenylphthalocyanine, copper pentaphenylphthalocyanine, lithium phthalocyanine, lutecium phthalocyanine, magnesium phthalocyanine, manganese phthalocyanine, mercury phthalocyanine, molybdenum phthalocyanine, naphthalocyanine, neodymium phthalocyanine, nickel phthalocyanine, nickel polyhalophthalocyanine, osmium phthalocyanine, palladium phthalocyanine, palladium chlorophthalocyanine, alkoxypthalocyanine, alkylaminophthalocyanine, alkylmercaptophthalocyanine, aralkylaminophthalocyanine, aryloxyphthalocyanine, arylmercaptophthalocyanine, copper phthalocyanine piperidine, cycloalkylaminophthalocyanine, dialkylaminophthalocyanine, diaralkylaminophthalocyanine, dicycloalkylaminophthalocyanine, hexadecahydrophthalocyanine, imidomethylphthalocyanine, 1,2 - naphthalocyanine, 2,3-naphthalocyanine, octaazaphthalocyanine, sulfur phthalocyanine, tetraazaphthalocyanine, tetra-4-acetylaminophthalocyanine, tetra-4-aminobenzoylphthalocyanine, tetra - 4 - aminophthalocyanine, tetrachloromethylphthalocyanine, tetradiazophthalocyanine, tetra - 4,4 - dimethyloctaazaphthalocyanine, tetra - 4,5 - diphenylenedioxide phthalocyanine, tetra-4,5-diphenyloctaazaphthalocyanine, tetra-(6-methyl-benzothiazoyl) phthalocyanine, tetra-p-methyl-phenylaminophthalocyanine, tetra-methylphthalocyanine, tetra-naphthotriazolylphthalocyanine, tetra-4-naphthylphthalocyanine, tetra-4-nitrophthalocyanine, tetra - peri-naphthylene-4,5-octaazaphthalocyanine, tetra-2,3-phenyleneoxide phthalocyanine, tetra-4-phenyloctaazaphthalocyanine, tetraphenylphthalocyanine, tetraphenylphthalocyanine tetracarboxylic acid, tetraphenylphthalocyanine

cyanine tetrabarium carboxylate, tetraphenylphthalocyanine tetra-calcium carboxylate, tetrapyritylphthalocyanine, tetra-4-trifluoro - methylmercaptophthalocyanine, tetra-4-trifluoromethylphthalocyanine, 4,5 - thionaphthene-octaazaphthalocyanine, platinum phthalocyanine, potassium phthalocyanine, rhodium phthalocyanine, samarium phthalocyanine, silver phthalocyanine and mixtures thereof.

Factors affecting the quantity of conductive particulate material to be incorporated in at least the surface of carrier particles include: the separation in the triboelectric series between the electroscopic marking particles and the carrier material; the average particle size of the conductive particulate additive; the concentration of the particular conductive material at the surface of the carrier particle; the average diameter of the carrier particle; and the conductivity of the finely-divided particulate additive.

The finely-divided conductive particulate material may be distributed only at the surface of a coated or uncoated carrier particle or uniformly distributed throughout an uncoated carrier particle or throughout the external coating of a coated carrier particle. When the finely-divided conductive particles are dispersed throughout the carrier particle or carrier particle coating rather than only contiguous to the surface of the carrier particle, proportionality more finely-divided conductive particles must necessarily be employed in order to maintain a sufficient quantity of exposed conductive particles at the surface of the carrier particle. The additional amount of finely-divided conductive particles necessary depends to a large extent on the surface area of the carrier particles, hence upon the particle diameter selected. Obviously, as the quantity of conductive particles actually available at the surface of the carrier particle is reduced to a negligible amount, the triboelectric properties of the carrier surface are substantially the same as a carrier which does not contain conductive particles. Obviously, with a given quantity of conductive particles based on the weight of the carrier, a greater volume of conductive particles is available at the surface of the carrier when the conductive particles are located only at the surface of the carrier particles than when the particles are intimately dispersed throughout each carrier particle.

In a preferred embodiment, the finely-divided conductive particulate material is incorporated into at least the outer surface of coated or uncoated carrier beads by bringing the finely-divided conductive particles into contact with the soft hardenable external surface of coated or uncoated beads and impacting the particulate additives therein by causing other beads to collide and roll across the soft surface thereof as disclosed in copending application Ser. No. 585,875 filed Oct. 11, 1966 now abandoned. As disclosed in the copending application, each carrier bead is subjected to thousands of collisions and rolling contacts with other beads during the impactation treatment. This impactation treatment is effected by suitable techniques such as tumbling a mixture of finely-divided conductive particles and carrier beads having a soft surface in hollow rotating cylinders; vibrating a mixture of finely-divided conductive particles and carrier beads having a soft surface linearly in high frequency reciprocating chambers; and contacting finely-divided particles with the soft external surfaces of carrier beads in an arcuate chamber vibrating in an oscillatory direction.

Where the finely-divided conductive particles are to be incorporated into a carrier bead having a preformed soft outer surface which is capable of being subsequently hardened, the carrier bead or carrier bead coating should comprise a material such as a soft curable prepolymer resin, gelled plastisol or certain soften materials. The softened materials may comprise materials softened by heat or solvents. The solvent or heat softenable materials may include natural resins, thermoplastic resins, and hard partially cured thermosetting resins. The soft curable prepolymers may comprise any suit-

able polymerized thermoplastic or thermosetting resin. Typical natural resins include: caoutchouc, colophony, copal, dammar, dragon's blood, jalap, storax, and the like. Typical thermoplastic resins include: the polyolefins such as polyethylene, polypropylene, chlorinated polyethylene, and chlorosulfonated polyethylene, polyvinyls and polyvinylidenes such as polystyrene, polymethylstyrene, polymethyl methacrylate, polyacrylonitrile, polyvinyl acetate, polyvinyl alcohol, polyvinyl butyral, polyvinyl chloride, polyvinyl carbazole, polyvinyl ethers, and polyvinyl ketones; fluorocarbons such as polytetrafluoroethylene, polyvinyl fluoride, polyvinylidene fluoride; and polychlorotrifluoroethylene; polyamides such as polycaprolactam and polyhexamethylene adipamide; polyesters such as polyethylene terephthalate; polyurethanes; polysulfides; polycarbonates; and the like. Typical thermosetting resins include: phenolic resins such as phenol-formaldehyde, phenol-furfural and resorcinol formaldehyde; amino resins such as urea-formaldehyde and melamine-formaldehyde; polyester resins; epoxy resins; and the like.

Where the finely-divided conductive particles are impacted into a softened surface of a carrier bead or carrier bead coating, the carrier surface is preferably a heat or solvent softenable material. The quantity of heat energy or solvent employed to soften the carrier surface should not exceed that quantity necessary to soften the carrier coating to a tacky or highly viscous state. When excessive quantities of heat energy or solvent is applied to the carrier coating, the coating material tends to flow and collect on the treatment chamber walls and, in some cases, cause agglomeration of the carrier particles. Thus, it is preferred that substantial fluidization of the coating is avoided during the impaction process. The carrier beads may be heated or treated with solvent prior to, during and/or subsequent to placement in the treatment chamber. Heating of the carrier beads may be effected by convection, conduction and/or radiation. Generally, heating by convection or radiation is preferred for softening carrier coatings because the danger of coating removal by hot heat transfer surfaces is eliminated. Conventional hot air blower systems and/or infrared heater banks may be employed to heat the carrier particles. Solvents or partial solvents may be used to soften the external surface of the bead. Generally, greater control of the softening process is achieved when solvent vapors or partial solvents for the coating material are employed. The use of solvents which rapidly dissolve external bead surface materials is less desirable because uniform surface softening of all the beads is difficult to attain, particularly at temperatures at which the solvents are most effective. Since the particulate materials to be incorporated into the bead surface are solids, care must be taken in selecting a solvent which will not completely dissolve the particulate additive. Any suitable solute bead material and solvent combination may be employed. Solvents for the solvent soluble beads or bead coatings employable in this invention are available in most handbooks of chemistry. Typical combinations of bead solute and solvent include: styrene-methyl-methacrylate-vinyl triethoxy silane terpolymer and toluene; polycarbonate and methylene chloride; phenoxy and tetrahydrofuran; nitrocellulose and methyl ethyl ketone; and the like.

Alternatively, the finely-divided conductive particles of this invention may be dispersed or suspended throughout a carrier bead or carrier bead coating material prior to bead or bead coating formation. The dispersion or suspension may be prepared by conventional techniques. It is to be understood that the material employed to form the matrix of the carrier bead or carrier bead coating may be in any suitable form such as a hot melt, a solution, an emulsion, a liquid monomer or a dispersion. When the ultimate product is to be a coated carrier bead, the carrier coating compositions with or without the finely-divided conductive particles may be applied to a carrier core by any conventional method such as spraying,

dipping, fluidized bed coating, tumbling, brushing and the like. The coating compositions may be applied as a powder, dispersion, solution, emulsion or hot melt. When applied as a solution, any suitable solvent may be employed. Solvents having relatively low boiling points are preferred because less energy and time is required to remove the solvent subsequent to application of the coating to the carrier core. If desired, the coating may comprise resin monomers which are polymerized in situ on the surface of the bead cores or plastisols gelled in situ to a non-flowable state on the surface of the bead cores. Any suitable coating thickness may be employed. However, the carrier coating should be sufficiently thick to resist flaking and chipping.

Any suitable well known coated or uncoated electrostatographic carrier bead material may be employed as the core of the beads of this invention. Typical carrier cores materials include sodium chloride, ammonium chloride, aluminum potassium chloride, Rochelle salt, sodium nitrate, potassium chlorate, granular zircon, granular silicon, methyl methacrylate, glass, silicon dioxide, flint-shot, iron, steel, ferrite, nickel, Carborundum and mixtures thereof. Many of the foregoing and other typical carriers are described by L. E. Walkup in U.S. Pat. 2,618,551; L. E. Walkup et al. in U.S. Pat. 2,638,415 and E. N. Wise in U.S. Pat. 2,618,552. An ultimate homogeneous or coated carrier bead diameter between about 30 microns to about 1,000 microns is preferred for electrostatographic use because the treated carrier bead then possesses sufficient density and inertia to avoid adherence to the latent electrostatic images during the cascade or magnetic brush development process. Although conductive carriers are suggested by Wise in U.S. Pat. 2,618,552 and Walkup et al. in U.S. Pat. 2,638,416, no suggestion is made by these patentees that combinations of carrier beads and toners which are unsuitable for electrostatographic developing processes because of their wide separation in the triboelectric series can be rendered suitable in a developing process by incorporating finely-divided conductive particles in at least the surface of the carrier bead.

Generally, an average conductive particle diameter of less than about 15 microns is preferred because the smooth surface of the ultimate treated bead is substantially uninterrupted by portions of relatively large diameter conductive particles extending above the external bead surface. Optimum surface characteristics and maximum reduction of triboelectric value are achieved with conductive particles having an average particle size of less than about 100 millimicrons. Although unexposed conductive particles remote from the external surfaces of carrier beads contribute in some cases to the density of the carrier, they do not appear to have any measurable effect on the carrier triboelectric properties. Thus, where high density matrices are employed, a monolayer of particles adjacent the external surface of a carrier or a gradient of particles comprising a dense region of particles adjacent the external surface of the carrier is preferred because less conductive material is consumed. Further, where the carrier bead is coated, maximum adhesion between the bead core and the coating layer is maintained with monolayers or gradients of conductive particles adjacent the external surface of the coating.

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, coumaroneindene 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. 2,659,670 to Copley; U.S. Pat. 2,753,308 to Landrigan;

U.S. Pat. 3,079,342 to Insalaco; U.S. Pat. Reissue 25,136 to Carlson and U.S. Pat. 2,788,288 to Rheinfrank et al. These toners generally have an average particle diameter between about 1 and about 30 microns.

The various features, advantages, and limitations of the invention will be further understood by reference to the drawings which show diagrammatic representations of the variations obtained in triboelectric value when various carrier coating materials are treated with conductive particulate additives under static and dynamic conditions.

In FIG. 1, the changes in static triboelectric value due to the presence of various quantities of two different types of carbon black conductive particle additives in two different organosilicon carrier coatings are represented by curves A and B. The technique employed to obtain the comparative data is set forth in detail in Examples II-VII below. As can be seen from the drawing, the static triboelectric values of the carrier coatings are rapidly reduced by the incorporation of a relatively small quantity of carbon black into the carrier coatings. It is believed that the triboelectric value of the carrier represented by curve B is reduced at a greater rate per a given incremental increase in carbon black content than the triboelectric value of the carrier represented by curve A because the average diameter of particles employed in the carrier of curve B is about 5 and one-half times smaller than the average diameter of the particles employed in the carrier of curve A.

Referring now to FIG. 2, the dynamic triboelectric values of the treated carrier beads of this invention represented by curves D, F, G and H are compared to the dynamic triboelectric values of untreated carrier beads represented by curves C and E. The dynamic triboelectric characteristics of an untreated carrier coated with an organosilicon terpolymer is represented by curve C. Curve D represents a carrier coated with the same type of organosilicon terpolymer employed in the carrier of curve C, but additionally containing 10 percent, based on the weight of the terpolymer, of aurintricarboxylic acid ammonium salt. As can be seen from the drawing, both the triboelectric value at a given point in time and the total change in dynamic triboelectric value of the treated carrier of curve D are lower than the triboelectric values of the carrier of curve C for a corresponding period of time. The dynamic triboelectric characteristics of an untreated carrier coated with a mixture of vinyl chloride-vinyl acetate copolymer and 25 percent based on the weight of the copolymer, of Luxol Fast Blue Dye is represented by curve E. Curves F and G represent carriers coated with the same type of coating mixture employed in the carrier of curve E, but additionally containing 15 and 20 percent, respectively, based on the weight of the coating mixture, of aurintricarboxylic acid ammonium salt. Curve H represents a carrier coated with the same type of coating mixture employed in the carrier of curve E, but additionally containing 20 percent by weight, based on the weight, of the coating mixture, of carbon black (Molacco H). As can be seen from the drawing, both the triboelectric value at a given point in time and the total change in dynamic triboelectric value of the treated carriers of curves F, G and H are lower than the triboelectric values of the carrier represented by curve E for a corresponding period of time.

The following examples further define, describe and compare methods of preparing the carrier 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, the relative triboelectric values generated by contact of carrier beads with toner particles is measured by means of a Faraday Cage. The device comprises a brass cylinder having a diameter of one inch and a length of one 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 a styrene-n-butyl methacrylate copolymer, polyvinyl butyral, and carbon black by the method disclosed by M. A. Insalaco in Example I of U.S. Pat. 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 I

A control sample is produced by mixing one part colored styrene copolymer toner particles having an average particle size of about 10 to about 20 microns with about 100 parts coated carrier particles having an average particle size of about 600 microns. The carrier comprises a glass bead core coated with the addition reaction product of about 15 parts styrene, about 85 parts methyl methacrylate and about 5 parts vinyl triethoxy silane. About 1 pound of carrier coating material is applied to about 100 pounds of carrier core material. The relative triboelectric value of the carrier measured by means of a Faraday Cage is about 29 micro-coulombs per gram of toner.

EXAMPLE II

A developer sample is produced by mixing one part colored styrene copolymer toner particles of the type described in Example I with about 100 parts coated carrier particles having an average particle size of about 600 microns. The carrier coating comprises the same type of addition reaction product described in Example I mixed on a three roll mill with about 5 percent by weight, based on the weight of the addition reaction product, of carbon black (Molacco H) having an average particle size of about 70 millimicrons. About 1 pound of coating material is applied to about 100 pounds of glass bead core material. The relative triboelectric value of the carrier measured by means of a Faraday Cage is about 19 micro-coulombs per gram of toner.

EXAMPLE III

A developer sample is produced by mixing one part colored styrene copolymer toner particles of the type described in Example I with about 100 parts coated carrier particles having an average particle size of about 600 microns. The carrier coating comprising the same type of addition reaction product described in Example I mixed on a three-roll mill with about 10 percent by weight, based on the weight of the addition reaction product, of carbon black (Molacco H) having an average particle size of about 70 millimicrons. About 1 pound of coating material is applied to about 100 pounds of glass bead core material. The relative triboelectric value of the carrier measured by means of a Faraday Cage is 17 micro-coulombs per gram of toner.

EXAMPLE IV

A developer sample is produced by mixing one part colored styrene copolymer toner particles of the type described in Example I with about 100 parts coated carrier particles having an average particle size of about 600 microns. The carrier coating comprises the same type of addition reaction product described in Example I mixed on a three-roll mill with about 15 percent by weight, based on the weight of the addition reaction product, of carbon black (Molacco H) having an average particle size of about 70 millimicrons. About 1 pound of coating material is applied to about 100 pounds of glass bead

core material. The relative triboelectric value of the carrier measured by means of a Faraday Cage is 10 micro-coulombs per gram of toner.

EXAMPLE V

A developer sample is produced by mixing one part colored styrene copolymer toner particles of the type described in Example I with about 100 parts coated carrier particles having an average particle size of about 600 microns. The carrier coating comprises the same type of addition reaction product described in Example I mixed on a three-roll mill with about 20 percent by weight, based on the weight of the addition reaction product of carbon black (Molacco H) having an average particle size of about 70 millimicrons. About 1 pound of coating material is applied to about 100 pounds of glass bead core material. The relative triboelectric value of the carrier measured by means of a Faraday Cage is 5 micro-coulombs per gram of toner.

EXAMPLE VI

A developer sample is produced by mixing one part colored styrene copolymer toner particles of the type described in Example I with about 100 parts coated carrier particles having an average particle size of about 600 microns. The carrier coating comprises the same type of addition reaction product described in Example I mixed on a three-roll mill with about 5 percent by weight, based on the total weight of the addition reaction product, of carbon black (Neo Spectra Mark II) having an average particle size of about 13 millimicrons. About 1 pound of coating material is applied to about 100 pounds of glass bead core material. The relative triboelectric value of the carrier measured by means of a Faraday Cage is about 18 micro-coulombs per gram of toner.

EXAMPLE VII

A developer sample is produced by mixing one part colored styrene copolymer toner particles of the type described in Example I with about 100 parts coated carrier particles having an average particle size of about 600 microns. The carrier coating comprises the same type of addition reaction product described in Example I mixed on a three-roll mill with about 10 percent by weight, based on the total weight of the addition reaction product of carbon black (Neo Spectra Mark II) having an average particle size of about 13 millimicrons. About 1 pound of coating material is applied to about 100 pounds of glass bead core material. The relative triboelectric value of the carrier measured by means of a Faraday Cage is about 11 micro-coulombs per gram of toner.

EXAMPLE VIII

A developer mixture is produced by mixing one part colored styrene copolymer toner particles of the type described in Example I with about 100 parts coated carrier particles having an average particle size of about 250 microns. The carrier comprises a glass bead core coated with the addition reaction product of about 15 parts styrene, about 85 parts methyl methacrylate and about 5 parts vinyl triethoxy silane. About 200 grams of coating material is applied to about 9 pounds of glass core. The relative triboelectric value of the coated carrier measured by means of a Faraday Cage is about 29 micro-coulombs per gram of toner. The developer mixture is cascaded across a selenium surface bearing a positively charge electrostatic image. The resulting developed image is transferred by electrostatic means to a sheet of paper whereon it is fused by heat. The resulting fused image is characterized by a faded washed out appearance.

EXAMPLE IX

A developer mixture is produced by mixing one part colored styrene copolymer toner particles of the type described in Example I with about 100 parts coated carrier particles having an average particle size of about 250

microns. The carrier comprises a glass bead core coated with the addition reaction product of about 15 parts styrene, about 85 parts methyl methacrylate and about 5 parts vinyl triethoxysilane mixed in a roll mill with about 10 percent by weight of carbon (Neo Spectra Mark II) having an average particle size of about 13 millimicrons. About 200 grams of coating material is applied to about 9 pounds of glass core material. The relative triboelectric value of the coated carrier measured by means of a Faraday Cage is about 11 micro-coulombs per gram of toner. The developer mixture is cascaded across a selenium surface bearing a positively charged electrostatic image. The resulting developed image is transferred by electrostatic means to a sheet of paper whereon it is fused by heat. The resulting fused image is dense and substantially free of background toner deposits.

EXAMPLE X

A developer mixture is produced by mixing one part colored styrene copolymer toner particles of the type described in Example I with about 100 parts coated carrier particles having an average particle size of about 250 microns. The carrier comprises a glass bead core coated with the addition reaction product of about 15 parts styrene, about 85 parts methyl methacrylate and about 5 parts vinyltriethoxysilane milled with about 40 percent by weight of carbon black (Neo Spectra Mark II) having an average particle size of about 13 millimicrons. About 200 grams of coating material is applied to about 9 pounds of glass core material. The relative triboelectric value of the coated carrier measured by means of a Faraday Cage is about 4 micro-coulombs per gram of toner. The developer mixture is cascaded across a selenium surface bearing a positively charged electrostatic image. The resulting developed image is transferred by electrostatic means to a sheet of paper whereon it is fused by heat. The resulting fused image is dense but possesses relatively high background toner deposition.

EXAMPLE XI

A control sample is produced by mixing one part colored styrene copolymer toner particles of the type described in Example I with about 100 parts coated carrier particles having an average particle size of about 600 microns. The carrier coating comprises a mixture of a vinyl chloride-vinyl acetate copolymer and 25 percent by weight, based on the weight of the copolymer of Luxol Fast Blue Dye. About 0.3 pound of the coating material is applied to about 100 pounds of steel cores. The relative triboelectric value of the carrier measured by means of a Faraday Cage is about -12 micro-coulombs per gram of toner.

EXAMPLE XII

A developer sample is produced by mixing one part colored styrene copolymer toner particles of the type described in Example I with about 100 parts of a portion of the coated carrier particles described in Example XI. The carrier coating is impacted with about 10 percent by weight, based on the weight of the carrier coating material, of hydrazine sulfate particles having an average particle size of about 1 millimicron. The hydrazine sulfate particles are impacted into the carrier coatings in a vibrating housing. The impactation process involves softening the carrier coating and vibrating the coated carrier particles and hydrazine sulfate particles at an oscillatory vibration frequency of about 2,000 cycles per minute. The vibration is maintained until the housing no longer contains free hydrazine sulfate particles. The relative triboelectric value of the impacted carrier particles measured by means of a Faraday Cage is about -7 micro-coulombs per gram of toner.

EXAMPLE XIII

A developer sample is produced by mixing one part colored styrene copolymer toner particles of the type

described in Example I with about 100 parts of a portion of the coated carrier particles described in Example XI. The carrier coating is impacted with about 10 percent by weight, based on the total weight of the carrier coating material, of aminoguanidine sulfate particles having an average particle size of about 2 microns. The aminoguanidine sulfate particles are impacted into the carrier coatings in a vibrating housing. The impaction process involves heat softening the carrier coating and vibrating the coated carrier particles and aminoguanidine sulfate particles at an oscillatory vibration frequency of about 2,000 cycles per minute. The vibration is maintained until the housing no longer contains free aminoguanidine sulfate particles. The relative triboelectric value of the impacted carrier particle is measured by means of Faraday Cage is about -6 micro-coulombs per gram of toner.

EXAMPLE XIV

A control sample is produced by mixing one part colored styrene copolymer toner particles of the type described in Example I with about 100 parts carrier particles having an average particle size of about 600 microns. The carrier particles comprise homogeneous beads of nitrocellulose resin. The relative triboelectric value of the carrier measured by means of a Faraday Cage is about -17 micro-coulombs per gram of toner.

EXAMPLE XV

A developer sample is produced by mixing one part colored styrene copolymer toner particles of the type described in Example I with about 100 parts carrier particles having an average particle size of about 600 microns. The carrier particles comprise a nitrocellulose matrix containing about 10 percent by weight, based on the total weight of the carrier, of aluminum particles having an average particle size of about 73 millimicrons uniformly dispersed throughout said matrix. The relative triboelectric value of the carrier measured by means of a Faraday Cage is about -12 micro-coulombs per gram of toner.

EXAMPLE XVI

A developer sample is produced by mixing one part colored styrene copolymer toner particles of the type described in Example I with about 100 parts carrier particles having an average particle size of about 600 microns. The carrier particles comprise a nitrocellulose matrix containing about 10 percent by weight, based on the total weight of the carrier, of lead dioxide particles having an average particle size of about 3 millimicrons uniformly dispersed throughout said matrix. The relative triboelectric value of the carrier measured by means of a Faraday Cage is about -8 micro-coulombs per gram of toner.

EXAMPLE XVII

Coated carrier particles having an average particle size of about 600 microns are coated with the same type of addition reaction product described in Example I. About 1 pound of coating material is applied to about 100 pounds of glass bead core material.

A developer sample is produced by mixing about 3 grams of colored styrene copolymer toner particles of the type described in Example I with about 300 grams of coated carrier particles. The 400 gram toner and carrier mixture is then placed in an electrically grounded standard Xerox Model D tray, available from the Xerox Corporation, Rochester, N.Y., and rocked back and forth at the rate of 20 cycles per minute. The tray is tilted in each direction approximately 45 degrees from the horizontal during each cycle. Samples are removed periodically for triboelectric value measurements in a Faraday Cage. The readings obtained are plotted to form curve C in FIG. 2.

EXAMPLE XVIII

Carrier particles having an average particle size of about 600 microns are coated with a coating comprising the same type of addition reaction product described in Example I, but additionally, containing dispersed therein about 10 percent by weight, based on the weight of the reaction product, of aurintricarboxylic acid ammonium salt. The aurin salt is dispersed in the coating material by adding a methyl alcohol solution of aurintricarboxylic acid ammonium salt to a toluene-acetone solution of the Example I addition reaction product. The aurin salt is incompatible with the acetone-toluene mixture and comes out of solution as a fine dispersion uniformly distributed throughout the solution. About 1 pound of coating solids is applied to about 100 pounds of glass bead core material. A developer sample is produced by mixing about 3 grams of colored styrene copolymer toner particles of the type described in Example I with about 300 grams of the coated carrier beads. The resulting mixture is subjected to conditions substantially identical to the conditions set forth in Example XVII and the resulting readings are plotted to form curve D in FIG. 2. The dynamic triboelectric value of the curve D treated carrier at any corresponding point in time is at least 6.5 micro-coulombs below the dynamic triboelectric value of the curve C untreated carrier. Further, the maximum change in triboelectric value of the curve C untreated carrier over a five hour period is about 25 percent greater than the change in triboelectric value of the curve D treated carrier.

EXAMPLE XIX

Carrier particles having an average particle size of about 600 microns are coated with a coating comprising a vinyl chloride-vinyl acetate copolymer and 25 percent by weight, based on the weight of the copolymer, of Luxol Fast Blue Dye. About 1 pound of coating solids is applied to about 100 pounds of glass bead core material. A developer sample is produced by mixing about 3 grams of colored styrene copolymer toner particles of the type described in Example I with about 300 grams of the coated carrier particles. The resulting mixture is subjected to conditions substantially identical to the conditions set forth in Example XVII and the resulting readings are plotted to form curve E in FIG. 2.

EXAMPLE XX

Carrier particles having an average particle size of about 600 microns are coated with a coating comprising the same type of vinyl chloride-vinyl acetate copolymer mixture described in Example XIX, but additionally containing uniformly dispersed therein about 15 percent, by weight, based on the weight of the copolymer mixture, of aurintricarboxylic acid ammonium salt. The aurin salt is dispersed in the coating material by adding a methyl ethyl ketone solution of the copolymer mixture to a methyl alcohol solution of aurintricarboxylic acid ammonium salt. The aurin salt is incompatible with the methyl ethyl ketone mixture and comes out of solution as a fine dispersion uniformly distributed throughout the solution. About 1 pound of coating solids is applied to about 100 pounds of glass bead core material. A developer sample is produced by mixing about 3 grams of colored styrene copolymer toner particles of the type described in Example I with about 300 grams of the coated carrier beads. The resulting mixture is subjected to conditions substantially identical to the conditions set forth in Example XVII and the resulting readings are plotted to form curve F in FIG. 2. The dynamic triboelectric value of the curve F treated carrier at any corresponding point in time is at least 8.5 micro-coulombs less than the dynamic triboelectric value of the curve E untreated carrier. Also, the maximum change in triboelectric value of the curve E untreated carrier over a five hour period is about 300 percent greater than the change in triboelectric value of the curve F treated carrier.

15 EXAMPLE XXI

The coating procedure described in Example XX is repeated with sufficient additional aurintricarboxylic acid ammonium salt to provide a carrier coating containing about 20 percent by weight, based on the weight of the copolymer mixture, of aurin salt. A developer sample is produced by mixing about 3 grams of colored styrene copolymer toner particles of the type described in Example I with about 300 grams of the coated carrier beads. The resulting mixture is subjected to conditions substantially identical to the conditions set forth in Example XVII and the resulting readings are plotted to form curve G in FIG. 2. The dynamic triboelectric value of the curve G treated carrier at any corresponding point in time is at least 9 micro-coulombs less than the dynamic triboelectric value of the curve E untreated carrier. Further, the maximum change in triboelectric value of the curve E untreated carrier over a five hour period of time is about 600 percent greater than the change in triboelectric value of the curve G treated carrier.

EXAMPLE XXII

Carrier particles having an average particle size of about 600 microns are coated with a coating comprising the same type of vinyl chloride-vinyl acetate copolymer mixture described in Example XIX, but additionally containing uniformly dispersed therein about 20 percent by weight, based on the weight of the copolymer mixture, of carbon black (Molacco H) having an average particle size of about 70 millimicrons. The carbon black particles are dispersed in the coating material on a roll mill. About 1 pound of coating material is applied to about 100 pounds of glass bead core material. A developer sample is produced by mixing about 3 grams of colored styrene copolymer toner particles of the type described in Example I with about 300 grams of the coated carrier beads. The resulting mixture is subjected to conditions substantially identical to the conditions set forth in Example XVII and the resulting readings are plotted to form curve H in FIG. 2. The dynamic triboelectric value of the curve H treated carrier is at least 7.5 micro-coulombs less than the dynamic triboelectric value of the curve E untreated carrier. Also, the maximum change in triboelectric value of the curve E untreated carrier over a five hour period of time is about 200 percent greater than the change in triboelectric value of the curve H treated carrier.

EXAMPLE XXIII

A carrier coating is prepared by mixing about 25 parts of the same type of addition reaction product described in Example I with 75 parts of polyphenylene oxide resin on a Kady Mill. About 1 pound of coating material is applied to about 100 pounds of 600 micron glass bead cores.

A developer sample is produced by mixing one part colored styrene copolymer toner particles of the type described in Example I with about 100 parts coated carrier particles having an average particle size of about 600 microns. The relative triboelectric value of the carrier measured by means of a Faraday Cage is about 14 micro-coulombs per gram of toner. Since 600 micron glass carrier beads coated with about 1 pound of polyphenylene oxide resin per 100 pounds of glass bead cores possess a triboelectric value of about 4 micro-coulombs per gram of toner, it is apparent that a highly excessive percentage of electrically non-conductive polyphenylene oxide resin is required to reduce the triboelectric value of the organo-silicon coating material of Example I by approximately one-half. Further, the altered coating possesses more of the physical characteristics of the non-conductive additive than of the original coating material.

EXAMPLE XXIV

A carrier coating is prepared by mixing about 20 parts vinyl acetate resin (Bakelite AYHA) with about 80 parts

16

of vinyl chloride resin (Bakelite VAGH) on a Kady Mill. About 1 pound of the resin mixture is applied to about 100 pounds of 600 micron glass bead cores. A developer sample is produced by mixing 1 colored styrene copolymer toner particles of the type described in Example I with about 100 parts coated carrier particles having an average particle size of about 600 microns. The relative triboelectric value of the carrier measured by means of a Faraday Cage is about 27.5 micro-coulombs per gram of toner. Since separate batches of 600 micron glass carrier beads coated with the above described vinyl acetate and vinyl chloride resins possess triboelectric values of about 28.5 and -5 micro-coulombs, respectively, it is apparent that an inordinate percentage of electrically non-conductive vinyl chloride resin is necessary to reduce the triboelectric value of the vinyl acetate coating material. Additionally, the vinyl acetate coating does not possess all of its original physical characteristics after the non-conductive additive is mixed therewith.

Although specific components, proportions and procedures have been stated in the above description of the preferred embodiments of the novel carrier system, other suitable materials, as listed above, may be used with similar results. Further, other materials and procedures may be employed to synergize, enhance or otherwise modify the novel system.

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

What is claimed is:

1. 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 electrostatographic developer mixture comprising finely-divided toner particles electrostatically clinging to the surfaces of grossly larger carrier beads having a particle size from about 30 to about 1,000 microns, each of said carrier beads comprising a matrix material adjacent to at least the external surface of said beads, said matrix material containing solid finely-divided electrically conductive particulate material having an average diameter less than about 15 microns whereby at least a portion of said finely-divided toner particles are attracted to and held on said surface in conformance to said electrostatic latent image.

2. 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 electrostatographic developer mixture comprising finely-divided toner particles electrostatically clinging to the surfaces of grossly larger carrier beads having a particle size from about 30 to about 1,000 microns, each of said carrier beads comprising finely-divided electrically conductive particulate material having an average diameter less than about 15 microns concentrated contiguous to the external surface of said bead whereby at least a portion of said finely-divided toner particles are attracted to and held on said surface in conformance to said electrostatic latent image.

3. 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 electrostatographic developer mixture comprising finely-divided toner particles electrostatically clinging to the surfaces of grossly larger carrier beads having a particle size from about 30 to about 1,000 microns, each of said carrier beads comprising a matrix having a finely-divided electrically conductive particulate material having an average diameter less than about 15 microns uniformly dispersed through said matrix whereby at least a portion of said finely-divided toner particles are attracted to and held on

said surface in conformance to said electrostatic latent image.

4. 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 electrostatographic developer mixture comprising finely-divided toner particles electrostatically clinging to the surfaces of loose, freely movable carrier particles, each of said carrier particles comprising a core surrounded by a substantially permanent thin outer coating of matrix material and solid finely-divided electrically conductive particulate material substantially uniformly dispersed throughout said thin outer coating, said carrier particles having an average diameter between about 30 microns and about 1,000 microns and said finely-divided electrically conductive particulate material having an average diameter less than about 15 microns, whereby at least a portion of said finely-divided toner particles are attracted to and held on said surface in conformance to said electrostatic latent image.

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 electrostatographic developer mixture comprising finely-divided toner particles electrostatically clinging to the surfaces of loose, freely movable carrier particles, each of said carrier particles comprising a glass core surrounded by a substantially permanent thin outer coating of a matrix material and solid finely-divided electrically conductive particulate material substantially uniformly dispersed throughout said outer coating, said carrier particle having an average diameter between about 30 microns and about 1,000 microns and said finely-divided electrically conductive particulate material having an average diameter less than about 15 microns, whereby at least a portion of said finely-divided toner particles are attracted to and held on said surface in conformance to 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 by contacting said electrostatic latent image with an electrostatographic developer mixture comprising finely-divided toner particles electrostatically clinging to the surfaces of loose, freely movable carrier particles, each of said carrier particles comprising a core surrounded by a substantially permanent thin outer coating a matrix material and solid finely-divided electrically conductive particulate material substantially uniformly dispersed throughout said thin outer coating, said carrier particle having an average diameter between about 30 microns and about 1,000 microns and said finely-divided electrically conductive particulate material having an average diameter less than about 15 microns and a volume resistivity of less than about 10^{10} ohm-cm. at about 23° C., whereby at least a portion of said finely-divided toner particles are attracted to and held on said surface in conformance to said electrostatic latent image.

7. 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 electrostatographic developer mixture comprising finely-divided toner particles electrostatically clinging to the surfaces of loose, freely movable carrier particles, each of said carrier particles comprising a core surrounded by a substantially permanent thin outer coating of matrix material and solid finely-divided electrically conductive particulate material substantially uniformly dispersed throughout said thin outer coating, said carrier particle having an average diameter between about 30 microns and about 1,000 microns and said solid finely-divided electrically conductive particulate material having a volume resistivity less than about

one ohm-cm. at about 23° C. and having an average diameter less than about 15 microns, whereby at least a portion of said finely-divided toner particles are attached to and held on said surface in conformance to said electrostatic latent image.

8. 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 electrostatographic developer mixture comprising finely-divided toner particles electrostatically clinging to the surfaces of loose, freely movable carrier particles, each of said carrier particles comprising a core surrounded by a substantially permanent thin outer coating of matrix material and solid finely-divided electrically conductive particulate material concentrated contiguous to the outer surface of said thin outer coating, said carrier particle having an average diameter between about 30 microns and about 1,000 microns and said finely-divided electrically conductive particulate material having an average diameter less than about 15 microns, whereby at least a portion of said finely-divided toner particles are attracted to and held on said surface in conformance to said electrostatic latent image.

9. An electrostatographic imaging process comprising the steps of forming an electrostatic latent image on an imaging surface and developing said electrostatic latent image by contacting said electrostatic latent image with an electrostatographic developer mixture comprising a dry mixture of loose movable particles of electrostatically attractable toner particles and separate loose, freely movable carrier particles, each of said carrier particles comprising a matrix material containing finely-divided conductive particulate material adjacent to at least the external surface of each of said carrier particles, said carrier particles having an average diameter between about 30 microns and about 1,000 microns and sufficient specific gravity whereby said carrier particles do not adhere to said imaging surface, said outer surface of each of said carrier particles and said toner particles having a triboelectric relationship of opposite polarity whereby said toner particles are electrostatically charged through triboelectric action by mixing with said carrier particles to electrostatically adhere said toner particles to the outer surface of each of said carrier particles, said toner particles being electrostatically attractable from said outer surface of said carrier particles to said imaging surface to form a toner particle deposit on said imaging surface in image configuration, said outer surface of said outer coating being correspondingly electrostatically charged to opposite polarity and adapted to electrostatically attract and remove by contact said charged toner particles from areas of said imaging surface other than the areas covered by said toner particle deposit whereby at least a portion of said finely-divided toner particles are attracted to and held on said imaging surface in conformance to said electrostatic latent image.

10. An electrostatographic imaging process comprising the steps of forming an electrostatic latent image on an imaging surface and developing said electrostatic latent image by contacting said electrostatic latent image with an electrostatographic developer mixture comprising a dry mixture of loose movable particles of electrostatically attractable toner particles and separate loose, freely movable carrier particles, each of said carrier particles comprising a core surrounded by a substantially permanent thin outer coating of matrix material and solid finely-divided electrically conductive particulate material substantially uniformly dispersed throughout said thin outer coating, said carrier particles having an average diameter between about 30 microns and about 1,000 microns and sufficient specific gravity whereby said carrier particles do not adhere to said imaging surface, said outer coating and said toner particles having a triboelectric relationship of opposite polarity whereby said toner particles are electrostatically charged through triboelectric action by mixing with said carrier particles to electrostatically adhere said toner parti-

cles to the outer surface of each of said carrier particles, said toner particles being electrostatically attractable from said outer surfaces of said carrier particles to said imaging surface to form a toner particle deposit on said imaging surface in image configuration, said outer surface of said outer coating being correspondingly electrostatically charged to opposite polarity and adapted to electrostatically attract and remove by contact said charged toner particles from areas of said imaging surface other than the areas covered by said toner particle deposit whereby at least a portion of said finely-divided toner particles are attracted to and held on said imaging surface in conformance to said electrostatic latent image.

11. An electrostatographic imaging process comprising the steps of forming an electrostatic latent image on an imaging surface and developing said electrostatic latent image by contacting said electrostatic latent image with an electrostatographic developer mixture comprising a dry mixture of loose movable particles of electrostatically attractable toner particles having an average particle size less than about 30 microns and separate loose, freely movable carrier particles, each of said carrier particles comprising a steel core surrounded by a substantially permanent thin outer coating of matrix material and solid finely-divided electrically conductive particulate material substantially uniformly dispersed throughout said thin outer coating, said carrier particles having an average particle diameter between about 30 microns and about 1,000 microns and sufficient specific gravity whereby said carrier particles do not adhere to said imaging surface, said outer coating and said toner particles having a triboelectric relationship of opposite polarity whereby said toner particles are electrostatically charged through triboelectric action by mixing with said carrier particles to electrostatically adhere said toner particles to the outer surface of each of said carrier particles, said toner particles being electrostatically attractable from said outer surfaces of said carrier particles to said imaging surface to form a toner particle deposit on said imaging surface in image configuration, said outer surface of said outer coating being correspondingly electrostatically charged to opposite polarity and adapted to electrostatically attract and remove by contact said charged toner particles from areas of said imaging surface other than the areas covered by said toner particle deposit whereby at least a portion of said finely-divided toner particles are attracted to and held on said imaging surface in conformance to said electrostatic latent image.

12. 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 electrostatographic developer mixture comprising loose, freely movable carrier particles substantially uniformly coated with smaller toner particles electrostatically clinging to and electrostatically removable from the outer surfaces of carrier particles having outer surfaces capable of retaining said toner particles by electrostatic attraction, said toner particles having an average particle size less than about 30 microns, each of said carrier particles comprising a matrix material adjacent to at least the external surface of each of said carrier particles, said carrier particles having an average diameter between about 30 microns and about 1,000 microns and said finely-divided electrically conductive particulate material having an average diameter less than about 15 microns whereby at least a portion of said finely-divided toner particles are attracted

to and held on said surface in conformance to said electrostatic latent image.

13. 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 electrostatographic developer mixture comprising loose, freely movable carrier particles substantially uniformly coated with smaller toner particles electrostatically clinging to and electrostatically removable from the outer surfaces of said carrier particles having outer surfaces capable of retaining said toner particles by electrostatic attraction, said toner particles having an average particle size less than about 30 microns, each of said carrier particles comprising a core substantially free of dispersed solid finely-divided electrically conductive particulate material, said core surrounded by a substantially permanent thin outer coating of matrix material and solid finely-divided electrically conductive particulate material substantially uniformly dispersed throughout said thin outer coating, said carrier particles having an average diameter between about 30 microns and about 1,000 microns and said finely-divided electrically conductive particulate material having an average diameter less than about 15 microns whereby at least a portion of said finely-divided toner particles are attracted to and held on said surface in conformance to said electrostatic latent image.

14. 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 electrostatographic developer mixture comprising loose, freely movable carrier particles substantially uniformly coated with smaller toner particles electrostatically clinging to and electrostatically removable from the outer surfaces of carrier particles having outer surfaces capable of retaining said toner particles by electrostatic attraction, said toner particles having an average particle size less than about 30 microns, each of said carrier particles comprising a core surrounded by a substantially permanent thin outer coating of matrix material and solid finely-divided electrically conductive particulate material concentrated contiguous to the outer surface of said thin outer coating, said carrier particle having an average diameter between about 30 microns and about 1,000 microns and said finely-divided electrically conductive particulate material having an average diameter less than about 15 microns whereby at least a portion of said finely-divided toner particles are attracted to and held on said surface in conformance to said electrostatic latent image.

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17—17.5; 252—62.1

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,752,666 Dated August 14, 1973

Inventor(s) Robert J. Hagenbach and Robert W. Madrid

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 4, line 53, following "finely-divided" and preceding "material" (line 54), please delete "particular" and substitute therefor--particulate--.

Column 17, line 30, following "of" and preceding "matrix", please delete "a".

Column 17, line 49, "a" should read -- of --.

Column 18, line 3, following "are" and preceding "to", please delete "attached" and substitute therefor --attracted--.

Column 19, line 56, following "the" and preceding "surfaces", please delete "other" and substitute therefor --outer--.

Signed and sealed this 10th day of September 1974.

(SEAL)
Attest:

McCOY M. GIBSON, JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents