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Madrid et al.

[11] **3,857,792**

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[54] **AN ELECTROSTATIC DEVELOPER MIXTURE WITH A COATED CARRIER**

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Related U.S. Application Data

[60] Division of Ser. No. 27,114, April 9, 1970, , which is a continuation-in-part of Ser. No. 585,793, Oct. 11, 1966, abandoned.

[52] **U.S. Cl.** ..... **252/62.1,** 117/17.5, 117/100 B, 117/100 M, 117/100 C

[51] **Int. Cl.** **G03g 9/02**

[58] **Field of Search** 252/60.1; 117/100, 17.5; 260/80.75, 824, 47

[56] **References Cited**

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[57] **ABSTRACT**

Development is obtained in an electrostatographic imaging system with a developer mixture wherein the carrier particles are coated with a thin layer of a solid polyphenylene oxide resin or a blend of a polyphenylene oxide resin and a thermoplastic or thermosetting resin.

3 Claims, No Drawings

AN ELECTROSTATIC DEVELOPER MIXTURE WITH A COATED CARRIER

This is a division of application Ser. No. 27,114, filed Apr. 9, 1970 which is a continuation-in-part of application Ser. No. 585,793, filed Oct. 11, 1966, now abandoned.

This invention relates in general to imaging systems and, more particularly to improved developing 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. 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 electrostatic 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 as by heat. Instead of latent image formation by uniformly charging the photoconductive layer and then exposing the layer to a light and shadow image, one may form the latent image by directly charging the layer in image configuration. The powder image may be fixed to the photoconductive layer if elimination of the powder image transfer step is desired. Other suitable means such as solvent or overcoating treatment may be substituted for the foregoing heat fixing step.

Several methods are known for applying the electroscopic particles to the latent electrostatic image to be developed. One development method, as disclosed by L. E. Walkup is U.S. Pat. No. 2,618,551 and E. N. Wise in U.S. Pat. No. 2,618,552, is known as "cascade" development. In this method, a developer material comprising relatively large carrier particles having fine toner particles electrostatically coated thereon is conveyed to and rolled or cascaded across the electrostatic image-bearing surface. The composition of the carrier particles is so chosen as to triboelectrically charge the toner particles to the desired polarity. As the mixture cascades or rolls across the image-bearing surface, the toner particles are electrostatically deposited and secured to the charged portion of a latent image and are not deposited on the uncharged or background portion of the image. Most of the toner particles accidentally deposited in the background areas are removed by the rolling carrier, due apparently, to the greater electrostatic attraction between the toner and carrier than between the toner and the discharge background. The carrier and excess toner are then recycled. This technique is extremely good for the development of line copy images.

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 method, a developer material containing toner and magnetic carrier particles is carried by magnets. The magnetic field of the magnet causes alignment of the magnetic carrier 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.

In most commercial processes, the cascade technique is carried out in automatic machines. In these machines, small buckets on an endless belt conveyor scoop the developer material from a sump and convey it to a point above an electrostatic image-bearing surface where the developer mixture is allowed to fall and cascade or roll by gravity across the image-bearing surface. The carrier beads along with any unused toner particles are then returned to the sump for recycling through the developing system. Small quantities of toner are periodically added to the developer mixture to compensate for the toner depleted during the development process. This process is repeated for each copy produced in the machine and is ordinarily repeated many thousands of times during the usable life of the developer. It is apparent that in this process, as well as in other development techniques the developer mixture is subjected to a great deal of mechanical attrition which tends to degrade both the toner and carrier particles. This degradation, of course, occurs primarily as a result of shear and impact forces due to the tumbling of the developer mixture on the xerographic plate and the movement of the bucket conveyor through the developer material in the sump. Deterioration or degradation of carrier particles is characterized by the separation of portions of or the entire carrier coating from the carrier core. The separation may be in the form of chips, flakes or entire layers and is primarily caused by fragile, poorly adhereing coating materials which fail upon impact and abrasive contact with machine parts and other carrier particles. Carriers having coatings which tend to chip and otherwise separate from the carrier core must be frequently replaced thereby increasing expense and consuming time. Print deletion and poor print quality occur when carrier particles having damaged coatings are not replaced. Fines and grit formed from carrier coating disintegration tend to drift and form unwanted deposits on critical machine parts. Many materials having high compressive and tensile strength either do not adhere well to the carrier core or do not possess the desired triboelectric characteristics. The triboelectric and flow characteristics of many carriers are adversely effected when relative humidity is high. For example, the triboelectric values of some carrier coatings fluctuate with changes in relative humidity and are not desirable for employment in xerographic systems, particularly in automatic machines which require carriers having stable predictable triboelectric values. Another factor affecting the stability of carrier triboelectric properties is the susceptibility of carrier coatings to "toner impaction." When the carrier particles are employed in automatic machines and recycled through many cycles, the many collisions which occur between the carrier particles and other surfaces in the machine cause the toner particles carried on the surface of the carrier particles to be welded or otherwise forced into carrier coatings. The gradual accumulation of permanently attached toner material to the surface of the carrier particles causes a change in the triboelectric value of the carrier particles and directly contributes to the degradation of copy quality by eventual destruction of the toner carrying capacity of the carrier. Further, many carrier coating materials are difficult to apply to carrier cores because they tend to form thin filaments rather than smooth continuous coatings.

Since developer materials must flow freely to facilitate accurate metering and even distribution during the development and developer recycling phases of the electrostatographic process, the presence of filaments and carrier having rough outer surfaces in developer materials is unsuitable because the developer materials tend to cake, bridge, and agglomerate. Some carrier coating materials having acceptable triboelectric and coating properties are unacceptable for employment on a commercial scale because they cannot be economically mass produced. For example,quality control of the triboelectric value of some resin blends is difficult to maintain because a slight deviation in component percentages causes the triboelectric value of the resulting product to change drastically. Carrier coating materials having close tolerance triboelectric values are particularly important in high speed automatic copying machines. Thus, there is a continuing need for a better system for developing latent electrostatic images.

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

It is another object of this invention to provide carrier coating materials which tenaciously adhere to carrier cores.

It is a still further object of this invention to provide carrier coatings having stable triboelectric values.

It is yet another object of this invention to provide carrier coatings having high tensile and compressive strength.

It is a further object of this invention to provide coated carriers having smooth outer surfaces.

It is still another object of this invention to provide toner impaction resistant carrier coatings.

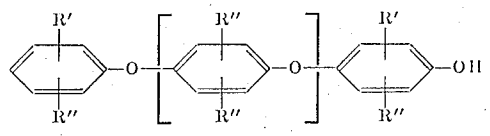
It is a further object of this invention to provide carrier coating materials having easily adjustable triboelectric values.

It is yet another object of this invention to provide carrier coatings which are more resistant to chipping and flaking.

It is another object of this invention to provide developers having physical and chemical properties superior to those of known developer materials.

The above objects and others are accomplished, generally speaking, by providing novel electrostatographic developer materials including carrier cores coated with a composition comprising a polyphenylene oxide resin. The resin component employed in the carrier coatings of this invention may comprise a polyphenylene oxide resin per se, or a polyphenylene oxide resin blended with one or more other resins. The polyphenylene oxide resin coating may be employed in any suitable thickness. Typically, the coating on the free flowing carrier particles is at least about 1 micron in thickness. However, a coating having a thickness of at least about 2.5 microns is preferred because the carrier coating will then possess sufficient thickness to resist abrasion and prevent any pinholes which would adversely affect the triboelectric properties of the coated carrier particles. The maximum coating thickness is generally determined by the amount of coating material capable of being coated on the core by any given coating technique which produces free flowing coated particles and which does not result in agglomeration. A practical maximum coating thickness for large size cores is therefore about 20 microns. Within these limits, a coating thickness of from about 3 to about 5 microns provides superior abrasion resistance and stable triboelectric properties. While not absolutely necessary, excellent abrasion resistance and stable triboelectric properties are generally achieved with a substantially smooth, continuous uniform coating of a polyphenylene oxide resin. However, superior abrasion resistance has been achieved with coatings which are neither uniform or continuous.

Any suitable linear polyphenylene oxide resin may be employed. These polyphenylene oxide resins have the general formula:



wherein: R′ and R″ are each selected from the group consisting of H and alkyl radicals having a total of up to 12 carbon atoms in R′ and R″ and *n* is a positive integer of at least about 25. Generally, the high molecular weight film-forming polyphenylene oxide resins employed in the carrier coatings of this invention are obtained by well known polymerization techniques such as the oxidative coupling of phenols. Oxidative coupling involves the reaction of oxygen with active hydrogens from different molecules to produce water and a dimer linked by an oxygen. In order to form polymers by the oxidative coupling technique, a polyphenylene oxide monomer must have at least two active hydrogens. Optimum impaction resistance is obtained with a polyphenylene oxide resin formed by the copper catalyzed oxidation of 2,6-dimethylphenol. The resulting polymer has methyl groups at R′ and R″ in the general formula set forth above. While a 2,6-xylenol monomer is preferred, any other suitable phenol may be used to produce useful resin carrier coatings. Typical phenols include: phenol; 2-methylphenol; 2-propyl phenol; 2-isobutyl phenol; 2,6-diethyl phenol; 2,6-diisopropyl phenol; 2-ethyl-6-methyl phenol; 2,5-dimethyl phenol; 3,5-dimethyl phenol; and the like.

Any suitable resin may be blended with a polyphenylene oxide resin to form the carrier coating materials of this invention. These resins may include natural resins, modified natural resins or synthetic resins prepared by addition, condensation or any other technique proving suitable. The polyphenylene oxide resin may be blended with other resins in any suitable amount. Generally to maintain the properties of the polyphenylene oxide resin as a coating it is present in the blend in at least the major proportion. Typical natural and modified natural resins include: gum copal, gum sandarac, rosin, fossil resins, zein, ethyl cellulose, cellulose acetate, cellulose nitrate, gum nitrate, oxidized rosin, pentaerythritol esters of rosin and the like. Typical synthetic resins include polymers, copolymers, terpolymers and other polymeric structures and modified polymeric structures including, for example, polyolefins such as polyethylene, polypropylene, chlorinated polyethylene, and chlorosulfonated polyethylene; polyvinyl and polyvinylidine compounds such as polystyrene, polymethylstyrene, polymethyl methacrylate, polyacrylic acid, polyacrylonitrile, polyvinyl acetate, polyvinyl alcohol, polyvinyl butyral, polyvinyl chloride, polyvinyl carbazole, polyvinyl ethers and polyvinyl ketones; fluorocarbons such as polytetrafluoroethylene,

polyvinylfluoride, polyvinylidenefluoride and polychlorotrifluoroethylene; polyamides such as polycaproloctamo and polyhexamethylene adipamide; polyesters such as polyethylene terephthalate; polyurethanes; polysulfides; polycarbonates; epoxies such as the condensation reaction product of epichlorohydrin with any one of a bisphenol A, resorcinol, hydroquinone and ethylene glycol; phenolic resins such as phenol formaldehyde, phenol furfural and resorcinol formaldehyde; amino aldehydes such as urea formaldehyde and melamine formaldehyde; and mixtures thereof.

Excellent results are obtained with a carrier coating containing a polyphenylene oxide resin blended with the products of an addition polymerization reaction between monomers or prepolymers of: (1) organo silanes, silanols or siloxanes having from one to three hydrolyzable groups and an organic group attached directly to the silicon atom containing less than eight carbon atoms and an unsaturated carbon to carbon linkage capable of addition polymerization and (2) one or more silicon free types of unsaturated polymerizable organic compounds. These addition reaction products have a weight average molecular weight of at least about 5,000. Outstanding results are obtained with a carrier coating containing a solid polymeric reaction product of monomers of prepolymers of: (1) styrene and homologues thereof, (2) acrylate or methacrylate esters and (3) organo silanes, silanols or siloxanes having from one to three hydrolyzable groups and an organic group attached directly to a silicon atom containing less than eight carbon atoms and an unsaturated carbon to carbon linkage capable of addition polymerization. These organosilicon terpolymers are preferred additives because the resulting blend possesses especially good triboelectric stability and synergistic resistance to toner impaction.

Typically a solid copolymer addition reaction product may be obtained from about 99.5 to about 50 percent, by weight, of an unsaturated silicon free organic compound and from about 0.5 to about 50 percent, by weight, of the above described polymerizable organosilicon composition. Typically the solid terpolymer comprises from about 5 to about 94.5 percent, by weight, of an unsaturated silicon free organic compound, from about 94.5 to about 5 percent, by weight, of an unsaturated silicon free organic compound different from the first mentioned silicon free compound and from about 0.5 to about 50 percent, by weight, of one of the above described polymerizable organosilicon compounds.

The unsaturated organic group attached to the silicon atom contains the unsaturation in a non-benzoid group and is preferably an unsaturated hydrocarbon group. Typical unsaturated organic groups include: vinyl, chlorvinyl, divinyl, distyryl, allyl, diallyl, triallyl, allyl phenyl, dimethyl allyl and methacryloxypropyl groups. Typical hydrolyzable groups include:: ethoxy, methoxy, chloro, bromo, propoxy, acetoxy and amino groups. Examples of typical unsaturated organo silanes having hydrolyzable groups attached to a silicon atom include: vinyl triethosy silane, vinyl trimethoxy silane, vinyl-tris, (beta-methoxyethoxy), silane, gamma-methacryloxypropyltrimethoxy silane, vinyl trichlorosilane, vinyl triacetoxy silane, divinyl dichloro silane, and dimethyl vinyl chloro silane. Suitable corresponding polymerizable hydrolysis products and the corresponding siloxanes may be substituted for the foregoing unsaturated organo silanes. Unsaturated organic groups having less than six carbon atoms attached to the silicon atom are preferred because of the unusually greater polymerization activities of these groups. If more than one organic group is attached to the silicon atom, only one of the organic groups need be unsaturated to enter into a polymerization reaction with other unsaturated monomers. Hence, compounds such as dimethyl vinyl chloro silanes are suitable. When more than one unsaturated organic group attached to the silicon atom are present, these unsaturated groups need not be identical. For example, vinyl allyl silicon chlorides and bromides may be employed. Partially condensed siloxanes in the liquid state having reactive unsaturated organic groups attached to a silicon atom may be employed as a terpolymer reactant.

Suitable silicon free monomers or prepolymers with which the above organosilicon compounds are particularly adapted to react to form the polymeric organosilicon resin additives of this invention include the unsaturated compounds which normally form resinous polymers by addition type polymerization. Monomers or prepolymers containing the unsaturation in a nonbenzoid group may be employed, such unsaturated monomers or prepolymers include those having ethylenic or acetylenic linkage. Thus, there are included olefins, diolefins, acetylenes and their derivatives, particularly derivatives having substituents such as halogen, alkyl, aryl, unsaturated alicyclic and other types of substituent groups including, for example, nitrile or nitro groups. The unsaturated organic monomers containing the unsaturation in a non-benzoid group also include unsaturated hydrocarbons, aliphatic carbocyclic, and heterocyclic compounds including unsaturated alcohols, aldehydes, ketones, quinones, acids, acid anhydrides, esters, nitriles or nitro compounds. Typical unsaturated monomers include: ethylene, propylene, butenes, isobutylene, pentenes, hexenes, methyl methacrylate, methyl acrylate, vinyl chloride, vinylidene chloride, acrylonitrile, chlorovinyl acetate, styrene, butadene, chloroprene, cyclopentadene, divinyl benzene, cyclohexadiene, ethyl methacrylate, vinyl acetate, vinyl toluene, acetylene, phenylacetylene, ethylvinyl benzene, allyl chloride, allyl benzene, maleic anhydride, ethyl acrylate, diethylmaleate, butyl acrylate, butyl methacrylate, isobutyl methacrylate, methacrylic anhydride, vinyl formate, and mixtures thereof.

Polymerization of the unsaturated organosilicon and unsaturated silicon free unsaturated compounds are effected with any suitable free-radical initiator or catalyst capable of polymerizing the monomers or prepolymers. By a "free-radical initiator or catalyst" is meant a compound which is capable of producing free-radicals under the polymerization conditions employed, such as compounds having an —O—O— or an —N=N— linkage. Examples of the more commonly employed free-radical initiators or catalysts include: alkyl peroxides, such as tert-butyl hydroperoxide, and di-tert-butyl peroxide, acyl and aroyl peroxides, such as dibenzoyl peroxide, perbenzoic acid, dilauroy peroxide, perlauric acid and acetyl benzoyl peroxide; azo compounds such as azo-bisisobutyronitrile, dimethaylazodiisobutyrate, azo-bis-1-phenylethane and alkali metal azodisulfonates; and the like.

Generally, the impaction resistance of most resin blends increases with an increase in the quantity of polyphenylene oxide resin present in the blend. The

polyphenylene oxide resin is therefore generally at least present in the major amount in resin blends. However, an exception to this general rule has been found with combinations of polyphenylene oxide resins with the organosilicon terpolymers described above. As illustrated in the Examples below, optimum synergistic results are obtained when the polyphenylene oxide resin-organosilicon terpolymer resin ratio is from about 90:10 to about 25:75. The extremely high resistance to toner impaction is completely unexpected because the polyphenylene oxide resin organosilicon terpolymer resin blend possesses higher toner impaction resistance than either the polyphenylene oxide resin or the organosilicon terpolymer resin alone. No satisfactory explanation for this surprising result has been found.

When the carrier coatings of this invention contain thermosetting resins blended with a polyphenylene oxide resin, the blending should be effected while the thermosetting resin is in a monomeric or partially polymerized stage. Polymerization of the thermosetting monomer or partially polymerized prepolymer may be completed in situ after the blend is applied to a carrier core. In situ polymerization may be effectuated by any well known technique as by application of heat. If a thermosetting resin prepolymer is employed, the prepolymer should be in a liquid or thermoplastic stage so that uniform blending of the prepolymer as a melt or in a solvent solution will be facilitated.

To achieve further variation in the properties of the final resinous product, well known additives such as plasticizers, reactive resins, dyes, pigments, wetting agents, and mixtures thereof may be mixed with the resin coating of this invention. When an organosilicon polymer is blended with the polyphenylene oxide resin, hydrolysis of the hydrolyzable groups attached to the silicon atoms may be promoted by pre-treating the carrier core with any suitable hydrolyzing medium such as a dilute solution of acetic acid or by mixing the hydrolyzing material with the organosilicon polymer prior to the coating operation.

Any suitable well known coated or uncoated carrier material may be employed as the core of the carriers of this invention. Typical carrier materials include sodium chloride, ammonium chloride, aluminum potassium chloride, Rochelle salt, sodium nitrate, potassium chlorate, granular zircon, granular silicon, methyl methacrylate, glass, silicon dioxide, flintshot, 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. No. 2,618,551; L. E. Walkup et al in U.S. Pat. No. 2,638,416 and E. N. Wise in U.S. Pat. No. 2,618,552. An ultimate coated carrier particle diameter between about 40 microns to about 600 microns is preferred because the carrier particles then possess sufficient density and inertia to avoid adherence to the electrostatic latent images during the cascade development process. Adherence of the carrier beads of an electrostatographic drum is undesirable because of the formation of deep scratches on the drum surface during the image transfer and drum cleaning steps, particularly when cleaning is accomplished by a web cleaner such as the web disclosed by W. P. Graff, Jr., et al in U.S. Pat. No. 3,186,838.

The surprisingly better results obtained from the employment of polymeric carrier coating materials containing polyphenylene oxide resins and blends thereof may be due to many factors. For example, it is postulated that the unusually low water absorption properties of the polyphenylene oxide resins contribute to the stable triboelectric properties thereof. Further, although it is not entirely clear, the high resistance of the carrier coatings to toner impaction may be at least partly due to the high tensile strength and heat resistance exhibited by polyphenylene oxide resins, particularly blends of polyphenylene oxide resins with organosilicon terpolymers. The polyphenylene oxide coatings of this invention adhere well to the carrier cores tested and are also highly resistant to chipping, and flaking.

The polyphenylene oxide resin coating compositions may be applied to a carrier core by any conventional method such as spraying, dipping, fluidized bed coating, brushing, and the like. The polyphenylene oxide resins or blends thereof 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. Typical solvents include the halogenated aliphatics such as chloroform and 1,2-dichloro ethane; aromatic hydrocarbons such as toluene and o-chlorobenzene; and the like. Any suitable coating thickness may be employed. However, the carrier coating should be sufficiently thick to resist flaking and chipping. The quantity of resin to be applied to the carrier cores depends upon the density and the surface area presented by the carrier cores. Typical coating weights include from about 20 to about 1,000 grams of coating material per 100 pounds of flintshot carrier cores haivng an average diameter of about 600 microns.

Any suitable pigmented dyed electroscopic toner material may be employed with the coated carrier of this invention. Typical toner materials include: cumarone-indene resin, asphaltum, phenolformaldehyde resins, rosin-modified phenolformaldehyde resins, methacrylic resins, polystyrene resins, polypropylene resins, epoxy resins, polyethylene resins and the like. Typical toner materials are disclosed by H. E. Copley in U.S. Pat. 2,659,670; R. B. Landrigan in U.S. Pat. No. 2,753,308; M. A. Insalaco in U.S. Pat. No. 3,079,342 and C. F. Carlson in U.S. Pat. No. Re. 25,136.

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.

EXAMPLE I

A control sample containing 1 part colored toner particles having an average particle size of about 10 to about 12 microns and about 99 parts coated carrier particles available in the Xerox 813 Developer sold by the Xerox Corporation, Rochester, New York is cascaded across an electrostatic imagebearing surface. The resulting developed image is transferred by electrostatic means to a sheet of paper whereon it is fused by heat. The residual powder is removed from the electrostatic imaging surface by a cleaning web of the type disclosed by W. P. Graff, Jr., et al in U.S. Pat. No. 3,186,838. After the copying process is repeated 8,000 times, the developer mix is examined for the presence of carrier coating chips and flakes. Numerous carrier chips and flakes are found in the developer mix.

EXAMPLE II

A coating solution containing about 20 grams, by weight, of polyphenylene oxide resin, PPO Grade C-1001 resin sold by the General Electric Company, Pittsfield, Massachusetts, dissolved in about 100 parts chloroform and 175 parts dichloro benzene is sprayed onto glass beads having an average diameter of about 600 microns. About 20 grams of polyphenylene oxide resin is applied to about 5 pounds of glass carrier cores. After drying, the developing procedure of Example I is repeated with the foregoing coated carriers substituted for the Xerox 813 carrier particles. An examination of the developer mix after test termination reveals substantially no carrier coating chips or flakes.

EXAMPLE III

A coating solution about 20 grams, by weight, of a resin blend comprising about 85 percent polyphenylene oxide resin and about 15 percent of an organosilicon terpolymer resin consisting essentially of the addition polymerization reaction product between about 15 parts sytrene, about 85 parts methyl methacrylate and about 5 parts of vinyl triethoxy silane dissolved in toluene is sprayed onto glass beads having an average diameter of about 600 microns. About 10 grams of resin blend is applied to about 5 pounds of glass carrier cores. After drying, the developing procedure of Example I is repeated with the foregoing coated carrier substituted for the Xerox 813 carrier particles, an examination of the developer mix after test termination reveals substantially no carrier coating chips or flakes.

EXAMPLE IV

A control sample containing one part pigmented resin toner particles having an average particle size of about 10 to about 12 microns and about 99 parts coated carrier particles available in the Xerox 813 Developer sold by the Xerox Corporation, Rochester, New York, is tumbled in a rotating cylindrical jar having a diameter of about 2 ½ inches and a surface speed of about 140 feet per minute. Most of the carrier coating separated in the form of flakes from the carrier core after about 100 hours after the test is initiated. The carrier coating remaining on the carrier core is almost completely impacted with toner.

EXAMPLE V

Glass carrier cores having an average diameter of about 600 microns are spray coated with a coating solution comprising about 10 percent, by weight, of polyphenylene oxide resin derived from the oxidative coupling of 2,6dimethylphenol. About 20 grams of the polyphenylene oxide resin is applied to about 5 pounds of glass cores. After drying, the milling procedure of Example IV is repeated with the foregoing coated carrier particles substituted for the Xerox 813 carrier particles. No chips or flakes are found. A slight amount of toner impaction is first observed after a milling time of about 144 hours.

EXAMPLE VI

The milling procedure described in Example V is continued until the cumulative milling time is about 240 hours. Upon termination of the milling, no chips or flakes are found. Examination of the carrier surfaces reveals complete impaction.

EXAMPLE VII

Glass carrier cores having an average diameter of about 600 microns are spray coated with a coating solution comprising about 10 percent, by weight, of a resin blend comprising about 85 percent polyphenylene oxide resin, PPO PR5311 resin sold by the General Electric Co., and about 15 percent of an organosilicon terpolymer resin consisting essentially of the addition polymerization reaction product between about 15 parts styrene, about 85 parts methyl methacrylate and about 5 parts vinyl triethoxy silane. About 20 grams of the resin blend is applied to about 5 pounds of glass cores. After drying, the milling procedure of Example IV is repeated with the foregoing coated carrier particles substituted for the Xerox 813 carrier particles. A slight amount of toner impaction is first observed after a milling time of about 144 hours. No chips or flakes are found.

EXAMPLE VIII

The milling procedure described in Example VII is continued until the cumulative milling time is about 240 hours. Upon termination of the milling, no chips or flakes are found. Examination of the carrier surfaces reveals almost complete toner impaction.

EXAMPLE IX

Glass carrier cores having an average diameter of about 600 microns are spray coated with a coating solution comprising about 10 percent, by weight, of a resin blend comprising about 75 percent polyphenylene oxide resin and about 25 percent of an organosilicon terpolymer resin consisting essentially of the addition polymerization reaction product between about 50 parts styrene, about 85 parts methyl methacrylate and about 5 parts vinyl triethoxy silane. About 20 grams of the resin blend is applied to about 5 pounds of glass cores. After drying, the milling procedure of Example IV is repeated with the foregoing coated carrier particles substituted for the Xerox 813 carrier particles. A slight amount of toner impaction is first observed after a milling time of about 192 hours. No chips or flakes are found.

EXAMPLE X

The milling procedure described in Example IX is continued until the cumulative milling time is about 240 hours. Upon termination of the milling, no chips or flakes are found. Examination of the carrier surfaces reveals only slight toner impaction.

EXAMPLE XI

Glass carrier cores having an average diameter of about 600 microns are spray coated with a coating solution comprising 10 percent, by weight, of a resin blend comprising about 50 percent polyphenylene oxide resin and about 50 percent of an organosilicon terpolymer resin consisting essentially of the addition polymerization reaction product between about 15 parts styrene, about 85 parts methyl metacrylate and about 5 parts vinyl triethoxy silane. About 20 grams of the resin blend is applied to about 5 pounds of glass cores. After drying, the milling procedure of Example IV is repeated with the foregoing coated carrier particles substituted for the Xerox 813 carrier particles. A slight amount of toner impaction is first observed after

a milling time of about 96 hours. No chips or flakes are found.

EXAMPLE XII

The milling procedure described in Example XI is continued until the cumulative milling time is about 192 hours. Upon termination of the milling, no chips or flakes are found. Examination of the carrier surfaces reveals almost complete toner impaction.

EXAMPLE XIII

Glass carrier cores having an average diameter of about 600 microns are spray coated with a coating solution comprising about 10 percent, by weight, of an organosilicon terpolymer resin consisting essentially of the addition polymerization reaction product between about 15 parts styrene, about 85 parts methyl methacrylate and about 5 parts vinyl triethoxy silane. About 20 grams of the resin is applied to about 5 pounds of glass cores. After drying, the milling procedure of Example IV is repeated with the foregoing coated carrier particles substituted for the Xerox 813 carrier particles. A slight amount of toner impaction is first observed after a milling time of about 96 hours. No chips or flakes are found.

EXAMPLE XIV

The milling procedure described in Example XIII is continued until the cumulative milling time is about 192 hours. Upon termination of the milling, no chips or flakes are found. Examination of the carrier surfaces reveals complete toner impaction.

EXAMPLE XV

Steel carrier cores having an average diameter of about 250 microns are spray coated with a coating solution comprising about 15 percent, by weight, of a resin blend comprising about 90 percent polyphenylene oxide resin NORYL resin sold by the General Electric Company, and about 10 percent of an organosilicon terpolymer resin consisting essentially of the addition polymerization reaction product between about 50 parts styrene, about 50 parts isobutyl methacrylate and about 5 parts gammamethacryloxypropyltrimethoxy silane. About 20 grams of the resin blend is applied to about 15 pounds of steel cores. After drying, the milling procedure of Example IV is repeated with the foregoing coated carrier particles substituted for the Xerox 813 carrier particles. A slight amount of toner impaction is first observed after a milling time of about 144 hours. No chips or flakes are found.

EXAMPLE XVI

Flintshot carrier cores having an average diameter of about 600 microns are spray coated with a coating solution comprising about 20 percent, by weight, of a resin blend comprising about 90 percent polyphenylene oxide resin and about 10 percent of polycarbonate resin. About 35 grams of the resin blend is applied to about 5 pounds of flintshot cores. After drying, the milling procedure of Example IV is repeated with the foregoing carrier particles substituted for the Xerox 813 carrier particles. A slight amount of toner impaction is first observed after a milling time of about 240 hours. No chips or flakes are found.

EXAMPLE XVII

Iron carrier cores having an average diameter of about 500 microns are spray coated with a coating solution comprising about 10 percent, by weight, of a resin blend comprising about 75 percent polyphenylene oxide resin and about 25 percent of ethylene-vinylacetate copolymer resin. About 20 grams of the resin blend is applied to about 10 pounds of iron cores. After drying, the milling procedure of Example IV is repeated with the foregoing coated carrier particles substituted for the Xerox 813 carrier particles. A slight amount of toner impaction is first observed after a milling time of about 144 hours. No chips or flakes are found.

Although specific materials and conditions were set forth in the above exemplary processes in making and using the developer 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 for those 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 particles, said carrier particles comprising particulate cores surrounded by a thin outer layer, said thin outer layer comprising from about 1 to about 20 microns in thickness of a blend of a polyphenylene oxide resin and a solid terpolymer of (1) from about 5 to about 94.5%, by weight of an unsaturated silicon free organic compound, (2) from about 94.5 to about 5% by weight of an unsaturated silicon free organic compound different from the compound of (1) and (3) from about 0.5 to about 50%, by weight of a polymerizable organosilicon compound selected from the group consisting of silanes, silanols and siloxanes having from one to three hydrolyzable groups and an organic group attached directly to a silicon atom containing less than 8 carbon atoms and an unsaturated carbon to carbon linkage, the weight ratio of said polyphenylene oxide to said terpolymer being from about 90:10 to about 25:75.

2. An electrostatographic developer mixture comprising finely divided toner particles electrostatically clinging to the surface of carrier particles, said carrier particles comprising particulate cores surrounded by a thin outer layer, said thin outer layer comprising from about 1 to about 20 microns in thickness of a blend of a polyphenylene oxide resin and a solid terpolymer of (1) from about 5 to about 94.5%, by weight, of a styrene composition, (2) from about 94.5 to about 5%, by weight, of a composition selected from the group consisting of acrylate and methacrylate esters and (3) from about 0.5 to about 50%, by weight, of a polymerizable organosilicon composition selected from the group consisting of organosilanes, silanols and siloxanes having from one to three hydrolyzable groups and an organic group attached directly to a silicon atom containing less than eight carbon atoms and an unsaturated carbon to carbon linkage, the weight ratio of said poly-

phenylene oxide to said terpolymer being from about 90:10 to about 25:75.

3. An electrostatographic developer mixture comprising finely divided toner particles electrostatically clinging to the surface of carrier particles, said carrier particles comprising particulate cores surrounded by a thin outer layer, said thin outer layer comprising from about 1 to about 20 microns in thickness of a blend of a solid polyphenylene oxide resin and a solid linear addition terpolymer of (1) from about 5 to about 94.5%, by weight, of a styrene composition, (2) from about 94.5 to about 5%, by weight, of a methacrylate composition selected from the group consisting of methyl, ethyl, propyl and butyl methacrylate and (3) from about 0.5 to about 50%, by weight, of a polymerizable organosilicon composition selected from the group consisting of silanes, silanols and siloxanes having from one to three hydrolyzable groups and an organic group attached directly to a silicon atom containing less than six carbon atoms and an unsaturated carbon to carbon linkage, the weight ratio of said polyphenylene oxide to said terpolymer being from about 90:10 to about 25:75, said carrier particles having a diameter of from about 40 to about 600 microns.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,857,792 Dated December 31, 1974

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

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

Cover page, first column, after "[76] Inventors: Robert W. Madrid, 160 Jacobs Rd., Macedon; Robert J. Hagenbach, 235 Westmoreland Dr., Rochester, both of N.Y.", insert -- Assignee: Xerox Corporation, Rochester, N.Y.--

Signed and sealed this 18th day of March 1975.

(SEAL)
Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents
and Trademarks

FORM PO-1050 (10-69)

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