

[54] CARRIER COMPOSITIONS

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Related U.S. Application Data

[63] Continuation of Ser. No. 814,437, April 8, 1969, abandoned.

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2,618,551 11/1952 Walkup..... 252/62.1

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[57]

ABSTRACT

A carrier for electrostatographic developer mixtures is provided comprising a core surrounded by a pre-coated partially cured thin film of a silicone, over-coated with an unsaturated polyester, said silicone chemically coupling said polyester to said core upon curing.

6 Claims, No Drawings

CARRIER COMPOSITIONS

This is a continuation of application Ser. No. 814,437, now abandoned, filed in the United States on Apr. 8, 1969.

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 fixing means such as solvent or overcoating treatment may be substituted for the foregoing heat fixing step.

Many methods are known for applying the electroscopic particles to the latent electrostatic image to be developed. One development method, as disclosed by E. N. Wise in U.S. Pat. No. 2,618,552 is known as "cascade" development. In this method, a 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 carrier particles. As the mixture cascades or rolls across the image-bearing surface, the toner particles are electrostatically deposited and secured to the charged portion of the latent image and are not deposited on the uncharged or background portions of the image. Most of the 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. No. 3,099,943.

Another technique for developing electrostatic images is the "magnetic brush" process as disclosed, for example, in U.S. Pat. Nos. 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.

Carrier Material Criteria

The criteria for selection of suitable carrier materials are extremely rigid in that these materials must exhibit a unique balance of electrostatic properties. The carrier must be capable of inducing a triboelectric charge on the toner particles opposite in polarity to that of the image being developed in order to effect deposition of the toner particles on the latent image. However, the carrier must also exhibit sufficient electrostatic attraction for the toner particles to enable the carrier to be an effective scavenger for toner particles deposited on the discharged background of the photoconductive insulating layer.

A property common to all carrier developers is a threshold force which the image developing forces must exceed in order to effect deposition. The retention force of the carrier is probably a combination of coulomb attraction between the toner and carrier, along with short-range "contact" forces. These retention forces account for the high contrast characteristic of all carrier developers as is desirable for line copy reproduction. It contributes to relatively clean, dust-free background or non-image areas, yet permits dense image development.

Residual charge is almost invariably present in the nominally discharged or background areas of the latent image. Relatively low as this charge density is, it may nevertheless be non-uniform, and such irregularities will be a source of small fields capable of trapping toner particles. This electrostatic "noise" in the background areas of the latent image is one of the primary sources of unwanted background toner.

As toner is removed from carrier by the development fields, the carrier becomes more capable of accepting loosely held toner, especially that not held by fields associated with the latent image. Removal of toner from the carrier leaves upon it an opposite, unbalanced charge that is not immediately neutralized. Thus developer is intrinsically its own scavenging agent.

Thus it is of critical importance in obtaining a suitable carrier material that it be capable of imparting charge to the toner particles through triboelectricity and yet exhibit sufficient electrostatic charge relative to the discharged portions of the photoconductor to attract stray toner particles thereby maintaining a clean background without interfering with the attraction of the toner particles by the latent image. Thus, the triboelectric relationship of the toner and carrier must be such that an acceptable development of the xerographic image is produced, i.e., a dense image with low background. An excessively high triboelectric relationship produces low density image with clean background because of the inability of the electrostatic image to attract sufficient toner particles from the carrier. A low triboelectric relationship produces a so-called "dusty" developer which will develop very low contrast electrostatic patterns but will also produce high background densities. In order to obtain a practical developer, these extremes must be avoided. In use, the average triboelectric relationship for the developer decreases with time because of cumulative physical damage to the carrier. Therefore, the ideal carrier is a

material exhibiting the proper triboelectric relationship with the toner and is resistant to physical damage and impaction which impairs this critical relationship.

While ordinarily capable of producing good quality images, conventional developing materials suffer serious deficiencies in certain areas. The developing materials must flow freely to facilitate accurate metering and even distribution during the development and developer recycling phases of the electrostatographic process. Some developer materials, though possessing desirable properties such as proper triboelectric characteristics, are unsuitable because they tend to cake, bridge and agglomerate during handling and storage. Adherence of carrier particles to reusable electrostatographic imaging surfaces causes the formation of undesirable scratches on the surfaces during image transfer and surface cleaning steps. The tendency of carrier particles to adhere to imaging surfaces is aggravated when the carrier surfaces are rough and irregular. The coatings of most carrier particles deteriorate rapidly when employed in continuous processes which require the recycling of carrier particles by bucket conveyors partially submerged in the developer supply such as disclosed in U.S. Pat. No. 3,099,943. Deterioration occurs when portions of or the entire coating separates from the carrier core. The separation may be in the form of chips, flakes or entire layers and is primarily caused by fragile, poorly adhering 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 having damaged coatings are not replaced. Fines and grit formed from carrier disintegration tend to drift and form unwanted deposits on critical machine parts and this coating has a positive charge which adds to the background on the selenium plate. Many carrier coatings 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 affected 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 and predictable triboelectric values. Another factor affecting the stability of carrier triboelectric properties is the susceptibility of carrier coatings to "toner impaction." When 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 the carrier coatings. The gradual accumulation of permanently attached toner material on 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. 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 developing materials which flow freely.

It is a further 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 which are more resistant to chipping, flaking and the like.

It is yet another object of this invention to provide carrier coatings having stable triboelectric values.

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

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

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

SUMMARY OF THE INVENTION

These, as well as other objects, are accomplished by the present invention which provides a carrier for electrostatographic developer mixtures comprising a core surrounded by a first layer comprising a hydrolyzed ambifunctional organo silane, silanol or siloxane and a second over-layer comprising an unsaturated polyester resin, said first layer chemically coupling said second layer to said core upon curing.

In general, the carriers of the present invention are prepared by pre-coating carrier cores with a first layer comprising an ambifunctional silicone-forming material such as organo silanes, silanols or siloxanes having from 1 to 3 hydrolyzable groups, hydrolyzing said material and at least partially curing the ambifunctional silicone thus formed to bond said first layer to said core. Thereafter, said pre-coated core is overcoated with an unsaturated monomeric ester or polyester prepolymer and the composite, multicoated core is finally cured to chemically couple the resulting polyester to the core.

DESCRIPTION OF THE INVENTION

Core Materials

Any suitable well known coated or uncoated carrier material can 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 50 microns to about 600 microns is preferred because the carrier particles then possesses sufficient density and inertia to avoid adherence to the electrostatic images during the cascade development process. Adherence of carrier beads to 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 where 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.

Pre-Coating Layer

The pre-coating layer surrounding the carrier core comprises an ambifunctional silicon compound. The ambifunctional silicon compounds useful in the present invention are those organo silanes, silanols and siloxanes containing from 1 to 3 hydrolyzable groups attached to a silicon atom and at least one functional organic group attached to a silicon atom. Functional sites in the organic groups attached to the silicon atom enable reaction to occur which are typically organic in nature. Molecules having such functional groups are generally referred to as organo-functional silicon compounds, denoting that their chemical reactions occur in the organic portion of the molecule. Compounds with both silicon-functional and organo-functional groups are generally referred to as ambifunctional silicon compounds and are the type of silicon compounds employed herein.

Typical hydrolyzable groups included in such silicon compounds are, for example, alkoxy groups such as methoxy, ethoxy, propyloxy and the like, halo groups such as chloro, bromo and the like, acetoxy, hydroxy and amino groups. Functional organic groups included in such compounds are the radical residue of such compounds as amines, glycidyl ethers, acrylates, methacrylates, vinyls and unsaturated aliphatics containing from 2 to about 8 carbon atoms such as butenyl, propenyl, hexenyl radicals and the like. If more than one organic group is attached to a silicon atom, only one of the organic groups need be functional. Hence, compounds such as dimethyl vinyl chlorosilane are suitable. When more than one functional group attached to the silicon atom is present, these groups need not be identical. For example, vinyl allyl silicon chlorides and bromides can be employed.

Exemplary of such ambifunctional silicon compounds are n-(trimethoxysilylpropyl)ethylene diamine, n-(dimethoxymethylsilylisobutyl) ethylene diamine, gamma-methacryloxypropyl trimethoxysilane, gamma-glycidyloxypropyltrimethoxysilane, vinyltrichlorosilane, vinyl triethoxy silane, vinyl trimethoxy silane, vinyltris(beta-methoxy-ethoxy)silane, divinyl dichlorosilane, dimethyl vinylchloro silane and the like. Also, the hydroxy silanes (silanols) such as trimethyl silanol, dimethyl silanediol, diphenyl silanediol and the like are useful.

Hydrolysis and/or condensation of the hydrolyzable groups attached to the silicon atoms gives rise to the formation of siloxane polymers generally called silicones. The corresponding partially condensed siloxanes can be readily employed in lieu of silanes or silanols. Hydrolysis can be promoted by pretreating the carrier core with any suitable hydrolyzing medium such as water, a dilute solution of acetic acid, sodium hydroxide, ammonium hydroxide, triethylamine, dioxane or a dialkyl ether, or simply by mixing the hydrolyzing medium with the silicon polymer prior to the coating operation. The silanols are easily condensed to the corresponding siloxanes by application of heat. Still further, two or more silicon compounds as hereinabove defined can be co-hydrolyzed. In such cases, siloxanes are formed representing each monomer separately and usually products containing two or more kinds of monomer units are also formed.

The resulting liquid hydrolyzates and/or condensates hereinafter collectively referred to as "hydrolyzates" can be readily applied to the carrier cores in any convenient manner such as by mixing, dipping, spraying or other similar means of application. Any suitable coating thickness can be employed. However, a coating having a thickness at least sufficient to form a continuous film is preferred because the carrier coating will then possess a uniform distribution of potential cross-linking sites with both the core and the over-coating. In addition, a coating of sufficient thickness is necessary to resist abrasion and prevent pinholes which adversely affect the triboelectric properties of the coated carrier particles.

Once applied, the hydrolyzates are at least partially cured to affect bonding between the carrier core and the precoated silicone layer. Curing is conducted by heating the mixture of carrier cores and hydrolyzates at temperatures ranging from about 100°C. to about 110°C.

Although not considered critical, peroxide-type catalysts as hereinafter further described as well as organic salts of certain reactive metals such as cobalt, lead, zinc and iron as, for example, zinc naphthenate, iron octoate, cobalt naphthenate and the like have been found useful in hastening the cure.

Over-Coating Layer

Over-coating of the pre-coated core materials is accomplished with monomer or prepolymer solutions which upon curing give rise to cross-linked unsaturated polyesters. The unsaturated polyesters useful as over-coating materials in the present invention are preferably those unsaturated polyesters derived from the allyl esters of unsaturated organic acids or anhydrides or the prepolymers thereof. Most preferably, however, the unsaturated polyesters are derived from the allyl esters of unsaturated cyclic organic acids and anhydrides. Illustrative of such materials are diallyl maleate, diallyl fumarate, diethylene glycol bis(allyl carbonate), diallyl benzene phosphonate. Preferably, however, materials such as diallyl phthalate, diallyl isophthalate and diallyl chlorendate are employed since they are solids and there is no chance of unreacted liquid monomer which may be accidentally present, contaminating and destroying the xerographic properties of the selenium plate. These latter materials can be readily prepared by esterification of phthalic or isophthalic anhydride or chlorendic anhydride with allyl alcohol. Chlorendic anhydride is the diels-alder adduct, 1, 4, 5, 6, 7, 7-hexachlorobicyclo-(2.2.1)-5-heptene-2,3-dicarboxylic anhydride prepared from hexachlorocyclopentadiene and maleic anhydride. Similar useful adducts can be prepared by reaction of hexachlorocyclopentadiene with such dienophiles as maleic acid, citraconic anhydride, chloro maleic anhydride, itaconic anhydride and the like.

While most of the allyl esters hereinabove described are useful primarily as positive carrier coatings, diallyl chlorendate and the other diels-alder adducts of hexachlorocyclopentadiene are especially useful as reversal carrier coatings because of their relative electronegativity.

These compounds can be polymerized alone under mild conditions using only one of the allyl groups to form linear polyesters which can undergo further polymerization to yield thermosetting, highly cross-linked compounds. It is, therefore, unnecessary to add any

other polymerizing monomer such as a glycol although additional monomers can be added if desired.

The allyl esters and prepolymers of the present invention undergo thermal polymerization in the presence of a free radical initiator. Since the materials easily undergo a vinyl type polymerization, free radical initiators, such as peroxides and azo compounds, can be employed. The action of the initiator can be modified by use of activators and promoters. Peroxide type initiators which will initiate polymerization at relatively low temperatures (30° to 60°C.) are those such as acetyl benzoyl peroxide, peracetic acid, methyl ethyl ketone peroxide, cumene hydroperoxide and the like. For polymerization at intermediate temperatures (60°-100°C.), peroxides such as tert.-butyl hydroperoxide, methyl amyl ketone peroxide, tert.-butyl perbenzoate and the like can be employed. At still higher temperatures (above 100°C.), peroxides such as p-chlorobenzoyl peroxide, ditert.-butyl peroxide, dibenzal diperoxide are suitably employed. Azo compounds such as azo-bisisobutyronitrile, dimethylazodiisobutyrate, azobis-1-phenylethane, alkali metal azodisulfonates and the like have been found useful. Catalytic activity is obtained when these free radical initiators are employed in an amount from about 0.0001 to about 5.0 percent based on the combined weight of the polymerizable ingredients.

It has been found in the present invention that better cross-linking between the silicon compounds used as a pre-coat and the unsaturated polyester over-coat can be promoted by selecting a peroxide initiator which is an active polymerization catalyst for both materials at the curing temperatures employed. Mixtures of peroxides can be employed if desired. For example, benzoyl peroxide is not a particularly effective catalyst for polymerization of vinyltriethoxy silane, as low conversion to polymer is obtained. Di-tert.-butyl peroxide is, however, a good catalyst for vinyl triethoxysilane at higher temperatures and can be employed by itself or in combination with another peroxide such as tert.-butyl perbenzoate which is especially active in allyl ester polymerization. A well established crosslinked network between the silicone and polyester coatings can thus be obtained during curing.

The rate of cure can be increased if desired through use of an activator. Cobalt, in the form of its ethyl hexanoate or naphthenate salt, is a good general purpose activator for use with ketone peroxides. Activators cause rapid curing at room temperature and tend to reduce surface tackiness. Concentrations as low as about 30 ppm of cobalt have been found effective.

A promoter can also be added to the curing system if desired to reduce the time usually required for gelling the resin. Pre-gelled structures have sufficient rigidity to be handled, and thus can be transferred to ovens to obtain final cure. Promoters used with acyl peroxides include tertiary dialkyl aryl amines such as diethyl aniline and aliphatic thiols as, for example, lauryl mercaptan. Concentrations in the range of about 0.05 to about 0.5 percent by weight of promoter have been found suitable.

In addition, inhibitors or antioxidants can be added to the polyester to improve environmental stability. Inhibitors found useful for this purpose are for example 5-butyl catechol, 2,6-di-tert.-butyl-p-cresol, hydroquinone, p-benzoquinone and similar sterically hindered phenols.

The polyester overcoating can be applied to the pre-coated carrier cores either as a monomeric solution or a prepolymer solution together with initiator, activator, promoter and/or inhibitor. The over-coating solution can be applied by mixing, dipping, spraying and other similar liquid application methods. The coating solution is generally applied hot, i.e., at about 100°C. to about 130°C. to promote rapid curing. Upon application of a continuous thin film of solution to the pre-coated core particles, the temperature is dropped below the softening point of the polyester and the curing is continued until integrally coated core particles having sufficient rigidity to be easily handled are obtained. Thereupon, the coated core particles are finally cured, generally in a vacuum oven at temperatures below the softening point of the polyester.

Any suitable coating thickness can be employed. A coating having a thickness at least sufficient to form a continuous film is preferred because the composite carrier coating will then possess sufficient thickness to resist abrasion and prevent pinholes which adversely affect the triboelectric properties of the coated carrier particles.

To achieve further variation in the properties of the final resinous product, well known additives such as plasticizers, reactive or non-reactive resins, dyes, pigments, wetting agents and mixtures thereof can be admixed with the overcoating solution.

Toner Particles

The electrostatographic developer mixtures of the present invention comprise finely-divided toner particles electrostatically clinging to the surface of carrier particles prepared in the manner hereinabove described. Generally, toner particles consist of a carbon black dispersed in a resin; however, other pigments of dyes can also be employed, including fluorescent materials. Toner can be given special adhesive (or in some cases, non-adhesive) properties to control transfer of still other material in an image pattern; it can also be made inert to acids or solvents in order to serve as a resist for selective etching applications. Toner particles, however, must be of sufficient electric charge so that forces exerted by the electrostatic image fields are sufficient to capture the particles from the developer mass.

Employing the pre-coating and over-coating materials and procedures described herein, a carrier is obtained which is composed of a tough, internally cross-linked over-coating chemically coupled through the pre-coat to the carrier core. These carriers have been found extremely durable and resistant to impaction. The surprisingly better results obtained from the employment of the multi-layer carrier materials of the present invention may be attributable to many factors. For example, the marked durability of the carrier may be due to the fact that the ambifunctional organo silicon pre-coating adheres extremely well to the carrier cores tested and forms an extensive cross-link network with the polyester over-coating forming, in essence, an integral structure tenaciously bound to the carrier. Outstanding adhesion is obtained when the organo silicon pre-coating of this invention is applied to glass or similar siliceous particles. The unsaturated polyester over-coatings of this invention exhibits a smooth, hard outer surface which is highly resistant to chipping and flaking. The smooth tough surface enhances the rolling action of the carrier particles across the electrostatographic

graphic surfaces and produces the tendency of the carrier particles to adhere to the surfaces. Employment of the present carrier coatings unexpectedly extends carrier life, particularly in respect to toner impaction resistance. Additionally, the hydrophobic properties of the resins of this invention especially those derived from diallyl chlorendate appear to contribute in some unknown manner to the stability of the triboelectric properties of the coated carrier over a wide relative humidity range.

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 1

Control Sample: Conventional Developer

A control sample containing one part colored toner particles having an average particle size of about 10 to about 20 microns and 99 parts coated carrier particles available in the Xerox 813 Developer sold by the Xerox Corporation, Rochester, New York is cascaded across an electrostatic image-bearing surface. The resultant 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 2

A coating solution (100 grams) having 2.22 grams of the hydrolysis product of gamma-methacryloxypropyltrimethoxy silane (Dow Corning Z-6030), prepared by mixing 1 g. of acetic acid (glacial)/100 g. H₂O (distilled) with 10 g. of methacryloxypropyltrimethoxysilane until both layers were completely miscible and diluting 22.2 grams of the product to 100 gms. with distilled water, was admixed with 15 lbs. of 600 micron glass carrier cores until said glass cores were uniformly coated. The resulting mixture was heated at 110°C. for about 30 minutes to partially cure said silane and affect a strong bond between said silane and the free hydroxyl groups on the surface of said glass cores.

Thereafter, 200 grams of an overcoating solution having the following composition was admixed with the precoated glass cores at about 110°C.

- 17.2 parts diallyl phthalate polyester prepolymer (Dapon 35 manufactured by FMC Corporation)
- 1.6 parts DuPont Oil Red Dye
- 180.0 parts 1,4-dioxane (solvent)
- 1.2 parts benzoyl peroxide
- 0.06 parts cobalt naphthenate

Mixing was continued until a uniform overcoating had been applied to the glass cores. The temperature was then dropped below the softening point of the prepolymer and held at such temperature (76°C.) for about one-half hour. The coated cores were then sufficiently rigid to be easily handled and were thereupon transferred to a vacuum oven and post heated for 70 hours at 30 mm. Hg and at a temperature about 5°C. below the initial softening point of the prepolymer..

The developing procedure of Example 1 is repeated with the foregoing coated carrier substituted for the Xerox 813 carrier. The copying process, however, is repeated 21,000 times rather than 8,000 times. An examination of the developer mix after test termination reveals substantially no carrier coating chips or flakes.

EXAMPLE 3

A coating solution of 1000 grams of the hydrolysis product of vinyltriacetoxysilane (Dow Corning Z-6075) was admixed with 50 lbs. of 600 micron glass carrier cores employing essentially the same procedure described in Example 2.

Thereafter, 2000 grams of an overcoating solution having the following composition was admixed with the pre-coated glass cores at about 130°C.

- 100 parts diallyl isophthalate (Dapon M manufactured by FMC Corporation)
- 1659.5 parts methyl isobutyl ketone
- 6 parts n-butyl acetate
- 0.25 parts t-butyl perbenzoate
- 0.25 parts di-tert.-butyl peroxide

Essentially the same overcoating and curing procedure described in Example 2 was employed except that curing was at 48°C. for one-half hour due to the lower softening point of Dapon M. The developing procedure of Example 1 is repeated with the foregoing coated carrier substituted for the Xerox 813 carrier. The copy process, however, is repeated 21,000 times rather than 8,000 times. An examination of the developer mix after test termination reveals substantially no carrier coating chips or flakes.

EXAMPLE 4

A coating solution (27.5 grams) having 2.75 g. of the hydrolysis product of vinyl silane (A-172 Union Carbide) was prepared by mixing 1 g. of acetic acid (glacial)/100 g. H₂O (distilled) with 10 g. of vinyl silane (A-172 Union Carbide) until both layers were completely miscible and diluting 27.5 gms. of above to 100 gms. with distilled water, was admixed with 9 lbs. of 450 micron glass carrier cores until said cores were uniformly coated. The resulting mixture was heated at 110°C. for about 30 minutes to partially cure said silane and affect a strong bond between said silane and said glass cores.

Thereafter, 200 grams of an overcoating solution having the following composition was admixed with the precoated glass cores at about 120°C.

- 17.2 parts diallyl chlorendate
- 1.6 parts DuPont Oil Red Dye
- 180.0 parts 1,4-dioxane
- 1.2 parts benzoyl peroxide
- 0.03 parts 2,5-dimethylhexyl-2,5-di(peroxybenzoate)
- 0.03 parts 2,6-di-tert.-butyl-p-cresol

Essentially the same overcoating and curing procedure described in Example 2 was employed to obtain about 20 grams of combined coating materials (pre-coat and overcoat) applied to about 2500 grams of glass cores. Carrier cores coated as above were designated carrier A.

Two other coating solutions, B and C, containing 10 percent by weight of polymeric material dissolved in appropriate solvents were prepared. Solution B contains a polycarbonate resin ("Lexan" sold by the Gen-

eral Electric Corporation) dissolved in ethylene dichloride. Solution C contains a copolymer of 87 percent vinylchloride and 13 percent vinylacetate dissolved in a mixture of methyl ethyl ketone and toluene. The coating solutions are sprayed onto two different batches of 450 micron glass carrier cores and the resulting coated cores heated to drive off the solvent. About 20 grams of polymeric material is applied to about 2500 grams of glass cores. About 99 parts of each carrier sample, A, B and C is mixed with 1 part colored styrene copolymer toner particles having an average particle size of about 10 to 20 microns and cascaded across an electrostatic image-bearing surface. The developed image is then electrostatically transferred to a receiving sheet. The development and transfer steps are repeated at different relative humidities in 10 percent increments from 20 percent to 80 percent. The resolution in lines per millimeter of each of the transferred images is plotted on a graph against the corresponding percent relative humidity. The change in resolution between 20 and 80 percent relative humidity for samples B and C is more than 4 times greater than the change in resolution for sample A.

EXAMPLE 5

Control Sample: Conventional Developer

A control sample containing one part pigmented toner particles having an average particle size of about 10 to about 20 microns and 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 an inside diameter of about 2.25 and a surface speed of 140 feet per minute. Toner impaction along with coating chips and flakes are observed within about 50 hours after the test is initiated.

EXAMPLE 6

Coated carrier cores prepared as described in Example 2 were subjected to the impaction testing procedure of Example 5 substituting said cores for the Xerox 813 carrier. Toner impaction is discovered after about 100 hours after the test was initiated. No chips or flakes are found.

EXAMPLE 7

Coated carrier cores were prepared as described in Example 3 using 250 micron steel carrier cores in lieu of the glass beads. The coated steel cores were subjected to the impaction testing procedure of Example 5 substituting said carrier for the Xerox 813 carrier. Toner impaction is discovered after about 100 hours after the test was initiated. No chips or flakes are found.

EXAMPLE 8

Coated carrier cores were prepared as described in Example 4 with respect to the preparation of Sample A. The coated glass cores were subjected to the impaction test procedure of Example 5 substituting said carrier cores for the Xerox 813 carrier. Toner impaction is observed within about 150 hours after the test was initiated. No chips or flakes are found.

Although specific materials and conditions were set forth in the above exemplary processes in making an using the developer material of this invention, these are merely intended as illustrations of the present inven-

tion. Various other toners, carrier cores, substituents and processes such as those listed above may be substituted for those in 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.

We claim:

1. In an electrostatographic developer mixture comprising finely-divided toner particles electrostatically clinging to the surface of free-flowing carrier particles, said carrier particles comprising a core having a diameter between about 50 microns to about 600 microns wherein the improvement comprises coating said core with a first substantially continuous uniform layer comprising an at least partially cured hydrolyzed ambifunctional silane, silanol or siloxane, and a second substantially continuous uniform over-layer comprising an unsaturated polyester resin, said over-layer being capable of triboelectrifying the toner particles, said core material being capable of reacting with the first layer and of forming a bond therewith, and said first layer chemically coupling said second layer to said core upon curing.
2. An electrostatographic developer mixture as defined in claim 1 wherein said first layer comprises the at least partially cured hydrolyzed product of an ambifunctional organosilane, silanol, or siloxane containing from 1 to 3 hydrolyzable groups attached to the silicon atom and at least one functional organic group attached to said silicon atom.
3. An electrostatographic developer mixture as defined in claim 1 wherein said unsaturated polyester resin is derived from the allyl esters of unsaturated organic acids or anhydrides.
4. In 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 latent image with an electrostatographic developer mixture comprising finely-divided toner particles electrostatically clinging to the surface of free-flowing carrier particles, said carrier particles comprising a core having a diameter between about 50 microns to about 600 microns wherein the improvement comprises coating said core with a first substantially continuous uniform layer comprising an at least partially cured hydrolyzed ambifunctional silane, silanol or siloxane, and a second substantially continuous uniform over-layer comprising an unsaturated polyester resin, said over-layer being capable of triboelectrifying the toner particles, said core material being capable of reacting with the first layer and of forming a bond therewith, and said first layer chemically coupling said second layer to said core upon curing, 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 as defined in claim 4 wherein said first layer comprises the at least partially cured hydrolyzed product of an ambifunctional organosilane, silanol, or siloxane containing from 1 to 3 hydrolyzable groups attached to the silicon atom and at least one functional organic group attached to said silicon atom.
6. An electrostatographic imaging process as defined in claim 4 wherein said unsaturated polyester resin is derived from the allyl esters of unsaturated organic acids or anhydrides.

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