

[54] **AN ELECTROSTATIC DEVELOPER
CONTAINING MODIFIED SILICON
DIOXIDE PARTICLES**
[75] Inventors: **Arun K. Chatterji; Marianne
Custozzo; Demosthenes K. Kiria-
zides**, all of Webster, N.Y.; **John J.
Russell, Jr.**, Tyrone, Pa.; **John P.
Serio**, Webster, N.Y.
[73] Assignee: **Xerox Corporation**, Stamford,
Conn.
[22] Filed: **May 20, 1970**
[21] Appl. No.: **39,856**

[52] U.S. Cl. **252/62.1, 117/17.5**
[51] Int. Cl. **G03g 9/02**
[58] Field of Search **252/62.1; 260/448.2**

[56] **References Cited**
UNITED STATES PATENTS

3,417,120	12/1968	Baissieras et al.	260/448.2
3,372,102	3/1968	Lennon	204/180
3,271,360	9/1966	Williams	260/448.2
3,246,629	4/1966	Shelffort et al.	252/62.1
3,041,169	6/1962	Wielichi et al.	252/62.1
2,381,366	8/1945	Patnode	260/448.2

FOREIGN PATENTS OR APPLICATIONS

275,616	4/1964	Australia	252/62.1
273,995	12/1962	Australia	252/62.1
914,703	1/1963	Great Britain	252/62.1
1,004,403	9/1965	Great Britain	252/62.1

OTHER PUBLICATIONS

Schaffert, Electrophotograph 1965 pp. 37 and 38.
Primary Examiner—George F. Lesmes
Assistant Examiner—J. P. Brammer
Attorney—James J. Ralabate, Albert A. Mahassel and
Peter H. Kondo

[57] **ABSTRACT**

A developer material comprising colored toner particles having a particle size less than about 30 microns and a minor proportion of submicroscopic silicon dioxide additive particles having at least a portion of the silicon atoms on the outside surface of the silicon dioxide particles directly attached through an oxygen atom to another silicon atom which is in turn directly attached through a carbon linkage to one to three organic groups.

7 Claims, No Drawings

AN ELECTROSTATIC DEVELOPER CONTAINING MODIFIED SILICON DIOXIDE PARTICLES

BACKGROUND OF THE INVENTION

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

The formation and development of images on the surface of photoconductor 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 electrostatic latent 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 electrostatic latent image. This powder image may then be transferred to a support surface such as paper. The transferred image may be 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 steps.

Several methods are known for applying the electroscopic particles to the electrostatic latent 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 coated thereon is conveyed to and rolled or cascaded across the electrostatic latent image bearing surface. The composition of the carrier particles is so selected 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 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 and excess toner are then recycled. This technique is extremely good for the development of line copy images.

Another method of 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 are carried by a magnetic. The magnetic field of the magnet causes alignment of the magnetic carrier into a brush-like configuration. This "magnetic brush" is engaged with the electrostatic image-bearing surface and the toner particles are drawn from the brush to the latent image by electrostatic attraction.

Still another technique for developing electrostatic latent images is the "powder cloud" process as disclosed, for example, by C. F. Carlson in U.S. Pat. No. 2,221,776. In this method, a developer material comprising electrically charged toner particles in a gaseous fluid is passed adjacent the surface bearing the electrostatic latent image. The toner particles are drawn by electrostatic attraction from the gas to the latent image. This process is particularly useful in continuous tone development.

Other development methods such as "touchdown" development as disclosed by R. W. Gundlach in U.S. Pat. No. 3,166,432 may be used where suitable.

Although some of the foregoing development techniques are employed commercially today, the most widely used commercial electrostatographic development technique is the technique known as "cascade" development. A general purpose office copying machine incorporating this development process is described in U.S. Pat. No. 3,301,126. In automatic electrostatographic imaging equipment, it is conventional to employ an electrophotographic plate in the form of a cylindrical drum which is continuously rotated through a cycle of sequential operations including charging, exposing, developing, transferring and cleaning. The plate is usually charged with corona of positive polarity by means of a corona generating device of the type disclosed by L. E. Walkup in U.S. Pat. No. 2,777,957 which is connected to a suitable source of high potential. After forming a powder image on the electrostatic latent 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 powder image is to be transferred is moved through the equipment at the same rate as the periphery of the drum and contacts the drum at the transfer position interposed between the drum surface and the corona generating device. Transfer is effected by a 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 the developing material employed to effect development. For example, where a positive reproduction is to be made of the positive original, it is conventional to employ a positive polarity corona to effect transfer of a negatively charged toner image to a 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 discharged area thereon to form a positive image which may be transferred by negative polarity corona. This imaging process is ordinarily repeated for each copy produced by the machine thousands of times during the usable life of the developer and drum surface.

Although automatic electrostatographic imaging machines are described above with reference to cascade development systems, it is apparent that other well known development techniques such as those described above would also utilize cycles of sequential operations including charging, exposure and develop-

ing. Generally, thousands of cycles of service free performance is expected of automatic machines today. Thus, the developer employed in automatic electrostatic imaging machines must be durable and exhibit stable and predictable performance for extended periods of time.

Many developer materials, though initially possessing desirable properties such as proper triboelectric characteristics, are unsuitable because they tend to exhibit a change in performance characteristics over extended periods of time. The change in performance characteristics is a result of numerous factors. For example, the electrical properties of some toner and carrier materials fluctuate with changes in relative humidity and are not desirable for employment in electrostatic imaging systems, particularly in precision high speed automatic machines which require toners and carriers having stable and predictable triboelectric values. Another factor affecting predictability of developer performance in automatic machines is the formation of contaminating films of toner material on reusable photoreceptor imaging surfaces and carrier particle surfaces. When toner and carrier particles are employed in automatic machines and recycled through many thousands of cycles, the millions of collisions which occur between the toner particles, carrier particles and other surfaces in the machine caused the toner particles to be welded or otherwise forced onto the surfaces of photoreceptors and carrier particles. It is apparent that the gradual accumulation of permanently attached toner material on the surfaces of carrier particles causes a change in the triboelectric value of the carrier particles and directly contributes to the degradation of the copy quality by eventual destruction of the toner carrying capacity of the carrier. Similarly, gradual accumulation of unwanted toner films on the surface of reusable photoreceptors alters the electrical properties of the photoreceptor thereby altering the overall performance of the automatic electrostatic imaging machine. Developer deterioration in automatic electrostatic imaging machines is visually detected on imaged copies in the form of increased toner deposits in the background areas, poor image resolution and low image density in solid areas. Thus, there is a continuing need for a better system for forming toner images in the electrostatic imaging machines.

SUMMARY OF THE INVENTION

It is, therefore an object of this invention to provide an imaging system which overcomes the above-noted deficiencies.

It is another object of this invention to provide an imaging system which stabilizes developer performance.

It is another object of this invention to provide an imaging system which forms images having reduced toner deposits in background areas.

It is another object of this invention to provide an imaging system which provides images having dense solid areas.

It is another object of this invention to provide an imaging system which forms higher resolution images.

It is another object of this invention to provide an imaging system which reduces the formation of toner films on carrier particle surfaces.

It is another object of this invention to provide an imaging system which reduces toner film formation on photoreceptor surfaces.

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

The above objects and others are accomplished, generally speaking, by providing a developer material comprising colored toner particles having a particle size less than about 30 microns and a minor proportion of submicroscopic silicon dioxide additive particles having at least a portion of the silicon atoms on the outside surface of the silicon dioxide particles directly attached through a silicon to carbon linkage to one to three organic groups.

The additive particles may be introduced into the ultimate developer material in any suitable manner to form a physical mix of additive particles with developing material particles. Thus, for example, the additive particles may be initially mixed with carrier particles or toner particles and thereafter introduced into the developer mix. Generally, when the additive is physically mixed with toner or carrier particles, satisfactory results are achieved when about 0.01 to about 15 percent additive based on the weight of the toner particles is employed. Greater stability of performance is achieved when the additive is present in an amount from about 0.05 percent to about 1.5 percent based on the weight of the toner in the final developer mixture. For optimum stability of performance for prolonged periods of operating time, about 0.25 to about 1 percent additive based on the weight of the toner should be employed.

Any suitable submicron particulate silicon dioxide additive having at least a portion of the silicon atoms on the outside surface of the additive particles directly attached to one to three hydrocarbon or substituted hydrocarbon groups may be employed in the developer of this invention. The silicon dioxide particles may be produced by any suitable technique such as the aqueous sodium silicate solution precipitation and silica tetrachloride high temperature oxidation processes. One well known high temperature technique for forming the silicon dioxide particles includes flame hydrolysis decomposition of pure silicon tetrachloride in the gaseous phase in an oxyhydrogen flame at about 1,100°C. Satisfactory results are obtained with treated silicon dioxide particles in a range of about 1 millimicron to about 100 millimicrons. Optimum stability under high humidity conditions and extended periods of use are achieved with particles having a size between about 2 and about 50 millimicrons. The additives of this invention may be of any suitable shape. Typical shapes include spherical, granular and irregular particles. Optimum results are obtained with additive particles having a spherical shape because more uniform developer flow properties are achieved. Although reference has been made to substantially pure silicon dioxide particles, it is apparent that other material may be present in minor amounts. For example, if desired, a mixture of silicon dioxide and aluminum oxide may be formed by mutual flame hydrolysis of silicon tetrachloride and aluminum chloride. Analysis by X-ray indicates that the silicon dioxide particles formed by flame hydrolysis are amorphous.

Prior to reaction with the organosilicon compounds, the submicroscopic silicon dioxide particles employed in the developers of this invention have numerous silanol groups available for reaction on the particle surfaces. For example, submicroscopic silicon dioxide particles having a diameter between about 10 and about 40 millimicrons formed by flame hydrolysis have about one silanol group per about 28 to about 33A.². This amounts to about 2,000 silanol groups per silicon dioxide particle. Upon exposure of freshly prepared submicroscopic silicon dioxide particles to the ambient atmosphere, chemisorbed water molecules become attached to the silanol groups. The presence of water molecules causes a chemical reaction to occur between the water molecules and the organosilicon compounds rather than between the silanol groups and the organosilicon compounds. Thus, the sooner freshly prepared colloidal silica particles are reacted with the organosilicon compounds, the greater number of silanol groups will be available for reaction with the organosilicon compound. The chemical attachment of hydrocarbon or substituted hydrocarbon groups to at least a portion of the silicon atoms on the surface of the silicon dioxide particles may be accomplished by any suitable technique. In one technique, silicon dioxide particles freshly obtained by the flame hydrolysis process described above is separated in a cyclone separator from the bulk of the hydrochloric acid also formed during the process. The silicon dioxide particles; at least one organosilicon compound having hydrocarbon or substituted hydrocarbon groups as well as hydrolyzable groups attached to a silicon atom such as dimethyl dichlorosilane; and steam are pneumatically introduced in parallel flow into a fluidized bed reactor heated to about 400°C by means of an inert gas such as nitrogen. The organosilicon compound reacts with silanol groups on the surface of the silicon dioxide particles and chemical attachment between the silicon atom in the organosilicon compound and a silicon atom in the silicon dioxide particle occurs through an oxygen atom. Where the organosilicon compounds have more than one hydrolyzable group attached to each silicon atom in the organosilicon compound, there is a possibility that (1) the silicon atom in the organosilicon compound may be chemically attached to two silicon atoms in the silicon particle through silicon-oxygen-silicon bonding; (2) the silicon atom in the organosilicon compound may be bonded to a silicon atom in the silicon dioxide particle and to a silicon atom in another organosilicon compound through silicon-oxygen-silicon bonding; or (3) the silicon atom in the organosilicon compound may be attached to a silicon atom in the silicon dioxide particle through a silicon-oxygen-silicon bond and the remaining hydrolyzable groups may be hydrolyzed leaving hydroxyl groups attached to the silicon atom of the organosilicon compound. Where an organosilicon compound having two hydrolyzable groups such as dimethyl dichlorosilane is employed, it is believed that the silicon atoms in two adjacent organosilicon compound molecules are attached through silicon-oxygen-silicon bonding to each other as well as to silicon atoms in a silicon dioxide particle. This belief is supported by measurements of hydroxyl group density before and after reaction and by the hydrophobic properties exhibited by the silicon dioxide particles

after treatment. In any event, at least one hydrophobic hydrocarbon or substituted hydrocarbon group is chemically attached by silicon-oxygen-silicon bonding to a silicon atom in the silicon dioxide particle. Obviously, some developer stability improvement occurs when at least some of the silanol groups available on the colloidal silica particles are reacted with the silane. For a noticeable improvement in stability, at least about 5 percent of the silanol groups on the surfaces of the silicon dioxide particles should be reacted with the organosilicon compounds. At least about 50 percent of the silanol groups should be reacted with organosilicon compound for significantly improved developer stability under high humidity conditions. Optimum results are achieved when at least about 70 percent of the silanol groups are reacted with the organosilicon compounds. The foregoing percentages are based on an average surface silanol group density of about 3 silanol groups per 100A.² of silicon dioxide particle surface area. Freshly prepared silicon dioxide particles formed by the flame hydrolysis technique described above have about 3 silanol groups per 100A.² of surface. The surface silanol group density on the surface of submicroscopic silicon dioxide particles formed by any of the techniques described above may be regulated by heat treatment in vacuo. The heat treatment removes chemisorbed water and depending on the temperatures employed, also removes some of the hydroxyl groups. Thus, at equilibrium in a heat treatment in vacuo, the number of silanol groups per unit area of surface is about 5 silanol groups per 100A.² of surface at 150°C and about 1 silanol group per 100A.² of surface at 800°C.

The marked difference in characteristics between ordinary silicon dioxide particles and silicon dioxide particles in which silanol groups have been reacted with organosilicon compounds may be illustrated by placing the reacted and unreacted particles in a beaker of water. When unreacted submicroscopic silicon dioxide particles formed by the flame hydrolysis process described above is placed in a beaker of water, the particles are immediately wetted by the water and sink to the bottom of the beaker. However, when another sample of substantially identical silicon dioxide particles are treated with dimethyl dichlorosilane so that approximately 75 percent of the silanol groups on the surface of the silicon dioxide particles are chemically reacted with the silane, the treated silicon dioxide particles will float indefinitely on the surface of the water in the beaker. When viewed from below, the mass of floating treated colloidal silica particles is similar in appearance to floating mercury because of the substantially total reflection of light. To further illustrate the unusual hydrophobic properties of silicon dioxide particles such as that described in the beaker of water test, a fine mist of water is mixed with a treated silicon dioxide particle and collected in a beaker. The particles of water are surrounded by the treated silicon dioxide particles and are prevented from reuniting with other particles of water to form larger particles. In a mixture of about 10 percent of treated colloidal silica particles and about 90 percent water droplets, the mixture takes on the appearance of a powder. Objects immersed in this mixture are not wetted by the water. To further illustrate the difference between treated and untreated sub-

microscopic silicon dioxide particles, the moisture adsorption in terms of mg/100m² at different relative humidities are compared. At 40 percent relative humidity, untreated silicon dioxide particles absorb 4.0 mg/100m² of water and the treated silicon dioxide particles absorb 0.4 mg/100m² of water. At 60 percent relative humidity, the untreated silicon dioxide particles absorb 10 mg/100m² of water and the treated particles absorb 0.9 mg/100m² of water. At 80 percent relative humidity, the untreated silicon dioxide particles absorb 30 mg/100m² and the treated particles absorb 1.5 mg/100m² of water. Thus, at 80 percent relative humidity, the untreated colloidal silica particles absorb about 20 times more water than the treated colloidal silica particles.

Any suitable hydrocarbon or substituted hydrocarbon organic group directly attached to a silicon atom in the organosilicon compound may be employed. The organic group is preferably hydrophobic to improve the stability of developer materials under varying humidity conditions. The organic groups may comprise saturated or unsaturated hydrocarbon groups or derivatives thereof. Saturated organic groups include methyl, ethyl, propyl, butyl, bromomethyl, chloromethyl, chloroethyl and chloropropyl groups. Typical unsaturated organic groups include: vinyl, chlorovinyl, allyl, allyl-phenyl, and methacryloxypropyl. The size of the organic group attached to a silicon atom in the organosilicon compound depends on numerous factors such as the number of organic groups attached to the silicon atom, the likelihood of steric hinderance occurring, the number of silanol groups to be reacted, and the like. The principle criteria is that at least about 5 percent of the silanol groups on the silicon dioxide particles are reacted with the organosilicon compound. Any suitable hydrolyzable groups may be attached to the silicon atom of the organosilicon compound. Typical hydrolyzable groups include: chloro, bromo, ethoxy, methoxy, propoxy, propyloxy, acetoxy and amino groups. Examples of typical organosilicon compounds having an organic group attached directly to a silicon atom and hydrolyzable groups attached to a silicon atom include: dimethyl dichlorosilane, trimethyl chlorosilane, methyl trichlorosilane, allyl dimethylchlorosilane, hexamethyldisilazane, allylphenyldichlorosilane, benzyl dimethylchlorosilane, bromomethyldimethylchlorosilane, alpha-chloroethyltrichlorosilane, beta-chloroethyltrichlorosilane, chloromethyldimethylchlorosilane, chloromethyltrichlorosilane, p-chlorophenyltrichlorosilane, 3-chloropropyltrichlorosilane, 3-chloropropyltrimethoxysilane, vinyltriethoxysilane, vinylmethoxysilane, vinyltris (beta-methoxyethoxy) silane, gamma-methacryloxypropyltrimethoxysilane, vinyltriacetoxysilane, divinyl-dichlorosilane, and dimethylvinylchlorosilane. Methylated chlorosilanes, particularly, dimethyl dichlorosilane, are preferred because a greater number of silanol groups per unit area on the silicon dioxide particles are reacted with the silanes thereby reducing the humidity sensitivity of the treated silicon dioxide particles of this invention. This high degree of reaction efficiency appears to be due to the reduced influence of steric hinderance.

Any suitable pigmented or dyed electroscopic toner material may be treated with the additives of this inven-

tion. Typical toner materials include polystyrene resin, acrylic resin, polyethylene resin, polyvinyl chloride resin, polyacrylamide resin, methacrylate resin, polyethylene terephthalate resin, polyamide resin, resinous condensation product of 2,2 bis-(4-hydroxyisopropoxy-phenyl) - propane and fumaric acid, and copolymers, polyblends and mixtures thereof. Vinyl resins having a melting point or melting range starting at least about 110°F. are especially suitable for use in the toner of this invention. These vinyl resins may be a homopolymer or a copolymer of two or more vinyl monomers. Typical monomeric units which may be employed to form vinyl polymers include styrene, vinyl naphthalene, mono-olefins such as ethylene, propylene, butylene, isobutylene and the like, vinyl esters such as vinyl acetate, vinyl propionate, vinyl benzoate, vinyl butyrate and the like, esters of aliphatic methylene aliphatic monocarboxylic acids such as methyl acrylate, ethyl acrylate, n-butylacrylate, isobutyl acrylate, dodecyl acrylate, n-octyl acrylate, phenyl acrylate methyl methacrylate; ethyl methacrylate, butyl methacrylate and the like; vinyl ethers such as vinyl methylether, vinyl isobutyl ether, vinyl ethyl ether, and the like; vinyl ketones such as vinyl methyl ketone, vinyl hexyl ketone, methyl isopropenyl ketone and the like; and mixtures thereof. Generally, suitable vinyl resins employed in the toner have a weight average molecular weight between about 3,000 to about 500,000.

Toner resins containing a relatively high percentage of styrene resin are preferred because a greater degree of image definition is achieved with a given quantity of additive material. Further, denser images are obtained when at least about 25 percent by weight, based on the total weight of resin in the toner, of a styrene resin is present in the toner. The styrene resin may be a homopolymer of styrene or styrene homologues or copolymers of styrene with other monomeric groups containing a single methylene group attached to a carbon atom by a double bond. Thus, typical monomeric materials which may be copolymerized with styrene by addition polymerization include: vinyl naphthalene; mono-olefins such as ethylene, propylene, butylene, isobutylene and the like; vinyl esters such as vinyl acetate, vinyl propionate, vinyl benzoate, vinyl butyrate and the like; esters of alpha-methylene aliphatic monocarboxylic acids such as methyl acrylate, ethyl acrylate, n-butylacrylate, isobutyl acrylate, dodecyl acrylate, n-octyl acrylate, phenyl acrylate, methyl methacrylate, ethyl methacrylate, butyl methacrylate and the like; vinyl ethers such as vinyl methyl ether, vinyl isobutyl ether, vinyl ethyl ether, and the like; vinyl ketones such as vinyl methyl ketone, vinyl hexyl ketone, methyl isopropenyl ketones and the like; and mixtures thereof. The styrene resins may also be formed by the polymerization of mixtures of two or more of these unsaturated monomeric materials with a styrene monomer.

The vinyl resins, including styrene type resins, may also be blended with one or more other resins if desired. When the vinyl resin is blended with another resin, the added resin is preferably another vinyl resin because the resulting blend is characterized by especially good triboelectric stability and uniform resistance against physical degradation. The vinyl resins

employed for blending with the styrene type or other vinyl resin may be prepared by the addition polymerization of any suitable vinyl monomer such as the vinyl monomers described above. Other thermoplastic resins may also be blended with the vinyl resins of this invention. Typical non-vinyl type thermoplastic resins include: rosin modified phenol formaldehyde resins, oil modified epoxy resins, polyurethane resins, cellulosic resins, polyether resins, polycarbonate resins and mixtures thereof. As indicated above, if the resin component of the toner contains styrene copolymerized with another unsaturated monomer or is a blend of polystyrene and other resins, a styrene component of at least about 25 percent, by weight, based on the total weight of the resin present in the toner is preferred because denser images are obtained and a greater degree of image definition is achieved with a given quantity of additive material.

It is to be understood that the specific description of components contained in the additives and resins of this invention represent the vast majority of the components present, but do not exclude the presence of other monomeric units or reactants than those which have been shown. For example, some commercial materials such as polystyrenes contain trace amounts of homologues or unreacted or partially reacted monomers. Similarly, additive particles containing trace amounts of impurities have been described above. Any minor amount of such substituents may be present in the materials of this invention.

Any suitable pigment or dye may be employed as the colorant for the toner particles. Toner colorants are well known and include, for example, carbon black, Resoform Red BN, Benzidine Yellow, nigrosine dye, aniline blue, Calco Oil Blue, chrome yellow, ultramarine blue, duPont Oil Red, Quinoline Yellow, methylene blue chloride, phthalocyanine blue, Malachite Green Oxalate, lamp black, Rose Bengal and mixtures thereof. The pigment or dyes should be present in the toner in a sufficient quantity to render it highly colored so that it will form a clearly visible image on a recording member. Thus, for example, where conventional xerographic copies of typed documents are desired, the toner may comprise a black pigment such as carbon black or a black dye such as Amaplast Black Dye, available from the National Aniline Products Inc. Preferably, the pigment is employed in an amount from about 1 percent to about 20 percent, by weight, based on the total weight of the colored toner. If the toner colorant employed is a dye, substantially smaller quantities of colorant may be used.

The combination of the resin component, colorant and additive, whether the resin component is a homopolymer, copolymer or blend, should have a blocking temperature of at least about 110°F. When the toner is characterized by a blocking temperature less than about 110°F, the toner particles tend to agglomerate during storage and machine operation and also form undesirable films on the surface of reusable photoreceptors which adversely affect image quality.

The toner compositions of the present invention may be prepared by any well known toner mixing and comminution technique. For example, the ingredients may be thoroughly mixed by blending, mixing and milling the components and thereafter micropulverizing the

resulting mixture. Another well known technique for forming toner particles is to spray-dry a ball-milled toner composition comprising a colorant, a resin and a solvent. When the toner mixtures of this invention are to be employed in a cascade or magnetic brush development process, the toner should have an average particle size by weight percent less than about 30 microns. For optimum results in cascade development, an average toner particle size between about 4 and about 20 microns is preferred.

Suitable coated and uncoated carrier materials for cascade development are well known in the art. The carrier particles comprise any suitable solid material, provided that the carrier particles acquire a charge having an opposite polarity to that of the toner particles when brought in close contact with the toner particles so that the toner particles cling to and surround the carrier particles. When a positive reproduction of the electrostatic images is desired, the carrier particle is selected so that the toner particles acquire a charge having a polarity opposite to that of the electrostatic image. Alternatively, if a reversal reproduction of the electrostatic image is desired, the carrier is selected so that the toner particles acquire a charge having the same polarity as that of the electrostatic image. Thus, the materials for the carrier particles are selected in accordance with its triboelectric properties in respect to the electroscopic toner so that when mixed or brought into mutual contact one component of the developer is charged positively if the other component is below the first component in the triboelectric series and negatively if the other component is above the first component in a triboelectric series. By proper selection of materials in accordance with their triboelectric effects, the polarities of their charge when mixed are such that the electroscopic toner particles adhere to and are coated on the surfaces of carrier particles and also adhere to that portion of the electrostatic image-bearing surface having a greater attraction for the toner than the carrier particles. Typical carriers, include steel, flintshot, aluminum potassium chloride, Rochelle salt, nickel, aluminum nitrate, potassium chlorate, granular zircon, granular silicon, methyl methacrylate, glass, silicon dioxide and the like. The carriers may be employed with or without a coating. Many of the foregoing and other typical carriers are described by 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 particle diameter between about 50 microns to about 2,000 microns is preferred because the carrier particles then possess sufficient density and inertia to avoid adherence to the electrostatic images during the cascade development process. Adherence of carrier beads to xerographic drums is undesirable because of the formation of deep scratches on the surface during the image transfer and drum cleaning steps. Also print deletion occurs when large carrier beads adhere to xerographic imaging surfaces. For magnetic brush development, carrier particles having an average particle size less than about 250 microns are satisfactory. Generally speaking, satisfactory results are obtained when about 1 part toner is used with about 10 to about 1,000 parts by weight of carrier in the cascade and magnetic brush developers.

The toner compositions of the instant invention may be employed to develop electrostatic latent images on

any suitable electrostatic latent image-bearing surface including conventional photoconductive surfaces. Well known photoconductive materials include vitreous selenium, organic or inorganic photoconductors embedded in a non-photoconductive matrix, organic or inorganic photoconductors embedded in a photoconductive matrix, or the like. Representative patents in which photoconductive materials are disclosed include U.S. Pat. No. 2,803,542 to Ullrich, U.S. Pat. No. 2,970,906 to Bixby, U.S. Pat. No. 3,121,006 to Middleton, U.S. Pat. No. 3,121,007 to Middleton, and U.S. Pat. No. 3,151,092 to Corrsin.

Although it is not entirely clear, numerous factors appear to affect the ability of the additive particles of this invention to stabilize the performance of developers in automatic machines. The stabilization of images as observed in terms of consistent high quality copies over extended periods of time reduces the need for servicing, extends the developer life, permits the construction of precision close tolerance automatic machines and eliminates the need to regulate machine environment. Factors which may be responsible for the ability of the additive to improve the stability of developer performance may include the enormous external surface area, extremely small particle size, relative chemical inertness, low water absorption, high electrical resistivity, high chemical purity, and chemical coupling of the organosilicon compound to the colloidal silica surface. The external surface area of the additive particles of this invention is enormous and ranges from below about 50 m²/g to above about 400 m²/g of external surface area (BET). In view of the results achieved, it is hypothesized that the enormous external surface area provided by the additive particles prevents contaminants from depositing and altering the electrical characteristics of the carrier, toner and photoreceptor surfaces. The extremely small size of the additive particles is believed to permit the formation of a barrier layer of additive particles around the toner particles. In support of this belief, it is observed that in a sample of toner particles having an average particle size of about 22 microns and containing 1 percent by weight based on the weight of the toner particles of treated additive particles having an average particle size of about 15 millimicrons, each toner particle is surrounded by about 3 million treated silicon dioxide particles. The high electrical resistivity of the treated sub-micron silicon dioxide particles even under exceptionally high humidity conditions appears to reduce fluctuations in the electrical properties of the developer under varying environmental conditions. The high chemical purity as well as the chemically bonded organosilicon compound helps reduce the deposition of contaminants from the treated additive onto the toner, carrier and photoreceptor surfaces. The chemical bonding between the organosilicon compound and the submicroscopic silicon dioxide particles is so strong that most boiling solvents will not remove the organosilicon compound from the colloidal silica particle surfaces.

Surprisingly, the developer additive of this invention restores untreated developers which have exhibited deterioration in performance over an extended period of time in automatic electrostatographic imaging machines. Thus, developers which have deteriorated to

the point where images have high background toner deposits, reduced resolution, poor image fill in solid areas, poor image fill in line copies and poor edge definition no longer have to be discarded. The mere addition of a small amount of additive to the deteriorated developer followed by the formation of about 10 to about 30 additional copies with the altered developer mixture restores the imaging performance of the developer to the level at which it initially performed when freshly introduced into the machine. The reason for the restorative powers of the additives of this invention is not entirely clear. Perhaps the additive particles remove some of the contaminants which may have deposited on the toner, carrier and photoreceptor. Possibly the additive particles alter the degraded electrical properties of the developer by electrically insulating the toner and carrier particles from each other or by altering the triboelectric properties of the toner and carrier particles. Although the mechanism through which improvement occurs is not positively established, the improved results are quite evident. The relative quantity of additive which may be employed to restore the developer is substantially the same as that which may be employed with fresh developer as described above.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The following examples further define, describe and compare exemplary methods of preparing the development system components of the present invention and of utilizing them in a development process. Parts and percentages are by weight unless otherwise indicated. The examples, other than the control examples, are also intended to illustrate the various preferred embodiments of the present invention.

EXAMPLE I

The vitreous selenium drum of an automatic copying machine is corona charged to a positive voltage of about 800 volts and exposed to a light-and-shadow image to form an electrostatic latent image. The selenium drum is then rotated through a cascade development station. A control developer comprising 1 part toner containing a polystyrene resin prepared by spray drying a solution of polystyrene and about 100 parts of sand core carrier beads prepared by the process disclosed in Example II of U.S. Pat. No. 3,467,634 is employed in the developer station. The toner particles have an average particle size of about 12 microns and the carrier beads have an average particle size of about 600 microns. After the electrostatic latent image is developed in the developing station, the resulting toner image is transferred to a sheet of paper at a transfer station. The residual toner particles remaining on the selenium drum after passage through the transfer station is removed by means of a rotating brush in a vacuum housing. The background density, resolution, image fill in solid areas, image fill in line copies and edge definition are good in the initial copies. However, after 2,000 copies are made, background density is very high, resolution has decreased, image fill in solid areas is poor, image fill in line copies is poor and edge definition is poor.

EXAMPLE II

The test described in Example I is repeated with substantially identical fresh developer mixed with about 0.5 percent by weight treated submicron silicon dioxide particles based on the weight of the toner. The treated silicon dioxide particles are produced by flame hydrolysis decomposition of pure silicon tetrachloride in the gaseous phase in an oxyhydrogen flame at about 1,100°C followed by reactions in a heated fluidized bed reactor with dimethyl dichlorosilane as described in detail above. About 75 percent of the silanol groups present on the surface of the freshly prepared silicon dioxide particles are reacted with the silane in the fluidized bed reactor. The freshly prepared silicon dioxide particles have about 3 silanol groups per 100Å.² of surface prior to reaction with the silane. Analysis of the treated silicon dioxide particles reveals that the particles contain more than about 99.8 percent SiO₂, about 0.9 to about 1.3 percent carbon, about 0.03 to about 0.05 percent Cl, less than about 0.003 percent heavy metals, less than about 0.003 percent Fe₂O₃, less than about 0.05 percent Al₂O₃, less than about 0.03 percent TiO₂ and less than about 0.01 percent Na₂O₃. The particle size of the treated silicon dioxide particles is between about 10 to about 30 millimicrons and the surface area of the particles is about 90 to about 150 m²/g. About 10,000 copies are produced with the treated developer. The image quality of all the copies produced are superior in every respect to the copies produced near the termination of the test in Example I.

EXAMPLE III

A Xerox 720 automatic copying machine is modified to replace the cascade development station with a magnetic brush development station. The vitreous selenium drum of the automatic copying machine is corona charged to a positive voltage of about 800 volts and exposed to a light-and-shadow image to form an electrostatic latent image. The selenium drum is then rotated through the magnetic brush development station. A control developer comprising one part toner containing about 88 percent styrene-butyl methacrylate copolymer and about 3 percent 1-amino-4-hydroxyanthraquinone colorant and about 9 percent polyvinyl butyral prepared by conventional blending and micropulverizing techniques and about 50 parts steel core carrier beads prepared by the process disclosed in Example II of U.S. Pat. No. 3,467,634 is employed in the development station. The toner particles have an average particle size of about 14 microns and the carrier beads have an average particle size of about 100 microns. After the electrostatic latent image is developed in the developing station, the resulting toner image is electrostatically transferred to a sheet of paper at a transfer station. The residual toner particles remaining on the selenium drum after passage through the transfer station is removed by a rotating cylindrical brush and vacuum system. The test is operated at an average temperature of about 75° and a relative humidity of about 32 percent. The background density, resolution, image fill in solid areas, image fill in line copies and edge definition are good in the initial copies. However, after 900 copies are made, background density has more than doubled, resolution has decreased,

image fill in solid areas is poor, image fill in line copies is poor and edge definition is poor.

EXAMPLE IV

The test described in Example III is repeated with fresh substantially identical developer mixed with about 1 percent of hydrophobic treated silicon dioxide particles based on the weight of the toner. The treated silicon dioxide particles have an average particle size of about 20 millimicrons. An average of at least about 2 silicon atoms per 100Å. of silicon dioxide particle surface area are chemically bonded through an oxygen linkage to silicon atoms having two methyl groups attached thereto. About 10,000 copies are produced with the treated developer. The image quality of all copies produced are superior in every respect compared to the copies produced near the termination of the test described in Example III.

EXAMPLE V

The procedure described in Example III is repeated with a developer comprising one part toner containing about 95 percent styrene-butyl methacrylate copolymer and about 5 percent Grasol Fast Yellow 3GL colorant prepared by conventional blending and micropulverizing techniques and about 100 parts by weight steel beads coated with a thin ethyl cellulose coating is employed in the development station. The test is operated at an average temperature of about 75 degrees and a relative humidity of about 24 percent. The background density, resolution, image fill in solid areas, image fill in line copy areas and edge definition are good in initial copies but extremely poor after 2,400 copies.

EXAMPLE VI

The procedure described in Example V is repeated with fresh substantially identical developer mixed with about 1.5 percent hydrophobic silicon dioxide particles based on the weight of the toner. This hydrophobic silicon dioxide material is substantially identical to the treated silicon dioxide particles described in Example IV. About 15,000 copies are produced with the treated developer. The image quality of all copies produced are superior in every respect compared to the copies produced near termination of the test described in Example V.

EXAMPLE VII

The procedure described in Example III is repeated with a different control developer. This new control developer comprises 1 part toner containing about 97 percent styrene-butyl methacrylate copolymer and about 3 percent purified Resoform Red BN colorant prepared by conventional blending and micropulverizing techniques and about 100 parts steel core carrier beads prepared by the process disclosed in Example II of U.S. Pat. No. 3,467,634. The toner particles have an average particle size of about 15 microns and the carrier beads have an average particle size of about 100 microns. The test is operated at an average temperature of about 76 degrees and a relative humidity of about 30 percent. The background density, resolution, image fill in solid areas, image fill in line images and

edge definition are good in the initial copies. However, after 4,000 copies are made, resolution has decreased, image fill in solid areas is poor, image fill in line images is poor and edge definition is poor.

EXAMPLE VIII

The test described in Example VII is momentarily stopped and about 3.5 percent of treated silicon dioxide particles based on the weight of the toner is mixed into the developer. The treated silicon dioxide particles have an average particle size between about 10 and about 30 millimicrons. An average of at least about 3 silicon atoms per 100A.² of the silicon dioxide particle surface area are chemically bonded through an oxygen linkage to silicon atoms having two hydrophobic organic groups attached thereto (Organ-O-Sil S-5, Cabot Corporation). After the treated silicon dioxide particles are added to the developer, 250 additional copies are made. The last 225 copies produced are superior in every respect compared to the copies produced near the termination of the test described in Example VI.

EXAMPLE IX

A control developer is tested in an automatic copying machine utilizing a web cleaning system. The photoreceptor of the automatic copying machine is corona charged to a positive voltage of about 700 volts and exposed to a light-and-shadow image to form an electrostatic latent image. The photoreceptor is then rotated through a cascade development station. The control developer comprises 1 part toner comprising about 7 parts styrene-butyl methacrylate copolymer, about 2 parts pentaerythritol tetrabenzoate and about 1 part carbon black colorant prepared by conventional blending and micropulverizing techniques and about 125 parts flintshot coated with a thin coating of ethylcellulose. The toner particles have an average particle size of about 12 microns and the carrier beads have an average particle size of about 700 microns. After the electrostatic latent image is developed in the developing station, the resulting toner image is electrostatically transferred to a sheet of paper at a transfer station. The residual toner particles remaining on the photoreceptor surface after passage through the transfer station is removed by a fibrous web rubbed against the photoreceptor surface. The image density is good in the initial copies with a density reading of about 1.2. However, the image density deteriorates to about 0.8 after about 1,500 copies are made.

EXAMPLE X

The procedure described in Example IX is repeated with fresh substantially identical developer mixed with about 0.5 percent by weight treated silicon dioxide additive based on the weight of the toner. The additive, Aerosil R-972, is substantially identical to the treated additive described in Example II. The initial images formed with this treated developer are very good with a density of about 1.3. The density of subsequent images through 4,000 copies remains good. All 4,000 copies exhibit a density of at least about 1.2.

EXAMPLE XI

A Xerox 720 automatic copying machine with a cascade development station is employed. The vitreous selenium drum of the automatic copying machine is corona charged to a positive voltage of about 800 volts and exposed to a light-and-shadow image to form an electrostatic latent image. The selenium drum is then rotated through the cascade development station. A control developer comprising one part toner containing about 90 percent of a resinous condensation product of 2,2 bis-(4-hydroxyisopropoxy-phenyl)-propane and fumaric acid and about 10 percent carbon black prepared by conventional blending and micropulverizing techniques, about 1 percent by weight untreated silicon dioxide additive based on the weight of the toner and about 100 parts flintshot carrier beads prepared by the process disclosed in Example II of U.S. Pat. No. 3,467,634 is employed in the development station. The toner particles have an average particle size of about 10 microns and the carrier beads have an average particle size of about 700 microns. Analysis of the additive, Aerosil 200, reveals that the particles contain more than 99.8 percent SiO₂, less than about 0.025 percent HCl, less than about 0.05 percent Al₂O₃, less than about 0.03 percent TiO₂ and less than about 0.003 percent Fe₂O₃. The particle size of the untreated silicon dioxide particles is about 12 millimicrons and the surface area of the particles is about 175 to about 225 m²/g. After the electrostatic latent image is developed in the developing station, the resulting toner image is electrostatically transferred to a sheet of paper at a transfer station. The residual toner particles remaining on the selenium drum after passage through the transfer station is removed by a rotating cylindrical brush and vacuum system. The test is operated at an average temperature of about 75° and a relative humidity of about 80 percent. The background density, resolution, image fill in line copies and edge definition are good in the initial copies. However, after about 900 copies are made, background density has more than doubled, resolution has decreased, image fill in line copies is poor and edge definition is poor. The photoreceptor is examined at this point. A dull damp clay-like film is observed which cannot be removed by ordinary cleaning techniques.

EXAMPLE XII

The procedure described in Example XI is repeated with fresh substantially identical developer mixed with about 1 percent by weight treated silicon dioxide additive based on the weight of the toner. The treated additive Aerosil R-972 is described in detail above in Example X. No clay-like film is observed on the photoreceptor surface even after about 2,500 copies.

Although the treated silicon dioxide particles of the invention are described in terms of individual particles, it is apparent that many of the particles agglomerate to form larger particles or chains. These agglomerates and chains of smaller particles are deemed within the scope of this invention.

The expression "developer material" as employed herein is intended to include electrosopic toner material or combinations of toner material and carrier material.

Although specific materials and conditions are set forth in the foregoing examples, these are merely intended as illustrations of the present invention. Various other suitable toner components, additives, colorants, carriers and development techniques such as those listed above may be substituted for those in the examples with similar results. Other materials may also be added to the toner or carrier to sensitize, synergize or otherwise improve the imaging properties or other desirable properties of the system.

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 developing material comprising particles, said particles including finely divided toner material having an average particle size from about 4 to 30 microns and from about 0.05–1.5 percent based on the weight of said toner material, of silicon dioxide particles having at least 0.15 silicon atoms per $A.^2$ on the surface of said silicon dioxide particles chemically attached through silicon-oxygen-silicon bonding to silicon atoms having 1 to 3 organic groups directly attached thereto by silicon-carbon bonding, said silicon dioxide particles having an average particle size of between about 1 millimicron and about 100 millimicrons.

2. An electrostatographic developing material according to claim 1 including from about 10 to about 1000 parts by weight per part by weight of said toner

material of carrier particles which are grossly larger than said finely divided toner material.

3. An electrostatographic developing material according to claim 1 wherein said developing material comprises from about 0.25 percent to about 1 percent by weight of said additive particles, based on the weight of said toner material.

4. An electrostatographic developing material according to claim 1 wherein said additive has an average particle size between about 2 millimicrons and about 50 millimicrons.

5. An electrostatographic developing material according to claim 1 wherein at least about 1.5 silicon atoms per $A.^2$ on the surface of said silicon dioxide particles are chemically attached through silicon-oxygen-silicon bonding to silicon atoms having one to three organic groups directly attached thereto by silicon-carbon bonding.

6. An electrostatographic developing material according to claim 1 wherein at least about 2.1 silicon atoms per $A.^2$ on the surface of said silicon dioxide particles are chemically attached through silicon-oxygen-silicon bonding to silicon atoms having one to three organic groups directly attached thereto by silicon-carbon bonding.

7. An electrostatographic developing material according to claim 1 wherein said organic groups are selected from the group consisting of hydrocarbon groups, substituted hydrocarbon groups and mixtures thereof.

* * * * *

35

40

45

50

55

60

65