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(54) Production of toners for use in electrophotography and method of developing electrostatic latent images using such toners.

(57) A method of producing toners for use in electrophotography comprising the following steps carried out in sequence :

(a) mixing colorant particles with a monomer and pulverizing the colorant particles in the monomer in the presence of a peroxide compound, thereby to disperse the colorant in the monomer eventy as finely divided particles :

(b) adding an azobisnitrile polymerization initiator to the monomer ;

(c) dispersing the monomer in an aqueous alkaline medium containing a first water soluble inorganic salt, to provide an aqueous alkaline dispersion of the monomer ;

(d) adding a second water soluble inorganic salt which reacts with the first water soluble inorganic salt to form a salt which is slightly soluble or insoluble in water, to the aqueous alkaline dispersion of the monomer, thereby to for such a salt under substantially neutral conditions ;

(e) adding an alkali to the aqueous dispersion of the monomer to make it alkaline, to stably disperse the monomer ; and

(f) suspension- polymerizing the monomer to polymer particles.

EP 0 524 016 A1

This invention relates to a method of production of toners for use in electrophotography, in particular suitable for use as non-magnetic one-component toner particles, and a method of developing electrostatic latent images using such toners.

Toners or developing agents in the form of finely divided particles for developing electrostatic latent images in electrophotography have been heretofore produced by a so-called crushing method. According to this method, a colorant such as carbon black, an electric charge controlling agent such as a certain dyestuff, and an anti-offset agent such as a wax are mixed and kneaded together with a melted thermoplastic resin, thereby to disperse them in the resin, cooling, crushing and pulverizing the resultant solid mixture with, for example, a jet mill, to powder of a desired particle size.

In this method, it is necessary that the resin used be brittle so that a mixture of the resin and the addtives as mentioned above be readily crushed. However, when a resin used is too brittle, the resultant toner is excessively finely divided during the use in an electrophotographic apparatus, and contaminates the inside of the apparatus or norms fog on developed positive images. On the other hand, when a resin used is readily melted, the resultant toner is apt to aggregate together and is undesirably reduced in fluidity, but also there takes place filming on an photoconductive member to deteriorate quality of positive images.

It is also necessary that individual toner particles have colorants and charge controlling agents equally and finely dispersed therein, and be capable of being equally electrified so as to produce high quality positive images. However, according to the conventional crushing method, colorants and charge controlling agents are unequally divided among individual toner particles with varied particle sizes. Thus, it is inevitable that positive images have background contamination as well as fog thereon. The apparatus is also contaminated.

In particular, a charge controlling agent has an important effect upon copying performance of toners, but since the known charge controlling agents are in many cases 1-20 μm in particle size, much time is needed to disperse the agent in a resin and thus producitivity is low. Moreover, as a matter on fact, the agent can not be uniformly dispersed in a resin even after kneading over a long period of time.

As above set forth, the conventional crushing method has many disadvantages, and therefore there have been proposed in recent years many methods to produce toners directly by suspension or emulsion polymerization of a radical polymerizable monomer which contains colorants therein such as carbon black.

In these methods, an oily monomer phase is polymerized in an aqueous phase containing a suspending agent dissolved therein such as polyvinyl alcohol. Accordingly, at least some portions of the suspending agent remain inevitably on the surface of the resultant polymer particles even after repeated washing, so that the polymer particles are very sensitive to humidity. Thus, such toners are low in triboelectricity under high humidity, and are apt to produce noncharged or reversely charged toners during the use, to provide a toner image with undesired fog or a tower image with an insufficient or uneven darkness.

Besides polyvinyl alcohol, many suspending agents have been heretofore known. In general, the suspending agents are divided into two. One is a water soluble organic polymer, and the other is a water insoluble or slightly soluble inorganic material. It is likely that the water soluble organic polymer is adsorbed or adheres to particles to form protective colloid around the particles, and thus produces repulsive force among the particles due to steric hindrance of the polymer, thereby to allow the particles to be dispersed stably in a medium. Polyvinyl alcohol, methylcellulose and gelatin, for example, are typical organic polymer suspending agents.

The water soluble or slightly soluble inorganic material as a suspending agent is usually used together with an anionic surfactant. It is likely that the inorganic material is adsorbed or adheres to particles to produce electrostatic repulsive force among the particles, thereby to allow the particles to be stably dispersed in a medium. The inorganic material useful as a suspending agent includes an inorganic salt compound such as barium sulfate, barium carbonate, calcium sulfate, calcium carbonate, calcium phosphate, or magnesium carbonate, an inorganic polymeric material such as talc, clay, silicic acid, or diatomaceous earth, and a metal oxide such as aluminum oxide or titanium oxide.

However, the suspension polymerization in the presence of a water soluble organic polymer as a suspending agent provides polymer particles which contain excessively or undesirably finely divided particles and have a wide particle size distribution. In addition, the water soluble organic polymer useful as a suspending agent is usually hydrophilic, so that it is difficult to remove such a water soluble organic polymer from the resultant polymer particles. The water soluble organic polymer rather remains on the surface of the resultant polymer particles, and makes the polymer particles water-absorptive and hence adversely affects the requisite properties of toners such as electric resistivity and triboelectricity.

The suspension polymerization in the presence of a water insoluble or slightly soluble inorganic material provides polymer particles of a narrowed particle size distribution. However, a large amount of such an inorganic material is needed to obtain polymer particles of a desired particle size. Moreover the inorganic material is used usually together with an anionic surfactant as a suspending aid, so that there arises a problem that excessively finely divided polymer particles are produced. The presence on such finely divided polymer par-

ticles in toners produce fog on electrophotographic images, or lowers fluidity of toners to cause unevenness in darkness on electrophotographic images when a large quantities of copies are made in succession.

To solve the problem as above, there have been proposed many improvements in the production of toners by suspension polymerization methods. For instance, a monomer and a colorant are dispersed in an aqueous medium which contains a suspending agent such as calcium phosphate and an anionic surfactant, suspension-polymerize the monomer, and then the resultant polymer particles are washed with a diluted inorganic acid solution to dissolve the calcium phosphate and then washed with water to remove the resultant water soluble calcium compound from the polymer particles, as disclosed in Japanese Patent Publication No. 63-45101. This method can provide polymer particles free from the suspending agent used, however, the method fails to present resolution regarding the problem of anionic surfactant remaining on the polymer particles.

A further method has also been proposed, as disclosed in Japanese Patent Application Laid-open No. 2-223960. In the method a mixture of a monomer and a colorant is added under stirring to an aqueous solution containing a water-soluble inorganic acid salt and an anionic surfactant, and then a water soluble salt of polyvalent metal is added to the solution thereby to deposit a water-insoluble or slightly soluble salt of the polyvalent metal under high shear agitation while the monomer is suspension-polymerized. There is used as the water-soluble inorganic acid salt, for example, sodium carbonate or sodium phosphate, while there is used as the water soluble salt of polyvalent metal, for example, calcium chloride. As the anionic surfactant, a fatty acid soap such as potassium oleate or sodium oleate.

This method also fails to present resolution regarding the problem of anionic surfactant remaining on the polymer particles produced.

On the other hand, it is an advantage of toners produced by a suspension or emulsion polymerization method that the toner is substantially spherical and has a high fluidity so that there is no need of adding a fluidizing agent such as silica to the toner. However, because of that sphericity, the toner is inferior in "blade cleanability".

In an electrophotographic process using plain paper as a substrate of which toner images are fixed, usually recording paper, an electrostatic latent image is formed on the surface on an photoconductive member to which electrostatic charge has been given, the latent image is developed by toner particles to a toner imaged and the toner image is transferred onto a substrate, and then the toner image is fixed thereon, to provide a copy image. Therefore, it is necessary that the toner remaining on the photoconductive member is removed therefrom after the toner image has been transferred and fixed onto the substrate to make copy image in succession. As one of the methods for removing the toner remaining on the photoconductive member, a blade cleaning method is widely known according to which the toner is scraped off with a cleaning blade after the toner image has been transferred onto the substrate. The blade may be formed of various elastomers, among which a polyurethane elastomer is most preferred from the stand-point of mechanical properties such as resistance to abrasion.

In such a blade cleaning method, spherical toner particles enter beneath the blade when the blade scrapes the photoconductive member, and roll between the blade and the surface of photoconductive member, so that the toner particles remain on the photoconductive member after the cleaning of the member with the blade.

Thus, in the production of toner particles by suspension polymerization, there has been proposed a method in which spherical polymer particles are agitated in a suspension medium at a high rate before the completion of the polymerization so that the spherical polymer particles are deformed, as described in Japanese Patent Application Laid-open No. 62-266560.

However, according to the method, the polymer particles tend to aggregate to each other on account of unreacted monomers remaining in the reaction system or the deformed polymer particles are restored to their original spherical particles at relatively high temperatures where the polymer particles are readily deformed, on account of surface tension they possess. Namely, effective deformation of spherical polymer particles is not attained. Agitation of the polymer particles as small rates or at low temperatures also fails to effectively deform the spherical polymer particles, although the aggregation of the particles is restrained.

Furthermore, the polymer particles produced by the suspension polymerization have rather a wide particle size distribution. Thus, large spherical particles might be readily deformed, but small particles are not, and accordingly there arises a wide distribution in degree of deformation. -Accordingly, as a further defect of the above method, small spherical particles remain undeformed and such small spherical particles elude cleaning by a blade on the photoconductive member.

A further method of producing toners has been recently proposed in which finely divided particles are adhered and fixed onto the toner particles by a so-called impact method, as described in Japanese Patent Application Laid-open No. 62-129866. however, since toner particles have a siginficantly wide size distribution, it is necessary that the finely divided particles are of not more than about one micron so that they are successfully fixed on the individual toner particles accoding to this method. Little improvement in blade cleanability is attained with such toner particles having such fine particles fixed thereon.

Meanwhile, an image forming process such as an electrophotographic process or an eletrostatic recording process using toners includes in general the following steps. A photoconductive member is electrified, an electrostatic latent image is formed on the photoconductive member by exposure of the member to the image, developing the latent image to a toner image using toners, transfer the toner image onto a recording substrate such as paper, and fix the toner image thereon by application of heat or pressure to the toner image. These steps are repeated.

In these processes, the developing methods are divided into two. One is a method wherein a two-component developing agent composed of toners and carriers is used, and the other is a method wherein a one-component developing agent is used which contains no carriers. It is necessary for the former method to use a mixture of toners and carries in a fixed ratio, so that it is difficult to make a developing device compact. In addition, there arises a farther problem that toners adhere to the carriers to deteriorate them.

In contrast, the method wherein the one-component developing agent is used has no such problems as above. In general, the method wherein the one-component developing agent is used is divided into two. one is a method wherein magnetic toners are used, and the other is a method wherein non-magnetic toners are used. The polymer method transfers the toners by a magnetic adsorptive means in a developing device, so that the device is expensive and complicated. Moreover, the toner particles contain therein magnetic powder, and hence need a large quantity of heat so that the toner image is fixed.

Under these circumstances, the method wherein one-component developing agent is used (which will be hereinafter referred to as the one-component method) is promising as a method of developing electrostatic latent images, as described in Japanese Patent Application Laid-open No. 47-13088 or No. 47-13089. But on the other hand, the method involves a number of problems and has not yet become widely utilized.

The one-component method contains a developing device as illustrated in Fig. 1. The device 4 includes a toner box 12 which contains toners 10 under stirring with a stirring blade 11. The toner box 12 is provided with a toner transfer member 13 adjacent to the photoconductive member 1, and the toner transfer member 13 rotates in the opposite direction to the photoconductive member 1. The toner transfer member 13 may be in contact with the photoconductive member 1 or placed close to the photoconductive member 1 with a small distance therebetween.

The toner transfer member 13 has a member 14 for regulating or controlling the thickness of toners forced on the member 13. In addition, there is provided a member 15 which rotates in the same direction as the toner transfer member 13 or in the opposite direction in contact therewith.

It is necessary to form a thin layer of toners on the toner transfer member 13 to evenly triboelectrify the toners thereon, and thus usually a doctor blade is suitably used as such a member 14 for regulating or controlling the thickness of toners. When the toners form a thick layer on the toner transfer member 13, the toners in the surface layer only are electrified while the towers inside the layer are unevenly electrified, so that the toners slightly electrified are scattered to contaminate the suroundings or produce fog on fixed toner images. Moreover, the one-component method uses no carriers to electrify toner particles, and consequently it is difficult to electrify toner particles sufficiently.

The toner particles produced by the crushing method are irregular in shape, or formless, and thus they are worn at corners to produce a large amount of finely divided powder when they are made adhere in a thin layer onto the toner transfer member 13. The powder adheres onto non-image areas on the photoconductive member thereby to produce fog on the resultant fixed toner images, or adheres onto the member 13 to cause insufficient electrification of toners or produce white lines on the resultant fixed toner image.

On the other hand, the toner particles produced by the polymerization method are free from such a problem as above mentioned attended by the toner particles produced by the crushing method. However, the toner particles produced by the polymerization method are truely spherical, and accordingly they readily pass through the regulating member 14 on the member 13 to fail to form an even and thin layer on the member 13. Thus, the toners are insufficiently electrified to produce fog on fixed images, but also when latent images on the photoconductive member are developed, the toners are excessively rotatable on the member 13 so that they produce fixed images with poor resolution of fine lines. When the thus formed toner images are transferred electrostatically onto recording paper or fixed thereonto by application of heat or pressure also, the toners readily rotate to provide blur with fine lines.

As hereinbefore set forth, the toner remaining on the photoconductive body is removed therefrom usually with a cleaning blade after the toner image has been transferred onto recording paper. The toner particles in the form of true spheres such as those produced by the polymerization method readily escape from cleaning with a cleaning blade, with consequence that the remaining toners are not completely removed from the photoconductive member.

To solve the problems as above, there have been proposed a method of producing deformed toner particles in which a polymerizable monomer is suspension polymerized in water containing polyvinyl alcohol as a sus-

pending agent, deforming the resultant polymer particles, and then saponifying and removing the polyvinyl alcohol remaining on the surface of the polymer particles, as described in Japanese Patent Laid-open No. 2-256068. However, even if a very small amount of polyvinyl alcohol remains on the surface of toner particles, the toner is insufficiently electrified especially under a high humidity, and thus it is virtually infeasible to use such deformed toners as above in such a developing method as uses no carriers, as in the non-magnetic one-component method.

It has been desired to provide a method of producing toners by suspension polymerization wherein not only a colorant and a charge controlling agent are finely and evenly dispersed in polymer particles, but also no surfactant is used in the stage of dispersing a monomer in an aqueous medium, to provide polymer particles having an improved particle size distribution.

It has been desired to provide a method of developing electrostatic latent images using non-magnetic one-component developing agent which can form an even and thin layer of toners on the toner transfer member without producing undesirably finely divided powder of toners and without adhesion of toners onto the member, thereby to provide high quality copy images including high resolution of fine lines attained.

It has been desired to provide a method of producing toners suitable for use in such a non-magnetic one-component developing method of electrostatic latent images on a photoconductive member in an electro-photographic process.

Other features and advantages of the invention will be apparent from the following description taken in connection with the accompanying drawings, in which:

Fig. 1 is a sectional view of an electrophotographic apparatus suitably used in the non-magnetic one-component method of developing electrostatic latent images on a photoconductive member; and

Fig. 2 is a sectional view of a continuous, wet type agitation mill preferably used nor the production of deformed polymer particles according to an embodiment of the present invention.

The invention provides a method of producing toners for use in electrophotography which comprises the following steps carried out in sequence:

(a) the step of mixing colorant particles with a monomer and pulverizing the colorant particles in the monomer in the presence of a peroxide compound, thereby to disperse the colorant in the monomer evenly as finely divided particles;

(b) the step of adding an azobisnitrile polymerization initiator to the monomer;

(c) dispersing the monomer in an aqueous alkaline medium containing a first water soluble inorganic salt, to provide an aqueous alkaline dispersion of the monomer;

(d) adding a second water soluble inorganic salt which reacts with the first water soluble inorganic salt to form a salt which is slightly soluble or insoluble in water, to the aqueous alkaline dispersion of the monomer, thereby to form such a salt under substantially neutral conditions;

(e) adding an alkali to the aqueous dispersion of the monomer to make it alkaline, to disperse the monomer stable again in the dispersion; and

(f) suspension-polymerise the monomer to polymer particles.

Any radical polymerizable monomer which is known as usable for the production of toner by suspension polymerization is usable in the invention. Therefore, such monomers include,for example, styrene, substituted styrenes such as o-methylstyrene, m-methylstyrene, p-methylstyrene or p-chlorostyrene; vinyl esters such as vinyl acetate or vinyl propionate; acrylic acid esters such as methyl acrylate, ethyl acrylate, propyl acrylate, n-butyl acrylate, isobutyl acrylate, n-octyl acrylate, dodecyl acrylate, 2-ethylhexyl acrylate, stearyl acrylate, phenyl acrylate or α-chloromethyl acrylate; methacrylic acid esters such as methyl methacrylate, ethyl methacrylate, propyl methacrylate; n-butyl methacrylate, isobutyl methacrylate, n-octyl methacrylate, dodecyl methacrylate, 2-ethylhexyl methacrylate, stearyl methacrylate, phenyl methacrylate, α-chloromethyl methacrylate, dimethylaminoethyl methacrylate, dimethylaminoethyl methacrylate or glycidyl methacrylate, unsaturated nitriles such as acrylonitrile or methacrylonitrile; α,β-unsaturated carboxylic acids such as acrylic acid or methacrylic acid; and vinylpyridines such as 2-vinylpyridine or 4-vinylpyridine. These monomers are used singly or as a mixture of two or more. Among these, however, styrene or a mixture of styrene and acrylic or methacrylic acid esters are preferred.

A polyfunctional monomer may be used together with the above mentioned monomers to improve fixation and anti-offset properties of toners. There may be mentioned as such a polyfunctional monomer, for example, divinylbenzene or ethylene glycol dimethacrylate. However, when the polyfunctional monomer is used in excess, the resultant polymer particles are too high in melting points, and poor in fixability. Thus, the polyfunctional monomer may be used normally in an amount of not more than about 1 % by weight based on the radical polymerizable mononer.

According to the invention, a colorant, for instance, carbon black, is mixed with and stirred in the monomer in the presence of a peroxide compound with, for example, a ball mill, and is dispersed minutely and finely in

the monomer. The preferred peroxide compound used are acyl peroxide which is derived from a fatty acid. For example, lauroyl peroxide is preferred. Usually the mixture of the monomer and carbon black is stirred in the presence of the peroxide compound over a period of several hours to disperse the carbon black evenly in the monomer as finely divided particles of not more than one micron in particle size, preferably of not more than 0.5 microns in particle size, the dispersion of carbon black in the monomer may be carried out at room temperatures, but if desired, at elevated temperatures, for example, at about 50-80°C to accelerate the dispersion.

Carbon black is used in amounts of about 2-10 parts by weight in relation to 100 parts by weight of the radical polymerizable monomer. In turn, the peroxide compound is used usually in an amount of about 10-50 parts, preferably of about 10-40 parts by weight, in relation to 100 parts by weight of carbon blank used. The use of the peroxide compound in an amount of less than about 10 parts by weight in relation to 100 parts by weight of carbon black used fails to disperse carbon black minutely and uniformly in the monomer, whereas the use of the peroxide compound in an amount of more than about 50 parts by weight in relation to 100 parts by weight of carbon black used, the decomposition fragments of the peroxide compound used remain in the resultant polymer particles. Such polymer articles undesirably smell bad when being heated and melted to fix on a recording paper during the electrophotographic process.

The use of an azobisnitrile polymerization initiator, such as azobisisobutyronitrile or azobisdimethylvaleronitrile, in place of a peroxide polymerization initiator as above mentioned in the step of the carbon black dispersion, fails to uniformly and minutely disperse carbon black in the monomer, but carbon black aggregates together, and most of the carbon black used is dispersed as large particles in the monomer. Furthermore, the monomer in part polymerizes in the presence of the azobisnitrile polymerization initiator, to increase the viscosity of the mixture of the monomer and the carbon black. This adversely affects the preparation of suspension of fine droplets of the monomer in an aqueous medium.

Any colorant may be used together with carbon black, if needed. Such colorants may or may not be soluble in the monomer. There are mentioned such colorants in, for example, Japanese Patent Application Laid-open No. 62-246073. When a colorant insoluble in the monomer is used, such a colorant may be dispersed minutely and uniformly in the monomer with aid of a peroxide compound or other suitable dispersing agent in the same manner as carbon black is dispersed in the monomer.

After the dispersion of carbon black in the monomer as set forth above, if necessary, a charge controlling agent may then be dispersed evenly as finely divided particles in the monomer mixture with carbon black.

For the purpopse, usually a charge controlling agent is added to the monomer mixture together with a dispersing agent soluble in the monomer, and the resultant mixture is stirred for, for example, about 50-200 hours, with a ball mill, thererby to pulverize and disperse the agent evenly as finely divided particles of not more than about 0.5 microns, preferably of not more than about 0.3 microns, in in the monomer. This dispersion may also be carried out at elevated temperatures such as at about 50-80°C to accelerate the dispersion.

The charge controlling agent is used usually in an amount of about 0.01-10 parts, preferably of about 0.05-5 parts, most preferably of about 0.1-1 part by weight, in relation to 100 parts by weight of the monomer used.

However, a charge controlling agent may be incorporated into polymer particles after the preparation of polymer particles. For instance, the charge controlling agent may be made to adhere physically to the particles.

Any charge controlling agent known in the art may be used, such as a powder of an inorganic compound, a powder of an organic compound including metallized dyes and pigments, and organic carboxylic acid metal salts, and a powder of an organic polymer.

In the method of the invention, carbon black and a charge controlling agent are dispersed evenly as finely divided particles in the monomer as hereinbefore described, and if necessary an additional amount of the monomer is further added to the dispersion, and then an azobisnitrile polymerization initiator is added to the dispersion, to form a monomer composition. Suitable azobisnitrile polymerization initiators include, for example, azobisdimethylvaleronitrile and azobisdimethylisobutyronitrile, however, azobisdimethylvaleronitrile is especially preferred since it is highly soluble in the monomer.

The monomer composition in the form of a dispersion thus containing an azobisnitrile polymerization initiator is then dispersed in an aqueous medium as small droplets by use of, for example, a homogenizer, and is heated so that suspension polymerization proceeds to produce spherical polymer particles.

When no azobisnitrile polymerization initiator is added anew to the monomer composition, substantially no suspension polymerization occurs even under heating, since substantially all the peroxide polymerization initiator which has been added to the monomer in the stage of the dispersion of carbon black in the monomer is decomposed during the dispersion, and therefore it is necessary that a polymerization initiator be anew added to the monomer in the stage of suspension polymerization. The polymerization initiator added in the stage of polymerization should be an azobisnitrile polymerization initiator, not a peroxide. The addition of a peroxide polymerization initiator is substantially useless since the initiator fails to polymerize the monomer, or if polymerization takes place, the resultant polymer has a very low molecular weight, and has no sufficient anti-offset

properties.

The azobisnitrile polymerization initiator is used usually in amounts of about 1-10 parts preferbly of about 2-5 parts by weight, in relation to 100 parts by weight of the monomer used. When the amount is less than about 1 part by weight in relation to 100 parts by weight of the monomer used, the polymerization proceeds only very slowly, and it is substantially impossible to polymerize the monomer in a high polymerization rate, while when the amount is more than about 10 parts by weight in relation to 100 parts by weight of the monomer used, the resultant polymer is low in molecular weight, and is insufficient in anti-offset properties.

According to the method of the invention, the mixture of the monomer, carbon black, an azobisnitrile polymerization initiator, and optionally a charge controlling agent, is added to an aqueous alkaline medium containing a first water soluble inorganic salt, and the mixture is vigorously stirred by use of, for example, a homogenizer, to provide an aqueous dispersion of droplets of the monomer composition of 1-30 microns, preferably in the range of 1-5 microns, in diameter, in the aqueous medium.

The first water soluble inorganic salt used includes, for example, sodium carbonate, sodium hydrogen carbonate, potassium carbonate, sodium phosphate, sodium dihydrogen phosphate, sodium pyrophosphate, potassium phosphate, sodium sulfate, potassium sulfate and sodium metasilicate.

Then a second water soluble inorganic salt which reacts with the first water soluble inorganic salt to form a salt which is slightly soluble or insoluble in water, is added to the aqueous dispersion of the above mentioned monomer composition, thereby to form such an inorganic salt which is slightly soluble or insoluble in water under substantially neutral pH conditions, preferably at a pH of 6-7.

According to a method of the invention, the pH of the aqueous alkaline solution of the first water soluble inorganic salt in advance arranged with a water soluble acid, preferablya a water soluble inorganic acid so that when the second water soluble inorganic salt is added to the aqueous dispersion of the monomer composition, a water insoluble or slightly soluble salt is formed under substantially neutral pH region or at a pH of 6-7. There may be used as such a water soluble inorganic acid, phosphoric acid.

The second water soluble inorganic salt used depends upon the first water soluble inorganic salt used, but there may be preferably used chlorides or sulfates of calcium, barium, magnesium, manganese, zinc, strontium or aluminum.

More specifically, it is preferred that sodium phosphate is used as the first water soluble inorganic salt, and calcium chloride as the second water soluble inorganic salt in the method of the invention. In this case, a water insoluble or slightly soluble calcium phosphate deposits in the aqueous medium.

The first water soluble inorganic salts are used in an amount of 0.1-20 parts by weight, preferably 0.5-15 parts by weight, in relation to 100 parts by weight of the monomer. In turn, the second water soluble inorganic salt is used in an amount equivalent to the amount of the first water soluble inorganic salt used and the inorganic acid used. It is further preferred that the amount of the second water soluble inorganic salt used is in the range of 0.1-20 parts by weight, preferably 0.5-15 parts by weight, in relation to 100 parts by weight of the monomer used.

According to the invention, the water insoluble or slightly soluble inorganic salt is deposited in the aqueous medium under the substantially neutral pH conditions, and the finely divided droplets of the monomer composition, preferably having a particle size of 1-5 microns as hereinbefore mentioned, are made unstable in the medium at a neutral pH region, and as results they are collected and coagulated to form droplets of larger particle size, preferably of 5-25 microns, most preferably 7-20 microns.

Then, an alkali such as ammonia water is again added to arrange the dispersion at an alkaline pH of more than 7 and not more than 12, preferably at a pH or more than 7 and not more than 10, thereby to allow the thus enlarged droplets of the monomer composition to be dispersed again stably in the medium with the particle size distribution being shifted to the direction of larger particle size and yet to the direction of a more narrow distribution, and with substantially no undesirably finely divided droplets of the monomer composition being present in the dispersion. Namely, the resultant droplets of the monomer composition have larger particle size and yet a such narrowed particle size distribution than they initially had.

However, when the second water soluble inorganic salt is added to the aqueous dispersion of the monomer composition containing the first water soluble inorganic salt to form the water insoluble or slightly soluble inorganic salt at an alkaline pH region, not at a neutral pH region, then the finely divided droplets of the mononer composition do not coagulate, but exist stably as they are, so that there are obtained droplets of the monomer composition containing such finely divided droplets, and thus still having a wide particle size distribution.

By way of example, an aqueous solution of sodium phosphate has a pH of about 12. When a monomer is dispersed in the solution to form a dispersion, and an aqueous solution of calcium chloride is added to the dispersion to deposit calcium phosphate, the dispersion usually has a pH more than 8. Consequently, the finely divided droplets of the monomer do not coagulate, but exist stably as they are, Even if a dispersing agent such as an anionic surfactant is added to the dispersion, the result is the same, and there is obtained a dispersion

of droplets of monomer containing a large amount of finely divided droplets, and thus having a wide particle size distribution.

According to the invention, in contrast to the above, a monomer is first dispersed as finely divided droplets in an aqueous medium, and then a water insoluble or slightly soluble inorganic salt is formed therein at a substantially neutral pH region to make the above finely divided droplets of the monomer unstable so that they coagulate to form droplets of a larger particle size, and then the aqueous dispersion is again arranged at an alkaline pH of more than 7 and not more than 12, preferably at a pH of more than 7 and not more than 11, thereby to allow the above formed droplets on the monomer to be dispersed again stably in the medium, The thus resultant aqueous dispersion contains droplets of the monomer having a enlarged particle size and a narrowed particle size distribution with substantially no undesirably finely divided droplets being present in the medium. Thus, the resultant dispersioncontains stable droplets of the monomer of a larger diameter and a more narrow particle size distribution than they initially had.

After the preparation of stable dispersion of the droplets of the monomer in an aqueous medium as above set forth, the dispersion is stirred at a temperature of 40-95°C, preferably 50-90°C, to suspension-polymerize the monomer, to provide polymer particles usually of particle size of 1-30 microns, and 3-25 microns in preferred embodiments, and 5-20 microns in the most preferred embodiments, and of a narrow particle size distribution. According to the invention, there can be obtained polymer particles having a particle size distribution more narrow than that of droplets of monomer dispersed in an aqueous medium.

The resultant polymer particles are first washed with an inorganic acid solution such as a hydrochloric acid solution to dissolve the water insoluble or slightly soluble salt, and then washed with water to remove the solubilized salt from the polymer particles. The polymer particles are then dried in vacuo to provide toners.

The thus prepared toners may be suitably used in a non-magnetic one-component developing agent in developing electrostatic latent images. However, there is obtained toners which are more suitably used as a non-magnetic one-component developing agent by deforming the polymer particles in accordance with the invention.

Thus, as a further aspect of the invention, there is provided a method of developing electrostatic latent images using a non-magnetic one-component developing agent, and a method of producing toners suitable for use in such a non-magnetic one-component method of developing electrostatic latent images on a photoconductive member in electrophotographic process.

According to the invention, there is provided an improvement in a method of developing electrostatic images in electrophotographic process which comprises providing eletrostatic charge on the surface of a photoconductive member, exposing the member to an image to form thereon an electrostatic latent image, forming a layer having a controlled, even and small thickness of non-magnetic one-component toner particles on the member while triboelectrifying the toner particles, and developing the latent image with the toner particles, the improvement comprising the use of toner particles mainly composed of disklike toner particles having a diameter of 3-30 μm, a thickness of 1-15 microns and a flatness of not more than 0.5 as the flatness of the disklike toner particles is defined as a ratio of average thickness to average diameter of the particles, or oval toner particles having a major axis of 3-30 microns in length, a minor axis of 1-25 microns in length and a flatness of not more than 0.5 as the flatness of the oval toner particles is defined as a ratio of twice the average thickness to the sum of length of average major axis and length of average minor axis, or a mixture of the disklike and oval toner particles.

As previously set forth, the suspension polymerization provides polymer particles which are 1-30 microns in diameter which have a flatness of not less than 0.98, the flatness being defined hereinafter. Thus, the resultant polymer particles are substantially true spherical.

In accordance with the invention, the suspension which contains the resultant substantially true spherical polymer particles may be further treated with a continuous wet type agitation mill in the presence of calcium phosphate as a suspending agent (before the resultant polymer particles are washed with a hydrochloric acid solution to remove the water insoluble or slightly soluble salt from the polymer particles).

The suspension of the polymer particles are treated with a continuous wet type agitation mill in the presence of calcium phosphate preferably at temperature in the range of ± 10°C of the glass transition temperatures of the polymer, thereby to deform or flatten the spherical particles into disklike or oval particles, or a mixture of these.

The continuous wet type agitation mill is known. As illustrated in Fig. 2, the mill contains an annular stator 21 having a triangular section and a rotor 22 therein similar to the stator in shape. A milling zone 23 is formed as an annular gap of a small breadth between the stator and the rotor. The milling zone contains a milling medium 24 therein to impart mechanical impact to suspended particles to deform them so that they get flat or flattened.

The suspension is introduced into the milling zone through an inlet 25 at the lower part of the mill and travels

along the gap, and is then separated from the medium at a separator 26. The suspension which contains deformed polymer particles is obtained from an outlet 27. While the polymer particles in the suspension are deformed in the milling zone, warm water is supplied to passages 28 within the stator and the rotor to control the temperature of the suspension. The milling medium also travels centrifugally along the milling zone having a W-shaped section and returns to the inlet. Zirconia, glass or steel spherules of, for example, about 0,5-3 mm in diameter are used as the milling medium, although not limited thereto.

It is preferred that treatment of the suspension containing the polymer particles with the annular, continuous, wet type agitation mill is carried out at temperatures in the range of ± 10°C of the glass transition temperature of the matrix which forms the polymer. When the suspension is treated at temperatures lower than the glass transition temperature of the polymer by 10°C, the polymer particles crushed, rather than deformed. On the other hand, when the suspension is treated at temperatures higher than the glass transition temperature of the polymer by 10°C, the polymer particles are apt to aggregate to each other to form mass, but also the polymer particles become spherical again on account of surface tension even after the particles have been deformed, so that deformation efficiency is low. The treatment is carried out usually over a period of 0.5-10 hours, preferably 2-5 hours.

The use of an annular, continuous, wet type agitation mill has an advantage that the rotor produces a larger shearing force in the direction of rotation than a ball mill or a sand mill, and can exert anisotropic stress on the particles, so that they are effectively deformed even when they have a significant particle size distribution. Namely, the particles are deformed irrespectively of their diameters, so that the resultant toner particles have a greatly improved blade cleanability. In addition, such particles make contact with a substrate with a large surface area when transferred from a photoconductive body, and thus fixed thereof at relatively low temperatures. Similarly, the individual particles have a large contact area on a substrate, so that a small amount of such particles produces dark images, and consumption of toner is reduced.

As above set forth, there is obtained a disklike polymer particle having a diameter of 3-30 μm, a thickness of 1-15 μm and a flatness of not more than 0.5, or an oval polymer particle having a major axis 3-30 μm in length, a minor axis 1-25 μm in length and a flatness of not more than 0.5, or a mixture of these, by the deforming or flattening treatment of spherical polymer particles produced by a suspension polymerization method with the annular, continuous, wet type agitation mill according to the invention.

In the specification, the flatness of disklike toner particles is defined as a ratio of average thickness to average diameter of the particles. The flatness of the oval toner particles is defined as a ratio of twice the average thickness to the sum of length of average major axis and length of average minor axis.

The thus deformed toners produced by the method of the invention are mainly composed of disklike or oval particles, or a mixture of these, contrast to truely spherical particles, so that the thus deformed or flattened toner particles form readily and certainly a thin and even layer of toners on the toner transfer member, and moreover the deformed toner is prevented from rotation when they are transferred from the toner transfer member to a photoconductive member so that they provide copy images with no fog. The deformed toner particles do not adhere to the transfer member and thus provide such high quality copy images as have no defects and have high resolution.

As a further feature of the deformed toner of the invention, the toner is deformed so that it does not pass through between the cleaning blade and the photoconductive member and has an improved blade cleanability.

However, when the toner has a flatness of more than 0.5, it is difficult to form a thin layer of toners on the toner transfer member, and moreover, the resultant copy images are apt to be blurred on account of rotation of toner particles when they are developed, transferred or fixed, as hereinbefore described. Further, it may happen that toner particles escape from cleaning with a cleaning blade to produce a variety of defects on the resultant copy images.

According to the invention, the toner is produced in the manner as above set forth, and the toner provides images with neither fog nor unevenness in darkness in solid images and with a high resolution. The toner also provides copy images with are the same in quality as that of initial stage of copying even after continuous copying in large quantities.

EXAMPLES

The invention will now be described with reference to examples, however, the invention is not limited thereto. In the examples, the RAT value is an index of particle size distribution, and is defined as D_{40}/D_{90} wherein D_{40} represents the 40% oversize particle size (diameter) in the cumulative distribution; and D_{90} represents the 90% oversize particle size (diameter) in the cumulative distribution. Thus, the nearer to 1 the RAT value, the more narrow the particle size distribution.

Example 1

An amount of 5.0 parts by weight of carbon black "Diablack" (tradename) #52 (volatile matters 0.8 %, pH 8.0, particle size 27 mμ, available from Mitsubishi Kasei Kogyo K.K., Japan) and 1 part by weight of lauroyl peroxide were added to and mixed with 50 parts by weight of styrene in a ball mill for 30 minutes to preliminarily disperse the carbon black in the monomer. The mixture was then further agitated in an autoclave at 70°C for 1 hour. After the dispersion operation as above, the carbon black was found to be about 0.1 micron in particle size and there took no sedimentation in the dispersion.

An amount of 0.4 parts by weight of an ethylene-vinyl acetate copolymer "Soablene CH" (tradename, available from Nippon Gosei Kagaku Kogyo K.K., Japan) as a dispersing agent and 1.0 part by weight of a negative charge controlling agent, a dyestuff named "Spiron Black TRH" (tradename, available from Hodogaya Kagaku Kogyo K.K., Japan) were added to the dispersion, and stirred with a ball mill for 100 hours, to disperse the charge controlling agent in the monomer. After the dispersion operation as above, the charge controlling agent was found to be of about 0.3 microns in particle size, and was found not to precipitate in the dispersion.

To the resultant monomer dispersion were then added 30 parts by weight of styrene, 20 parts by weight of butyl methacrylate, 0.2 parts by weight of divinylbenzene, 3 parts by weight of polypropylene wax as an anti-offset agent, and then 3 parts by weight of azobisdimethylvaleronitrile, to form a monomer composition.

An amount of 400 parts by weight of an aqueous solution of 12 parts by weight of sodium phosphate $Na_3PO_4 \cdot 12H_2O$) was prepared and arranged at pH of 11.0 by use of phosphoric acid.

The above monomer composition was added to the solution, and the mixture was agitated for 10 minutes using a homogenizer "Model TK-M available from Tokushu Kakoki Kogyo K.K., Japan) at 6000 rpm to disperse the monomer composition in the aqueous solution, to prepare an aqueous dispersion containing finely divided droplets of the monomer composition of about 3 microns in number average particle size.

Then an amount of 10 parts by weight of an aqueous solution of 8 parts by weight of calcium chloride ($CaCl_2 \cdot 2H_2O$) was added under stirring to the above aqueous dispersion of the monomer composition, thereby to deposit calcium phosphate, whereupon the resultant dispersion was found to have a pH of 6.4. Thus, the finely divided droplets of the monomer composition were made unstable and the finely divided droplets were collected and coagulated to form droplets of a larger particle size. Then, ammonia water was added under stirring to the dispersion to arrange the dispersion at a pH of 8.5, so that the enlarged droplets of the monomer composition were made stable again whereupon the droplets were found to have a volume average particle size of 8.3 microns and an RAT value of 1.56.

The thus prepared aqueous dispersion on the monomer composition was gently stirred at 70°C for 6 hours to polymerize the monomer. The resultant polymer particles were found to have a volume average particle size of 8.1 microns and an RAT value of 1.46.

The polymer particles were washed with a hydrochloric acid solution, and then with water several times, followed by drying in vacuo to provide toners having a triboelectric charge of -28 μC (microcoulomb)/g. The polymer was found to have a glass transition temperature of 65°C.

An amount of 100 parts by weight of the toners was mixed with 0.3 parts by weight on hydrophobic silica (R 972 available from Japan Aerosil K.K.) to provide a developing agent of which toner content was 5% by weight. The developing agent was used in an electrophotographic device (Model LED Printer K-II available from Nippon Kentech K.K.), and was found to provide high quality copy images with no fog or no unevenness in darkness in solid images and with high resolution, There were also made 10000 sheets of copies in succession to provide high quality copy images substantially the same in quality as that of initial stage of copying.

Example 2

An amount of 0.5 parts by weight of lauroyl peroxide were used to disperse the same carbon black as before, and otherwise in the same manner as in Example 1, an aqueous dispersion of the monomer composition was prepared. The droplets of the monomer composition in the dispersion was found to have a volume average particle size of 11.8 microns and an RAT value of 1.55.

The momoner was suspension-polymerized in the same manner as in Example 1 to provide toners having a volume average particle size of 11.7 microns, an RAT value of 1.48, and a triboelectric charge of -23.2 μC/g. The polymer was found to have a glass transition temperature of 65°C.

Using the toners thus prepared and in the same manner as in Example 1, a developing agent of which toner content was 5% by weight was prepared. The agent was also found to provide high quality copy images in the same test as in Example 1.

Reference Example 1

An amount of 12 parts by weight of sodium phosphate ($Na_3PO_4 \cdot 12H_2O$) was dissolved in 500 parts by weight of ion-exchanged water. An amount of 8 parts by weight of calcium chloride ($CaCl_2 \cdot 2H_2O$) was added under gentle stirring to the above aqueous solution, thereby to deposit calcium phosphate, whereupon the resultant dispersion was found to have a pH of 11.1.

There was prepared a monomer composition containing the same carbon black and charge controlling agent as before in the same manner as in Example 1. The monomer composition was added to the above dispersion of calcium phosphate, whereupon the dispersion was found to have a pH of 8.46, and stirred vigorously at a rate of 6000 rpm for 10 minutes with the same homogenizer as hereinbefore to prepare an aqueous dispersion of the monomer composition. The resultant droplets of the monomer composition were found to have a volume average particle size of 9.7 microns and an RAT value of 1.78. The droplets were further found to contain finely divided droplets of about 5 microns or less in size in an amount of 30%.

The aqueous dispersion of the monomer composition was stirred gently at 70°C for 6 hours to polymerize the monomer. The resultant polymer particles were found to have a volume average particle size of 9.6 microns and an RAT value of 1.75. These values were almost the same as those of the droplets of the monomer composition before the polymerization. The polymer particles were also found to have a wide particle size distribution.

The polymer particles were washed with a hydrochloric acid solution, and then with water several times, followed by drying in vacuo to provide toners.

Using the toners thus prepared and in the same manner as in Example 1, a developing agent of which toner content was 5% by weight was prepared.

The agent was found to provide copy images having much fog thereon and poor resolution in the same test as in Example 1.

Reference Example 2

An amount of 12 parts by weight of sodium phosphate ($Na_3PO_4 \cdot 12H_2O$) and 0.03 parts by weight of sodium dodecylbenzenesulfonate were dissolved in 500 parts by weight of ion-exchanged water. An amount of 8 parts by weight of calcium chloride ($CaCl_2$-$2H_2O$) was added under gentle stirring to the above aqueous solution, thereby to deposit calcium phosphate, whereupon the resultant dispersion was found to have a pH of 11.0.

There was prepared a monomer composition containing carbon black and charge controlling agent in the same manner as in Example 1. The monomer composition was added to the above dispersion of calcium phosphate, whereupon the dispersion was found to have a pH of 8.37, and stirred vigorously at a rate of 6000 rpm for 10 minutes with the same homogenizer as hereinbefore to prepare an aqueous dispersion of the monomer composition. the resultant droplets of the monomer composition were found to have a volume average particle size of 8.5 microns and an RAT value of 1.76. The droplets were further found to contain finely divided droplets of about 5 microns or less in size in an amount of 25%.

The aqueous dispersion of the monomer composition was stirred gently at 70°C for 6 hours to polymerize the monomer. The resultant polymer particles were found to have a volume average particle size of 8.2 microns and an RAT value of 1.77, and also a wide particle size distribution.

The polymer particles were washed with a hydrochloric acid solution, and then with water several times, followed by drying in vacuo to provide toners.

Using the toners thus prepared and in the same manner as in Example 1, a developing agent of which toner content was 5% by weight was prepared.

The agent was found to provide copy images having much fog thereon and poor resolution in the sane test as in Example 1.

Reference Example 3

An amount of 5.0 parts by weight of carbon black "Diablack" (tradename) #52 (volatile matters 0.8 %, pH 8.0, particle size 27 mμ, available from Mitsubishi Kasei Kogyo K.K., Japan) and 1 part by weight of lauroyl peroxide were added to and mixed with 50 parts by weight of styrene in a ball mill for 30 minutes to preliminarily disperse the carbon black in the monomer. The mixture was then further agitated in an autoclave at 70°C for 1 hour. After the dispersion operation as above, the carbon black was found about 0.1 μm in particle size and there took no sedimentation in the dispersion.

An amount of 0.4 parts by weight of an ethylene-vinyl acetate copolymer "Soablene CH" (tradename, available from Nippon Gosei Kagaku Kogyo K.K., Japan) as a dispersing agent and 1.0 part by weight of a negative

charge controlling agent, a dyestuff named "Spiron Black TRH" (tradename, available from Hodogaya Kagaku Kogyo K.K., Japan) were added to the dispersion, and stirred with a ball mill for 100 hours, to disperse the charge controlling agent in the monomer, After the dispersion operation as above, the charge controlling agent was found of about 0.3 μm in particle size, and was found not to sediment in the dispersion.

To the resultant monomer dispersion were when added 30 parts by weight of styrene, 20 parts by weight of butyl methacrylate, 0.2 parts by weight of divinylbenzene, 3 parts by weight of polypropylene was as an anti-offset agent, and then 3 parts by weight of azobisdimethylvaleronitrile, to form a monomer composition.

An amount of 400 parts by weight of an aqueous solution of 12 pats by weight of sodium phosphate ($Na_3PO_4 \cdot 12H_2O$) (having a pH of about 12) was prepared.

The above monomer composition was added to the aqueous alkaline solution of sodium phosphate under stirring at a rate of 6000 rpm for 10 minutes to disperse the monomer composition in the aqueous solution, to prepare an aqueous dispersion containing finely divided droplets of the monomer composition of about 3 microns in number average particle size.

Then an amount of 10 parts by weight of an aqueous solution of 8 parts by weight of calcium chloride ($CaCl_2 \cdot 2H_2O$) was added under stirring to the above aqueous dispersion of the monomer composition, thereby to deposit calcium phosphate, whereupon the resultant dispersion was found to have a pH of 9.10. The droplets of the mononer composition were found not to coagulate, but they were found to be stable as they were. The droplets were found to have a volume average particle size of 11.25 microns and contain a large quantities of finely divided particles of less than about 5 microns or less in size. Thus, the droplets were found to have a wide particle size distribution, and an RAT value of 2.372.

The monomer composition was polymerized in the same manner as in Example 1. The resultant polymer particles were found to have a volume average particle size of 11.20 microns and an RAT value of 2.063, and also a wide particle size distribution.

Using the toners thus prepared and in the same manner as in Example 1, a developing agent on which toner content was 5% by weight was prepared.

The agent was found to provide copy images having much fog thereon and poor resolution in the same test as in Example 1.

Example 3

The aqueous suspension of polymer particles prepared in Example 2 was continuously fed into an contiuous, annular, wet type agitation mill (Kobol Mill available from Shinko Pantech K.K.), as an example of such a mill is shown in Fig. 2, and the polymer particles were deformed under the conditions of temperature, suspension travelling speed and rotor peripheral speed shown in the Table 1. Zirconia spheres of 0.75-1.0 mm in diameter were used as a milling medium. The charge rate of the medium in the milling zone was 70%.

Thereafter a hydrochloric acid solution was added to the suspension of the thus deformed polymer particles to dissolve calcium phosphate. Then the polymer particles were washed with water, dried in vacuo, and classified to provide deformed toner particles.

The toner thus deformed was used in electrophotographic copying under the conditions of temperature of 23°C and relative humidity of 60% (normal temperature and normal humidity) and under the conditions of temperature of 30°C and relative humidity of 80% (high temperature and high humidity). The performance at the initial stage and after making 10000 sheets of copies were examined. Namely, the triboelectric charge of toners on the toner transfer member, adhesion of toner particles onto the member and quality of fixed images were measured. The results are shown in Tables 2 and 3.

The shape, average size and flatness of toner particles were measured with randomly selected 50 particles on through electromicrophotographs. The triboelectric charge of the toner particles on the toner transfer member was measured with the use of specific electric charge measuring device. Namely, the toner particles in a thin layer on the toner transfer member were absorbed and trapped into a gauge, and the specific electric charge of the absorbed toners were measured.

TABLE 1

	Examples		Comparative Examples			
	3	4	4[1]	5	6	7[2]
Polymer Particles[3]						
Average size (microns)	11.7	11.7	12.0	11.7	11.7	12.1
RAT Value	1.48	1.48	1.50	1.48	1.48	1.81
Deformation	Yes	Yes	No	No	Yes	Yes
Deformation Conditions						
Temperature (°C)	67	70	—	—	60	65
Peripheral speed of rotor (m/min.)	13	20	—	—	10	13
Average stay time (min.)	15	15	—	—	15	15
Form of Toner	disk	oval	formless	spherical	disk	disk
Average diameter (microns)	12.3	major 14.7 minor 9.9	—	—	12.2	13.0
Average thickness (microns)	5.8	5.1	—	—	7.6	6.0
Flatness	0.47	0.41	—	1.0	0.62	0.46

Notes 1) Produced by a crushing method.
2) Produced using polyvinyl alcohol as a suspendng agent.
3) As produced.

EP 0 524 016 A1

TABLE 2

Results under Normal Temperature and Normal Humidity	Examples		Comparative Examples			
	3	4	4[1]	5	6	7[2]
Electric charge (μC/g)						
Initial stage	−15	−15	−8	−6	−11	−11
After copying 10000 sheets	−14	−15	−4	—	—	−9
White lines on images						
After copying 10000 sheets	No	No	Yes	—	—	—
Adhesion of toners to toner transfer member	No	No	Yes	—	—	—
Image darkness						
Initial stage	1.42	1.41	1.20	1.02	1.30	1.30
After copying 10000 sheets	1.43	1.43	0.91	—	—	1.20
Fog darkness						
Initial stage	0.001	0.001	0.006	0.006	0.004	0.004
After copying 10000 sheets	0.001	0.001	0.010	—	—	0.007
Resolution of fine lines	Excellent	Excellent	Bad	Bad	No Good	No Good
Scattering of toners	No	No	Much	Much	Some	Some
Thickness of toners on toner transfer member (microns)	26	24	44	56	35	30

EP 0 524 016 A1

TABLE 3

Results under High Temperature and High Humidity	Examples		Comparative Examples			
	3	4	4[1]	5	6	7[2]
Electric charge (μC/g)						
Initial stage	−13	−13	−7	−5	−9	−8
After copying 10000 sheets	−13	−14	−2	—	—	−4
White lines on images						
After copying 10000 sheets	No	No	Yes	—	—	—
Adhesion of toners to toner transfer member	No	No	Yes	—	—	—
Image darkness						
Initial stage	1.43	1.42	1.15	0.99	1.25	—
After copying 10000 sheets	1.44	1.44	0.72	—	—	—
Fog darkness						
Initial stage	0.001	0.001	0.008	0.006	0.005	0.006
After copying 10000 sheets	0.002	0.002	0.013	—	—	0.011
Resolution of fine lines	Excellent	Excellent	Bad	Bad	No Good	Bad
Scattering of toners	No	No	Much	Much	Some	Much
Thickness of toners on toner transfer member (microns)	26	24	44	56	35	30

Example 4

The polymer particles were deformed under the conditions as indicated in Table 1, and otherwise in the same manner as in Example 3, a toner was prepared. The performance of the toner was examined in the same manner as in Example 3.

Reference Example 4

The performance of toner produced by a crushing method and available on the market was examined in

the same manner as in Example 3.

Reference Example 5

The performance of a toner prepared in Example 2 was examined as it was in the sane manner as in Example 3.

Reference Example 6

The aqueous suspension of polymer particles prepared in Example 2 was treated under the conditions as shown in Table 1 to provide deformed toner particles having a flatness of 0.62. The performance of the toner was examined in the same manner as in Example 3.

Reference Example 7

An amount of 0.5 parts by weight of lauroyl peroxide were used to disperse the same carbon black as before in the monomer. The thus prepared mixture of the monomer and carbon black was dispersed in 300 parts by weight of water containing 3 parts by weight of polyvinyl alcohol (having an average polymerization degree of 1700 and saponification degree of 80 mol%) as a suspending agent.

The suspension polymerization was carried out in the same manner as before to provide polymer particles wherein the polymer had a glass transition temperature of 63°C.

The aqueous suspension of polymer particles was treated under the conditions as shown in Table 1. Then, a mixture of 77% by volune of water and 23% by volume of methanol containing sodium hydroxide in an amount of ten times equivalent of the vinyl acetate component in the polyvinyl alcohol used was added to the suspension and stirred at 50°C for 3 hours to saponify the polyvinyl alcohol.

The resultant deformed polymer particles were recovered and washed with water, and then with aqueous solution containing hydrochloric acid in an amount equivalent to the amount of sodium hydroxide used to neutralize the sodium hydroxide. The polymer particles were dried under reduced pressures to provide toner particles having a flatness of 0.46.

The performance of the toner was examined in the same manner as in Example 3.

The results with the example 4 and reference examples 4-7 are indicated in Tables 2 and 3.

Toner particles made by a method according to a first aspect of the invention give, when deformed and used in a method according to a second aspect of the invention, an even layer of controllable thickness on the toner transfer member 13. The particles are then transferred by electrostatic attraction onto the photoconductive member 1 to develop its latent image to form a positive image, otherwise known as a toner image. The toner image is then transferred and fixed onto paper to give the desired hard copy.

As discussed above, an even thin layer of toner particles on the toner transfer member 13 gives a fog-free, high resolution copy, whose solid images are uniformly dark. Further, the quality of the image produced after many consecutive copies is the same as that of the copie first produced.

Claims

1. A method of producing toner particles for use in electrophotography which comprises carrying out the following steps in sequence:
   (a) mixing colorant particles with a momoner and pulverising the colorant particles in the monomer in the presence of a peroxide compound to disperse the colorant in the monomer evenly as finely divided particles;
   (b) adding an azobisnitrile polymerization initiator to the monomer;
   (c) dispersing the monomer in an aqueous alkaline medium containing a first water soluble inorganic salt to provide an aqueous alkaline dispersion of the monomer;
   (d) adding a second water soluble inorganic salt, which reacts with the first water soluble inorganic salt to form a salt which is insoluble or slightly soluble in water, to the aqueous alkaline disperion of the monomer to form such a salt under substantially neutral conditions;
   (e) adding an alkali to the aqueous dispersion of the monomer to stably disperse the monomer; and
   (f) suspension-polymerising the monomer to form polymer particles.

2. A method according to claim 1, in which the pH of the aqueous alkaline solution containing the first water

soluble inorganic salt is such that, when the second water soluble inorganic salt is added to the aqueous alkaline dispersion of the monomer, a water insoluble or slightly soluble salt deposits in the suspension under a substantially neutral pH of 6-7.

3. A method according to claim 1 or 2 in which the first and the second water insoluble salts are each used in an amount of 0.1-20 parts by weight in relation to 100 parts by weight of the monomer used.

4. A method according to any preceding claim in which the first water soluble inorganic salt is sodium phosphate and the second water soluble inorganic salt is calcium chloride.

5. A method of developing electrostatic images in an electrophotographic process which comprises providing an electrostatic charge on the surface of a photoconductive member (1), exposing the member (1) to an image to form thereon an electrostatic latent image, forming a layer having a controlled thickness of non-magnetic one-component toner particles (10) on the member while triboelectrifying the toner particles, and developing the latent image with the toner particles, the toner particles being composed mainly of disk-like toner particles having a diameter of 3-30 micrometres, a thickness of 1-15 micrometres and a flatness of not more than 0.5, the flatness of the disk-like toner particles being defined as the ratio of the average thickness to average diameter of the particles, or oval toner particles having a major axis of 3-30 micrometres in length, a minor axis of 1-25 micrometres in length and a flatness of not more than 0.5, the flatness of the oval particles being defined as the ratio of twice the average thickness to the sum of the lengths of the major and minor axes, or a mixture of the disk-like and oval particles.

6. A method of developing electrostatic images in an electrophotographic process which comprises providing an electrostatic charge on the surface of a photoconductive member (1), exposing the member (1) to an image to form thereon an electrostatic latent image, forming a layer having a controlled thickness of non-magnetic one-component toner particles (10) on a toner transfer member (13) while triboelectrifying the toner particles, and developing the latent image with toner particles transferred from the toner transfer member (13), the toner particles being composed mainly of disk-like toner particles having a diameter of 3-30 micrometres, a thickness of 1-15 micrometres and a flatness of not more than 0.5, the flatness of the disk-like toner particles being defined as the ratio of the average thickness to average diameter of the particles, or oval toner particles having a major axis of 3-30 micrometres in length, a minor axis of 1-25 micrometres in length and a flatness of not more than 0.5, the flatness of the oval particles being defined as the ratio of twice the average thickness to the sum of the lengths of the major and minor axes, or a mixture of the disk-like and oval particles.

7. A method of developing electrostatic images according to claim 5 or 6 characterised in that the toner particles are produced by a method according to any of claims 1 to 4.

FIG. 1

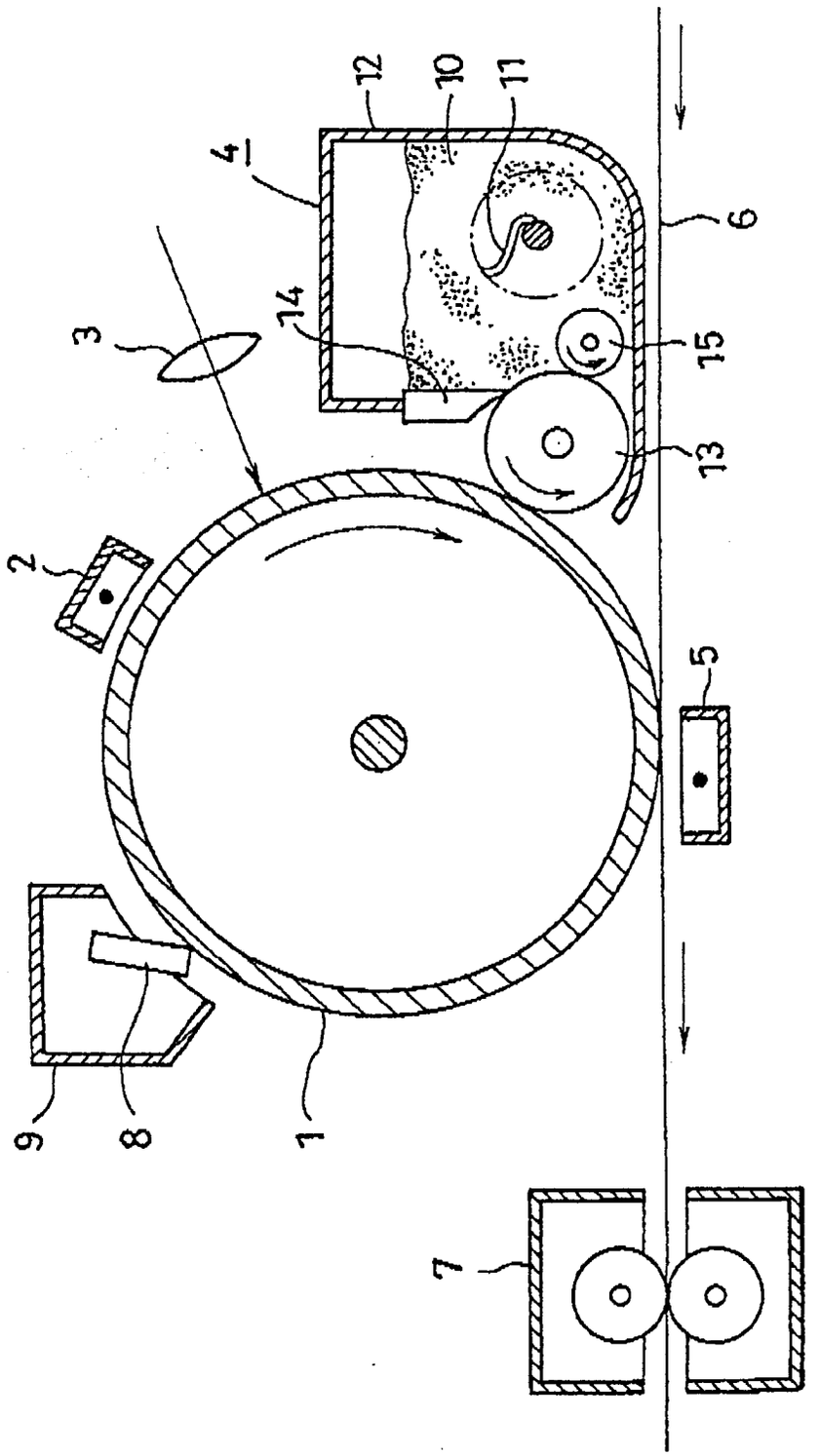
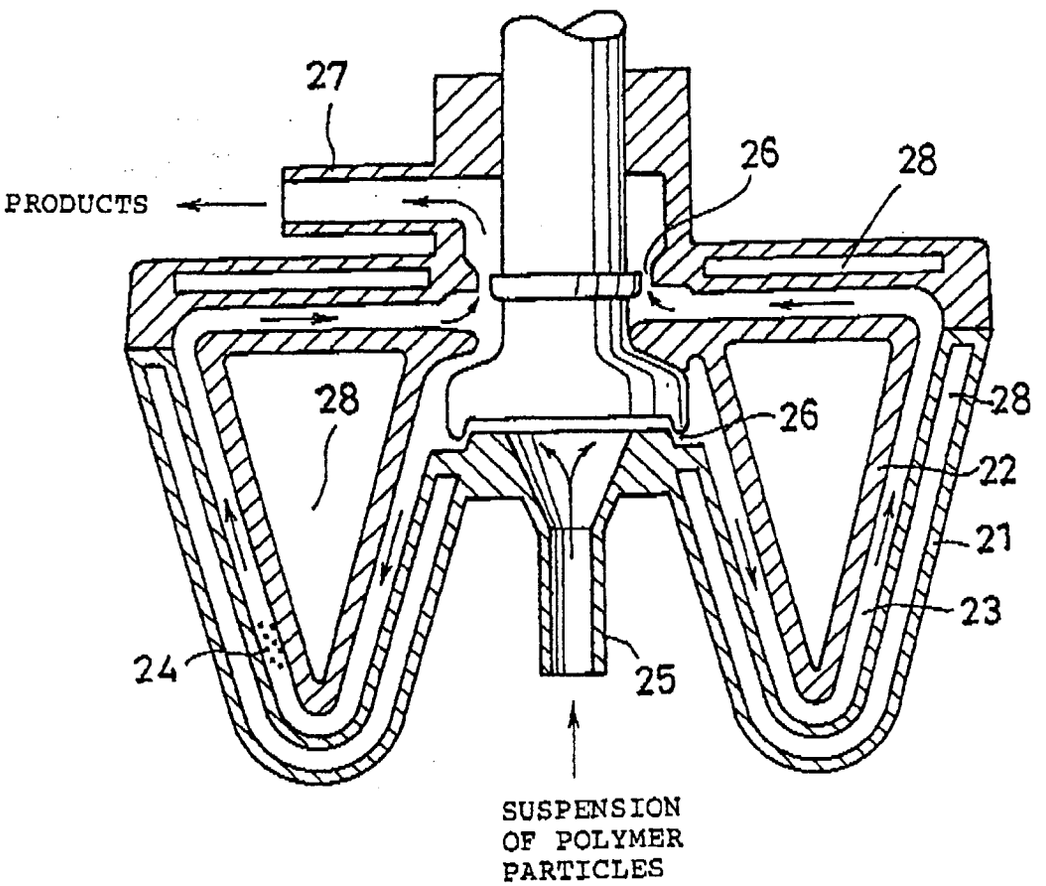


FIG. 2


27
PRODUCTS
26
28
28
26
28
22
21
23
24
25
SUSPENSION
OF POLYMER
PARTICLES

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 92 30 6582

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	EP-A-0 038 208 (XEROX CORPORATION) * page 5, line 1 - page 6, line 23; claims 1-8 *	1-7	G03G9/08
A	DE-A-2 026 390 (FUJI PHOTO FILM CO., LTD.) * example 1* * claims 1-14 *	1-7	
A	EP-A-0 297 839 (BANDO CHEMICAL INDUSTRIES, LIMITED) * page 8, line 3 - line 53; claims 1-12 *	1-7	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			G03G

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	22 SEPTEMBER 1992	HINDIAS E.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

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EPO FORM 1503 03.82 (P0401)