Description

The present invention relates to a developer for developing electrostatic images and to the combination of the aforesaid developer with an image forming device for developing electrostatic images on an electrostatic image-holding member. The invention also provides a method of developing an electrostatic image on an electrostatic image-forming member. The electrostatic latent images to be developed in this invention can be produced by electrophotography and electrostatic recording.

As image forming apparatus such as electrophotographic copying machines have come into increasingly widespread use, and as their range of uses has become extended, demand has arisen for improved image quality. For example in the copying of original images which are ordinary documents or books, it is desirable that even minute letters can be reproduced in fine and faithful detail without the reproduced image becoming thickened, distorted or broken. However, when an ordinary image forming apparatus such as a plain paper copying machine is used to form a latent image on a photosensitive member, and when that image comprises thin-line images of width a 100 microns or below, the thin-lines may be poorly reproduced and the clarity of the line images can be inadequate.

In particular, in recently developed image forming apparatus such as an electrophotographic printer using digital image signals, the desired latent image is formed by an array of dots of constant potential, and solid, half-tone and highlight portions of the image are expressed by variation in the dot density. However, if the dots are not correctly covered by toner particles and toner particles protrude from the dots, the problem can arise that there is not obtained a toner image having a gradation corresponding to the dot density ratio of the black portions and the white portions in the digitally produced latent image. Furthermore, as resolution is increased by decreasing the dot size in an attempt to improve image quality, reproduction of the small dot size latent image becomes poorer so that the image loses sharpness, is of low resolution and poor gradational characteristics.

On the other hand, in an electrophotographic copying machine or other image forming apparatus the phenomenon sometimes happens that that good quality images are produced initially, but the images deteriorate as copying or printing is continued. The reason for this phenomenon is believed to be that in successive copying operation only those toner particles which contribute to the developing operation become consumed, and toner particles having poor development characteristics remain in the developing device and accumulate.

A number of developers have been proposed for the purpose of improving image quality. For example, Japanese Laid Open Patent Application (JP-A KOKAI No. 3244/1976) corresponding to US Patent Nos. 3942979, 3969251 and 4112024) discloses a non-magnetic toner in which the particle size distribution is adjusted for the purpose of improvement in image quality. This toner comprises relatively coarse particles, about 25% or more of the toner particles by number having a particle size in the range 8 to 12 microns. However, our investigations have revealed that it is difficult to produce uniform and dense coverage of a latent image with toner particles using a toner having such particle sizes. Furthermore, the above-mentioned toner contains 30% or less by number (e.g. about 29% by number) of particles of size 5 microns or less and 5% or less by number (e.g. about 5% by number) of particles of size 20 microns or above. The toner therefore has a broad particle size distribution which tends to decrease the uniformity of the resulting image. In order to form a clear image using a toner having such relatively coarse particles and such a broad particle size distribution, it is necessary that any gaps between the toner particles should be filled by superposing the toner particles thickly one upon another, thereby enhancing the apparent image density. This gives rise to the further problem that the consumption of toner to give a desired image density is increased.

Japanese Laid Open Patent Application No. 72054/1979 (corresponding to US Patent No. 4284701) discloses a non-magnetic toner having a sharper particle size distribution than the toner mentioned above. In this toner, particles of intermediate weight have a relatively large particle size of 8.5-11 microns, which still leaves room for improvement from the standpoint of resolution.

Japanese Laid Open Patent Application No. 129437/1983 (corresponding to British Patent No. 2114310) discloses a non-magnetic toner in which the average particle size is 6-10 microns and the mode particle size is 5 to 8 microns. However, this toner only contains 15% by number or less of particles of size 5 microns or below which is a relatively small amount, and it tends to produce an insufficiently sharp image.

US Patent No. 4299900 discloses a jump development method using a developer containing 10 to 50 weight percent of magnetic toner particles of size 20 to 35 microns. In this method, the particle size distribution of the toner has been selected in order to improve the triboelectric charging of the magnetic toner, to enable a uniform and thin toner layer to form on a sleeve (developer carrying member) and to enhance the resistance of the toner to adverse environmental conditions. However, this toner does not fully satisfy the need for reproduction of thin lines at high resolution and there is room for further improvement.

Our investigations have revealed that toner particles having a particle size of 5 microns or below are pri-

marily responsible for clear reproduction of the outline of a latent image and of providing accurate and complete coverage of the whole of the latent image with the toner.

In particular, in the case of an electrostatic latent image formed on a photosensitive member, the field intensity at an edge portion thereof varies more sharply than that in inner portion thereof because the electric lines of force are more concentrated, so that the sharpness of the resultant image is determined by the quality of the toner particles that collect at the edge portion. Our investigations have shown that an effective solution to the problem of image sharpness can be provided by adjusting the quantity and state of distribution of toner particles of 5 microns or below.

Our investigations have further shown at relatively long ears or chains composed of magnetic toner particles can develop, and disturbances in the form of such ears can be present on the surface of a developer sleeve in the developing region which is undesirable. We have studied this problem in the light of the above-mentioned knowledge and thereby arrived at the present invention.

In one aspect the present invention provides a developer for developing electrostatic latent images having the features set out in claim 1.

In a further aspect the invention provides in combination a developer having the features set out in claim 1 and an image forming device having the features set out in claim 24.

In a further aspect the invention provides a method of developing an electrostatic latent image on an electrostatic image-holding member, the method comprising the steps of:

providing a developer having the features set out in claim 1, and carrying out the further steps set out in claim 26.

The invention also resides in the use of a developer as aforesaid in a process for developing images.

Embodiments of the invention can have a number of advantages. Such embodiments can provide a developer comprising a magnetic toner which can provide excellent thin-line reproducibility and gradational characteristics and provide high image density. Embodiments of such a magnetic toner can exhibit little change in performance even when used over an extended period, or under changing environmental conditions. Such embodiments can provide a toner having excellent transfer characteristics, and which in use is economic in terms of toner consumption, and embodiments of the present toner are suitable for use with an image forming apparatus using a digital image signal to provide good resolution, gradational characteristics and thin-line reproducibility.

BRIEF DESCRIPTION OF THE DRAWINGS

Figures 1 and 2 are a front sectional view and a sectional perspective view, respectively, of an apparatus embodiment for practicing multi-division classification;

Figure 3 is a schematic sectional view showing a developing device used for image formation in Examples and Comparative Examples;

Figure 4 is a graph obtained by plotting values of % by number (N)/% by volume (V) against % by number with respect to magnetic toner particles having a particle size of 5 microns or below;

Figure 5 is a graph showing the particle size distribution in the magnetic toner of Example 1; and

Figure 6 is a graph showing the particle size distribution in the magnetic toner of Comparative Example 1.

Various embodiments of the invention will now be described, by way of example only, with reference to the accompanying drawings, in which:

DETAILED DESCRIPTION OF THE INVENTION

The magnetic toner according to the present invention having the above-mentioned particle size distribution can faithfully reproduce thin lines in a latent image formed on a photosensitive member, and is excellent in reproduction of dot latent images such as halftone dot and digital images, whereby it provides images excellent in gradation and resolution characteristics. Further, the toner according to the present invention can retain a high image quality even in the case of successive copying or print-out, and can effect good development by using a smaller consumption thereof as compared with the conventional magnetic toner, even in the case of high-density images. As a result, the magnetic toner of the present invention is excellent in economical characteristics and further has an advantage in miniaturization of the main body of a copying machine or printer. Particularly, the developer of the present invention is useful as a one-component type developer without using carrier particles.

The reason for the above-mentioned effects of the magnetic toner of the present invention is not necessarily clear but may assumably be considered as follows.

The magnetic toner of the present invention is first characterized in that it contains 17 - 60 % by number of magnetic toner particles of 5 microns or below. Conventionally, it has been considered that magnetic toner particles of 5 microns or below are required to be positively reduced because the control of their charge amount is difficult, they impair the fluidity of the magnetic toner, and they cause toner scattering to contaminate the machine.

However, according to our investigation, it has been found that the magnetic toner particles of 5 microns or below are an essential component to form a high-quality image.

For example, we have conducted the following experiment.

Thus, there was formed on a photosensitive member a latent image wherein the surface potential on the photosensitive member was changed from a large developing potential contrast at which the latent image would easily be developed with a large number of toner particles, to a small developing potential contrast at which the latent image would be developed with only a small number of toner particles.

Such latent image was developed with a magnetic toner having a particle size distribution ranging from 0.5 to 30 microns. Then, the toner particles attached to the photosensitive member were collected and the particle size distribution thereof was measured. As a result, it was found that there were many magnetic toner particles having a particle size of 8 microns or below, particularly 5 microns or below. Based on such finding, it was discovered that when magnetic toner particles of 5 microns or below were so controlled that they were smoothly supplied for the development of a latent image formed on a photosensitive member, there could be obtained an image truly excellent in reproducibility, and the toner particles were faithfully attached to the latent image without protruding therefrom.

The magnetic toner of the present invention is secondly characterized in that it contains 1 - 23 % by number of magnetic toner particles of 8 - 12.7 microns. Such second feature relates to the above-mentioned necessity for the presence of the toner particles of 5microns or below.

As described above, the toner particles having a particle size of 5 microns or below have the ability to strictly cover a latent image and to faithfully reproduce it. On the other hand, in the latent image per se, the field intensity in its peripheral edge portion is higher than that in its central portion. Therefore, toner particles sometimes cover the inner portion of the latent image in a smaller amount than that in the edge portion thereof, whereby the image density in the inner portion appears to be lower. Particularly, the magnetic toner particles of 5 microns or below strongly have such tendency. However, we have found that when 1 - 23 % by number (preferably 8 - 20 % by number) of toner particles of 8 - 12.7 microns are contained in a toner, not only the above-mentioned problem can be solved but also the resultant image can be made clearer.

According to our knowledge, the reason for such phenomenon may be considered that the toner particles of 8 - 12.7 microns have suitably controlled charge amount in relation to those of 5 microns or below, and that these toner particles are supplied to the inner portion of the latent image having a lower field intensity than that of the edge portion thereby to compensate the decrease in cover-up of the toner particles to the inner portion as compared with that in the edge portion, and to form a uniform developed image. As a result, there may be provided a sharp image having a high-image density and excellent resolution and gradation characteristic.

The third feature of the magnetic toner of the present invention is that toner particles having a particle size of 5 microns or smaller contained therein satisfy the following relation between their percentage by number (N) and percentage by volume (V):

$$N/V = -0.04\,N + k,$$

wherein $4.5 \leqq k \leqq 6.5$, and $17 \leqq N \leqq 60$.

The region satisfying such relationship is shown in Fig. 4. The magnetic toner according to the present invention which has the particle size distribution satisfying such region, in addition to the above-mentioned features, can attain excellent developing characteristic.

According to our investigation on the state of the particle size distribution with respect to toner particles of 5 microns or below, we have found that there is a suitable state of the presence of fine powder in magnetic toner particles. More specifically, in the case of a certain value of N, it may be understood that a large value of N/V indicates that the particles of 5 microns or below (e.g., 2 - 4 microns) are significantly contained, and a small value of N/V indicates that the frequency of the presence of particles near 5 microns (e.g., 4 - 5 microns) is high and that of particles having a smaller particle size is low. When the value of N/V is in the range of 2.1 - 5.82, N is in the range of 17 - 60, and the relation represented by the above-mentioned formula is satisfied, good thin-line reproducibility and high resolution are attained.

In the magnetic toner of present invention, magnetic toner particles having a particle size of 16 microns or larger are contained in an amount of 2.0 % by volume or below. The amount of these particles may preferably be as small as possible.

As described hereinabove, the magnetic toner of the present invention alleviates the problems encountered in the prior art from a viewpoint utterly different from that in the prior art, and can meet the recent severe

demand for high image quality.

Hereinbelow, the present invention will be described in more detail.

In the present invention, the magnetic toner particles having a particle size of 5 microns or smaller are contained in an amount of 17 - 60 % by number, preferably 25 - 50 % by number, more preferably 30 - 50 % by number, based on the total number of particles. If the amount of magnetic toner particles is smaller than 17 % by number, the toner particles effective in enhancing image quality is insufficient. Particularly, as the toner particles are consumed in successive copying or print-out, the component of effective magnetic toner particles is decreased, and the balance in the particle size distribution of the magnetic toner shown by the present invention is deteriorated, whereby the image quality gradually decreases. On the other hand, the above-mentioned amount exceeds 60 % by number, the magnetic toner particles are liable to be mutually agglomerated to produce toner agglomerates having a size larger than the original particle size. As a result, roughened images are provided, the resolution is lowered, and the density difference between the edge and inner portions is increased, whereby an image having an inner portion with a little low density is liable to occur.

In the magnetic toner of the present invention, the amount of particles in the range of 8 - 12.7 microns is 1 - 23 % by number, preferably 8 - 20 % by number. If the above-mentioned amount is larger than 23 % by number, not only the image quality deteriorates but also excess development (i.e., excess cover-up of toner particles) occurs, thereby to invite an increase in toner consumption. On the other hand, the above-mentioned amount is smaller than 1 %, it is difficult to obtain a high image density.

In the present invention, the percentage by number (N %) and that by volume (V %) of magnetic toner particles having a particle size of 5 micron or below satisfy the relationship of $N/V = -0.04 N + k$, wherein k represents a positive number satisfying $4.5 \leqq k \leqq 6.5$. The number k may preferably satisfy $4.5 \leqq k \leqq 6.0$, more preferably $4.5 \leqq k \leqq 5.5$. Further, as described above, the percentage N satisfies $17 \leqq N \leqq 60$, preferably $25 \leqq N \leqq 50$, more preferably $30 \leqq N \leqq 50$.

If $k < 4.5$, magnetic toner particles of 5.0 microns or below are insufficient, and the resultant image density, resolution and sharpness decrease. When fine toner particles in a magnetic toner, which have conventionally been considered useless, are present in an appropriate amount, they attain closest packing of toner in development (i.e., in a latent image formed on a photosensitive drum) and contribute to the formation of a uniform image free of coarsening. Particularly, these particles fill thin-line portions and contour portions of an image, thereby to visually improve the sharpness thereof. If $k < 4.5$ in the above formula, such component becomes insufficient in the particle size distribution, the above-mentioned characteristics become poor.

Further, in view of the production process, a large amount of fine powder must be removed by classification in order to satisfy the condition of $k < 4.5$. Such process is disadvantageous in yield and toner costs.

On the other hand, if $k > 6.5$, an excess of fine powder is present, whereby the resultant image density is liable to decrease in successive copying. The reason for such phenomenon may be considered that an excess of fine magnetic toner particles having an excess amount of charge are triboelectrically attached to a developing sleeve and prevent normal toner particles from being carried on the developing sleeve and being supplied with charge.

In the magnetic toner of the present invention, the amount of magnetic toner particles having a particle size of 16 microns or larger is 2.0 % by volume or smaller, preferably 1.0 % by volume or smaller, more preferably 0.5 % by volume or smaller.

If the above amount is larger than 2.0 % by volume, these particles impair thin-line reproducibility. In addition, toner particles of 16 microns or larger are present as protrusions on the surface of the thin layer of toner particles formed on a photosensitive member by development, and they vary the transfer condition for the toner by irregulating the delicate contact state between the photosensitive member and a transfer paper (or a transfer-receiving paper) by the medium of the toner layer. As a result, there occurs an image with transfer failure.

In the present invention, the number-average particle size of the toner is 4 - 9 microns, preferably 4 - 8 microns. This value closely relates to the above-mentioned features of the magnetic toner according to the present invention. If the number-average particle size is smaller than 4 microns, there tend to occur problems such that the amount of toner particles transferred to a transfer paper is insufficient and the image density is low, in the case of an image such as graphic image wherein the ratio of the image portion area to the whole area is high. The reason for such phenomenon may be considered the same as in the above-mentioned case wherein the inner portion of a latent image provides a lower image density than that in the edge portion thereof. If the number-average particle size exceeds 9 microns, the resultant resolution is not good and there tends to occur a phenomenon such that the image quality is lowered in successive use even when it is good in the initial stage thereof.

The particle distribution of a toner is measured by means of a Coulter counter in the present invention, while it may be measured in various manners.

Coulter counter Model TA--II (available from Coulter Electronics Inc.) is used as an instrument for meas-

urement, to which an interface (available from Nikkaki K.K.) for providing a number-basis distribution, and a volume-basis distribution and a personal computer CX-1 (available from Canon K.K.) are connected.

For measurement, a 1 %-NaCl aqueous solution as an electrolytic solution is prepared by using a reagent-grade sodium chloride. Into 100 to 150 ml of the electrolytic solution, 0.1 to 5 ml of a surfactant, preferably an alkylbenzenesulfonic acid salt, is added as a dispersant, and 2 to 20 mg, of a sample is added thereto. The resultant dispersion of the sample in the electrolytic liquid is subjected to a dispersion treatment for about 1 - 3 minutes by means of an ultrasonic disperser, and then subjected to measurement of particle size distribution in the range of 2 - 40 microns by using the above-mentioned Coulter counter Model TA-II with a 100 micron-aperture to obtain a volume-basis distribution and a number-basis distribution. Form the results of the volume-basis distribution and number-basis distribution, parameters characterizing the magnetic toner of the present invention may be obtained.

In the present invention, the true density of the magnetic toner may preferably be 1.45 - 1.70 g/cm^3, more preferably 1.50 - 1.65 g/cm^3. When the true density is in such range, the magnetic toner according to the present invention having a specific particle size distribution functions most effectively in view of high image quality and stability in successive use.

If the true density of the magnetic toner particles is smaller than 1.45, the weight of the particle per se is too light and there tend to occur reversal fog, and deformation of thin lines, scattering and deterioration in resolution because an excess of toner particles are attached to the latent image. On the other hand, the true density of the magnetic toner is larger than 1.70, there occurs an image wherein the image density is low, thin lines are interrupted, and the sharpness is lacking. Further, because the magnetic force becomes relatively strong in such case, ears of the toner particles are liable to be lengthened or converted into a branched form. As a result, the image quality is disturbed in the development of a latent image, whereby a coarse image is liable to occur.

In the present invention, the true density of the magnetic toner is measured in the following manner which can simply provide an accurate value in the measurement of fine powder, while the true density can be measured in some manners.

There are provided a cylinder of stainless steel having an inside diameter of 10mm and a length of about 5cm, and a disk (A) having an outside diameter of about 10mm and a height of about 5mm, and a piston (B) having an outside diameter about 10 mm and a length of about 8cm, which are capable of being closely inserted into the cylinder.

In the measurement, the disk (A) is first disposed on the bottom of the cylinder and about 1 g of a sample to be measured is charged in the cylinder, and the piston (B) is gently pushed into the cylinder. Then, a force of 400 Kg/cm^2 is applied to the piston by means of a hydraulic press, and the sample is pressed for 5 min. The weight (Wg) of thus pressed sample is measured and the diameter (D cm) and the height (L cm) thereof are measured by means of a micrometer. Based on such measurement, the true density may be calculated according to the following formula:

$$\text{True density (g/cm}^3\text{)} = W/(\pi \times (D/2)^2 \times L)$$

In order to obtain better developing characteristics, the magnetic toner of the present invention may preferably have the following magnetic characteristics: a residual magnetization σ_r of 1 - 5 emu/g, more preferably 2 - 4.5 emu/g; a saturation magnetization σ_s of 20 - 40 emu/g; and a coercive force Hc of 40 - 100 Öe. These magnetic characteristics may be measured under a magnetic field for measurement of 1,000 Öe.

The binder for use in constituting the toner according to the present invention, when applied to a hot pressure roller fixing apparatus using an oil applicator, may be a known binder resin for toners. Examples thereof may include: homopolymers of styrene and its derivatives, such as polystyrene, poly-p-chlorostyrene, and polyvinyltoluene; styrene copolymers, such as styrene-p-chlorostyrene copolymer, styrene-vinyltoluene copolymer, styrene-vinylnaphthalene copolymer, styrene-acrylate copolymer, styrene-methacrylate copolymer, styrene-methyl α-chloromethacrylate copolymer, styrene-acrylonitrile copolymer, styrene-vinyl methyl ether copolymer, styrene-vinyl ethyl ether copolymer, styrene-vinyl methyl ketone copolymer, styrene-butadiene copolymer, styrene-isoprene copolymer, and styrene-acrylonitrile-indene copolymer; polyvinyl chloride, phenolic resin, natural resin-modified phenolic resin, natural resin-modified maleic acid resin, acrylic resin, methacrylic resin, polyvinyl acetate, silicone resin, polyester resin, polyurethane, polyamide resin, furan resin, epoxy resin, xylene resin, polyvinylbutyral, terpene resin, coumarone-indene resin and petroleum resin.

In a hot pressure roller fixing system using substantially no oil application, serious problems are provided by an offset phenomenon that a part of toner image on toner image-supporting member is transferred to a roller, and an intimate adhesion of a toner on the toner image-supporting member. As a toner fixable with a less heat energy is generally liable to cause blocking or caking in storage or in a developing apparatus, this should be also taken into consideration. With these phenomenon, the physical property of a binder resin in a toner is most concerned. According to our study, when the content of a magnetic material in a toner is de-

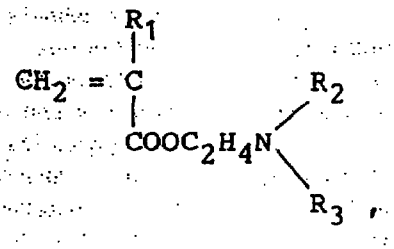
creased, the adhesion of the toner onto the toner image-supporting member mentioned above is improved, while the offset is more readily caused and also the blocking or caking are also more liable. Accordingly, when a hot roller fixing system using almost no oil application is adopted in the present invention, selection of a binder resin becomes more serious. A preferred binder resin may for example be a crosslinked styrene copolymer, or a crosslinked polyester. Examples of comonomers to form such a styrene copolymer may include one or more vinyl monomers selected from: monocarboxylic acid having a double bond and their substituted derivatives, such as acrylic acid, methyl acrylate, ethyl acrylate, butyl acrylate, dodecyl acrylate, octyl acrylate, 2-ethylhexyl acrylate, phenyl acrylate, methacrylic acid, methyl methacrylate, ethyl methacrylate, butyl methacrylate, octyl methacrylate, acrylonitrile, methacrylonitrile, and acrylamide; dicarboxylic acids having a double bond and their substituted derivatives, such as maleic acid, butyl maleate, methyl maleate, and dimethyl maleate; vinyl esters, such as vinyl chloride, vinyl acetate, and vinyl benzoate; ethylenic olefins, such as ethylene, propylene, and butylene; vinyl ketones, such as vinyl methyl ketone, and vinyl hexyl ketone; vinyl ethers, such as vinyl methyl ether, vinyl ethyl ether, and vinyl isobutyl ethers. As the crosslinking agent, a compound having two or more polymerizable double bonds may principally be used. Examples thereof include: aromatic divinyl compounds, such as divinylbenzene, and divinylnaphthalene; carboxylic acid esters having two double bonds, such as ethylene glycol diacrylate, ethylene glycol dimethacrylate, and 1, 3-butanediol diacrylate; divinyl compounds such as divinyl ether, divinyl sulfide and divinyl sulfone; and compounds having three or more vinyl groups. these compounds may be used singly or in mixture. In view of the fixability and anti-offset characteristic of the toner, the crosslinking agent may preferably be used in an amount of 0.01 - 10 wt. %, preferably 0.05 - 5 wt. %, based on the weight of the binder resin.

For a pressure-fixing system, a known binder resin for pressure-fixable toner may be used. Examples thereof may include: polyethylene, polypropylene, polymethylene, polyurethane elastomer, ethylene-ethyl acrylate copolymer, ethylene-vinyl acetate copolymer, ionomer resin, styrene-butadiene copolymer, styrene-isoprene copolymer, linear saturated polyesters and paraffins.

In the magnetic toner of the present invention, it is preferred that a charge controller may be incorporated in the toner particles (internal addition), or may be mixed with the toner particles (external addition). By using the charge controller, it is possible to most suitably control the charge amount corresponding to a developing system to be used. Particularly, in the present invention, it is possible to further stabilize the balance between the particle size distribution and the charge. As a result, when the charge controller is used in the present invention, it is possible to further clarify the above-mentioned functional separation and mutual compensation corresponding to the particle size ranges, in order to enhance the image quality.

Examples of the charge controller may include; nigrosine and its modification products modified by a fatty acid metal salt, quaternary ammonium salts, such as tributylbenzyl-ammonium-1 hydroxy-4-naphthosulfonic acid salt, and tetrabutylammonium tetrafluoroborate; diorganotin oxides, such as dibutyltin oxide, dioctyltin oxide, and dicyclohexyltin oxide; and diorganotin borates, such as dibutyltin borate, dioctyltin borate, and dicyclo-hexyltin borate. These positive charge controllers may be used singly or as a mixture of two or more species. Among these, a nigrosine-type charge controller or a quaternary ammonium salt charge controller may particularly preferably be used.

As another type of positive charge controller, there may be used a homopolymer of a monomer having an amino group represents by the formula;



wherein R_1 represents H or CH_3; and R_2 and R_3 each represent a substituted or unsubstituted alkyl group (preferably C_1 - C_4); or a copolymer of the monomer having an amine group with another polymerizable monomer such as styrene, acrylates, and methacrylates as described above. In this case, the positive charge controller also has a function of a binder.

On the other hand, a negative charge controller can be used in the present invention. Examples thereof may include an organic metal complex or a chelate compound. More specifically there may preferably be used aluminum acethyl-acetonate, iron (II) acetylacetonate, and a 3,5-di-tertiary butylsalicylic acid chromium. There may more preferably be used acetylacetone complexes, or salicylic acid-type metal salts or complexes. Among

these, salicylic acid-type complexes or metal salts may particularly preferably be used.

It is preferred that the above-mentioned charge controller is used in the form of fine powder. In such case, the number-average particle size thereof may preferably be 4 microns or smaller, more preferably 3 microns or smaller.

In the case of internal addition, such charge controller may preferably be used in an amount of 0.1 - 20 wt. parts, more preferably 0.2 - 10 wt. parts, per 100 wt. parts of a binder resin.

It is preferred that silica fine powder is added to the magnetic toner of the present invention.

In the magnetic toner of the present invention having the above-mentioned particle size distribution characteristic, the specific surface area thereof becomes larger than that in the conventioned toner. In a case where the magnetic toner particles are caused to contact the surface of a cylindrical electroconductive non-magnetic sleeve containing a magnetic field-generating means therein in order to triboelectrically charge them, the frequency of the contact between the toner particle surface and the sleeve is increased as compared that in the conventional magnetic toner, whereby the abrasion of the toner particle or the contamination of the sleeve is liable to occur. However, when the magnetic toner of the present invention is combined with the silica fine powder, the silica fine powder is disposed between the toner particles and the sleeve surface, whereby the abrasion of the toner particle is remarkably reduced.

Thus, the life of the magnetic toner and the sleeve may be lengthened and the chargeability may stably be retained. As a result, there can be provided a developer comprising a magnetic toner showing excellent characteristics in long-time use. Further, the magnetic toner particles having a particle size of 5 microns or smaller, which play an important role in the present invention, may produce a better effect in the presence of the silica fine powder, thereby to stably provide high-quality images.

The silica fine powder may be those produced through the dry process and the wet process. The silica fine powder produced through the dry process is preferred in view of the anti-filming characteristic and durability thereof.

The dry process referred to herein is a process for producing silica fine powder through vapor-phase oxidation of a silicon halide. For example, silica powder can be produced according to the method utilizing pyrolytic oxidation of gaseous silicon tetrachloride in oxygen-hydrogen flame, and the basic reaction scheme may be represented as follows:

$$SiCl_4 + 2H_2 + O_2 \rightarrow SiO_2 + 4HCl.$$

In the above preparation step, it is also possible to obtain complex fine powder of silica and other metal oxides by using other metal halide compounds such as aluminum chloride or titanium chloride together with silicon halide compounds. Such is also included in the fine silica powder to be used in the present invention.

Commercially available fine silica powder formed by vapor phase oxidation of a silicon halide to be used in the present invention include those sold under the trade names as shown below.

AEROSIL	130
(Nippon Aerosil Co.)	200
	300
	380
	OX 50
	TT 600
	MOX 80
	COK 84

Cab-O-Sil (Cabot Co.)	M-5
	MS-7
	MS-75
	HS-5
	EH-5
Wacker HDK (WACKER-CHEMIE GMBH)	N 20
	V 15
	N 20E
	T 30
	T 40
D-C Fine Silica (Dow Corning Co.)	
Fransol (Fransil Co.)	

On the other hand, in order to produce silica powder to be used in the present invention through the wet process, various processes known heretofore may be applied. For example, decomposition of sodium silicate with an acid represented by the following scheme may be applied:

$$Na_2O \cdot xSiO_2 + HCl + H_2O \rightarrow SiO_2 \cdot nH_2O + NaCl.$$

In addition, there may also be used a process wherein sodium silicate is decomposed with an ammonium salt or an alkali salt, a process wherein an alkaline earth metal silicate is produced from sodium silicate and decomposed with an acid to form silicic acid, a process wherein a sodium silicate solution is treated with an ion-exchange resin to form silicic acid, and a process wherein natural silicic acid or silicate is utilized.

The silica power to be used herein may be anhydrous silicon dioxide (silica), and also a silicate such as aluminum silicate, sodium silicate, potassium silicate, magnesium silicate and zinc silicate.

Commercially available fine silica powders formed by the wet process include those sold under the trade names as shown below:

Carplex (available from Shionogi Seiyaku K.K.)
Nipsil (Nippon Silica K.K.)
Tokusil, Finesil (Tokuyama Soda K.K.)
Bitasil (Tagi Seihi K.K.)
Silton, Silnex (Mizusawa Kagaku K.K.)
Starsil (Kamishima Kagaku K.K.)
Himesil (Ehime Yakuhin K.K.)
Siloid (Fuki Devison Kagaku K.K.)
Hi-Sil (Pittsuburgh Plate Glass Co.)
Durosil, Ultrasil (Fulstoff-Gesellshaft Marquart)
Manosil (Hardman and Holden)
Hoesch (Chemische Fabrik Hoesch K-G)
Sil-Stone (Stoner Rubber Co.)
Nalco (Nalco Chem. Co.)
Quso (Philadilphia Quartz Co.)
Imsil (Illinois Minerals Co.)
Calcium Silikat (Chemische Fabrik Hoesch, K-G)

Calsil (Fullstoff-Gesellschaft Marquart)
Fortafil (Imperial Chemical Industries)
Microcal (Joseph Crosfield & Sons. Ltd.)
Manosil (Hardman and Holden)
Vulkasil (Farbenfabriken Bayer, A.G.)
Tufknit (Durham Chemicals, Ltd.)
Silmos (Shiraishi Kogyo K.K.)
Starlex (Kamishima Kagaku K.K.)
Furikosil (Tagi Seihi K.K.)

Among the above-mentioned silica powders, those having a specific surface area as measured by the BET method with nitrogen adsorption of 30 m^2/g or more, particularly 50 - 400 m^2/g, provides a good result.

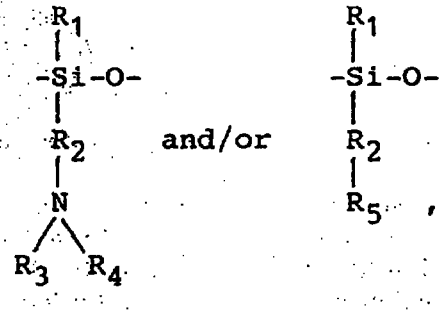
In the present invention, the silica fine powder may preferably be used in an amount of 0.01 - 8 wt. parts, more preferably 0.1 - 5 wt. parts, with respect to 100 wt. parts of the magnetic toner.

In case where the magnetic toner of the present invention is used as a positively chargeable magnetic toner, it is preferred to use positively chargeable fine silica powder rather than negatively chargeable fine silica powder, in order to prevent the abrasion of the toner particle and the contamination on the sleeve surface, and to retain the stability in chargeability.

In order to obtain positively chargeable silica fine powder, the above-mentioned silica powder obtained through the dry or set process may be treated with a silicone oil having an organic groups containing at least one nitrogen atom in its side chain, a nitrogen-containing silane coupling agent, or both of these.

In the present invention, "positively chargeable silica" means one having a positive triboelectric charge with respect to iron powder carrier when measured by the blow-off method.

The silicone oil having a nitrogen atom in its side chain to be used in the treatment of silica fine powder may be a silicone oil having at least the following partial structure:



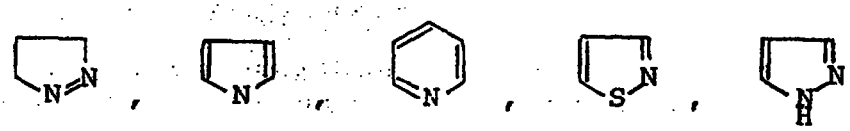
wherein R_1 denotes hydrogen, alkyl, aryl or alkoxyl; R_2 denotes alkylene or phenylene; R_3 and R_4 denotes hydrogen, alkyl, or aryl; and R_5 denotes a nitrogen-containing heterocyclic group. The above alkyl, aryl, alkylene and phenylene group can contain an organic group having a nitrogen atom, or have a substituent such as halogen within an extent not impairing the chargeability. The above-mentioned silicone oil may preferably be used in an amount of 1 - 50 wt. %, more preferably 5 - 30 wt. %, based on the weight of the silica fine powder.

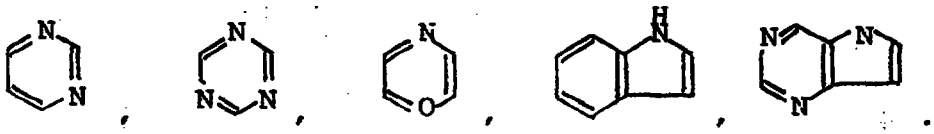
The nitrogen-containing silane coupling agent used in the present invention generally has a structure represented by the following formula:

$$R_mSiY_n,$$

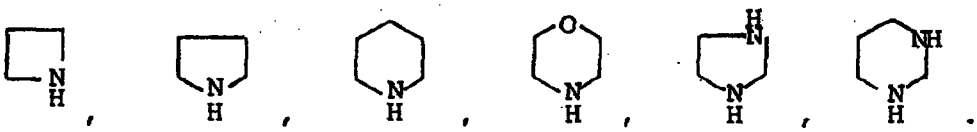
wherein R is an alkoxy group or a halogen atom; Y is an amino group or an organic group having at least one amino group or nitrogen atom; and m and n are positive integers of 1 - 3 satisfying the relationship of m + n = 4.

The organic group having at least one nitrogen group may for example be an amino group having an organic group as a substituent, a nitrogen-containing heterocyclic group, or a group having a nitrogen-containing heterocyclic group. The nitrogen-containing heterocyclic group may be unsaturated or saturated and may respectively be known ones. Examples of the unsaturated heterocyclic ring structure providing the nitrogen-containing heterocyclic group may include the following:





Examples of the saturated heterocyclic ring structure include the following:



The heterocyclic groups used in the present invention may preferably be those of five-membered or six-membered rings in consideration of stability.

Examples of the silane coupling agent include:
aminopropyltrimethoxysilane, aminopropyltriethoxysilane, dimethylaminopropyltrimethoxysilane, diethylaminopropyltrimethoxysilane, dipropylaminopropyltrtimethoxysilane, dibutylaminopropyltrimethoxysilane, monobutylaminopropyltrimethoxysilane, dioctylaminopropyltrimethoxysilane, dibutylaminopropyldimethoxysilane, dibutylaminopropylmonomethoxysilane, dimethylaminophenyltriethoxysilane, trimethoxysilyl-γ-propylphenylamine, and trimethoxysilyl-γ-propylbenzyl-amine. Further, examples of the nitrogen-containing heterocyclic compounds represented by the above structural formulas include:
trimethoxysilyl-γ-propylpiperidine, trimethoxysilyl-γ-propylmorpholine, and trimethoxysilyl-γ propylimidazole.
The above-mentioned nitrogen-containing silane coupling agent may preferably be used in an amount of 1 - 50 wt. %, more preferably 5 - 30 wt. %, based on the weight of the silica fine powder.

The thus treated positively chargeable silica powder shows an effect when added in an amount of 0.01 - 8 wt. parts and more preferably may be used in an amount of 0.1 - 5 wt. parts, respectively with respect to the positively chargeable magnetic toner to show a positive chargeability with excellent stability. As a preferred mode of addition, the treated silica powder in an amount of 0.1 - 3 wt. parts with respect to 100 wt. parts of the positively chargeable magnetic toner should preferably be in the form of being attached to the surface of the toner particles. The above-mentioned untreated silica fine powder may be used in the same amount as mentioned above.

The silica fine powder used in the present invention may be treated as desired with another silane coupling agent or with an organic silicon compound for the purpose of enhancing hydrophobicity. The silica powder may be treated with such agents in a known manner so that they react with or are physically adsorbed by the silica powder. Examples of such treating agents include hexamethyldisilazane, trimethylsilane, trimethylchlorosilane, trimethylethoxysilane, dimethyldichlorosilane, methyltrichlorosilane, allyldimethylchlorosilane, allylphenyldichlorosilane, benzyldimethylchlrosilane, bromomethyldimethylchlorosilane, α-chloroethyltrichlorosilane, β-chloroethyltrichlorosilane, chloromethyldimethylchlorosilane, triorganosilylmercaptans such as trimethylsilylmercaptan, triorganosilyl acrylates, vinyldimethylacetoxysilane, dimethylethoxysilane, dimethyldimethoxysilane, diphenyldiethoxysilane, hexamethyldisiloxane, 1,3-divinyltetramethyldisiloxane, 1,3-diphenyltetramethyldisiloxane, and dimethylpolysiloxane having 2 to 12 siloxane units per molecule and containing each one hydroxyl group bonded to Si at the terminal units. These may be used alone or as a mixture of two or more compounds. The above-mentioned treating agent may preferably be used in an amount of 1 - 40 wt. % based on the weight of the silica fine powder. However, the above treating agent may be used so that the final product of the treated silica fine powder shows positive chargeability.

In the present invention, it is preferred to add fine powder of a fluorine-containing polymer such as polytetra-fluoroethylene, polyvinylidene fluoride, or tetrafluoroethylene-vinylidene fluoride copolymer. Among these, polyvinylidene fluoride fine powder is particularly preferred in view of fluidity and abrasiveness. Such powder of a fluorine-containing polymer may preferably be added to the toner in an amount of 0.01 - 2.0 wt.%,

particularly 0.02 - 1.0 wt.%.

In a magnetic toner wherein the silica fine powder and the above-mentioned fluorine-containing fine powder are combined, while the reason is not necessarily clear, there occurs a phemomenon such that the state of the presence of the silica attached to the toner particle is stabilized and, for example, the attached silica is prevented from separating from the toner particle so that the effect thereof on toner abrasion and sleeve contamination is prevented from decreasing, and the stability in chargeability can further be enhanced.

An additive may be mixed in the magnetic toner of the present invention as desired. More specifically, as a colorant, known dyes or pigments may be used generally in an amount of 0.5 - 20 wt. parts per 100 wt. parts of a binder resin. Another optional additive may be added to the toner so that the toner will exhibit further better performances. Optional additives to be used include, for example, lubricants such as zinc stearate; abrasives such as cerium oxide and silicone carbide; flowability improvers such as colloidal silica and aluminum oxide; anti-caking agent; or conductivity-imparting agents such as carbon black and tin oxide.

In order to improve releasability in hot-roller fixing, it is also a preferred embodiment of the present invention to add to the magnetic toner a waxy material such as low-molecular weight polyethylene, low-molecular weight polypropylene, microcrystalline wax, carnauba wax, sasol wax or paraffin wax preferably in an amount of 0.5 - 5 wt. %.

The magnetic toner of the present invention contains a magnetic material which may also function as a colorant. The magnetic material to be contained in the magnetic toner may be one or a mixture of: iron oxides such as magnetite, hematite, ferrite and ferrite containing excess iron; metals such as iron, cobalt and nickel, alloys of these metals with metals such as aluminum, cobalt, copper, lead, magnesium, tin, zinc, antimony, beryllium, bismuth, cadmium, calcium, manganese, selenium, titanium, tungsten and vanadium.

These ferromagnetic materials may preferable be in the form of particles having an average particle size of the order of 0.1 - 1 micron, preferably 0.1 - 0.5 microns and be used in the toner in an amount of about 60 - 110 wt. parts, particularly 65 - 100 wt. parts, per 100 wt. parts of a resin component (or per 100 wt. parts of a binder resin in a case where the magnetic toner does not contain a resin other than the binder resin).

The magnetic toner for developing electrostatic images according to the present invention may be produced by sufficiently mixing magnetic powder with a vinyl on non-vinyl thermoplastic resin such as those enumerated hereinbefore, and optionally, a pigment or dye as colorant, a charge controller, another additive, etc., by means of a mixer such as a ball mill, etc.; then melting and kneading the mixture by hot kneading means such as hot rollers, kneader and extruder to disperse or dissolve the pigment or dye, and optional additives, if any, in the melted resin; cooling and crushing the mixture; and subjecting the powder product to precise classification to form magnetic toner according to the present invention.

The magnetic toner according to the present invention may preferably be applied to an image forming apparatus for practicing an image forming method wherein a latent image is developed while toner particles are caused to fly from a toner-carrying member such as a cylindrical sleeve to a latent image carrying member such as a photosensitive member.

The magnetic toner is supplied with triboelectric charge mainly due to the contact thereof with the sleeve surface and applied onto the sleeve surface in a thin layer form. The thin layer of the magnetic toner is formed so that the thickness thereof is smaller than the clearance between the photosensitive member and the sleeve in a developing region. In the development of a latent image formed on the photosensitive member, it is preferred to cause the magnetic toner particles having triboelectric charge to fly from the sleeve to the photosensitive member, while applying an alternating electric field between the photosensitive member and the sleeve.

Examples of the alternating electric field may include a pulse electric field, or an electric field based on an AC bias or a superposition of AC and DC biases.

Incidentally, in the present invention, the thin-line reproducibility may be measured in the following manner.

An original image comprising thin lines accurately having a width of 100 microns is copied under a suitable copying condition, i.e., a condition such that a circular original image having a diameter of 5 mm and an image density of 0.3 (halftone) is copied to provide a copy image having an image density ofo 0.3 - 0.5, thereby to obtain a copy image as a sample for measurement. An enlarged monitor image of the sample is formed by means of a particle analyzer (Luzex 450, mfd. by Nihon Regulator Co. Ltd.) as a measurement device, and the line width is measured by means of an indicator. Because the thin line image comprising toner particles has unevenness in the width direction, the measurement points for the line width are determined so that they correspond to the average line width, i.e., the average of the maximum and minimum line widths. Based on such measurement, the value (%) of the thin-line reproducibility is calculated according to the following formula:

$$\frac{\text{Line width of copy image obtained by the measurement}}{\text{Line width of the original (100 microns)}} \times 100$$

Further, in the present invention, the resolution may be measured in the following manner.

There is formed ten species of original images comprising a pattern of five thin lines which have equal

line width and are disposed at equal intervals equal to the line width. In these ten species of original images, thin lines are respectively drawn so that they provide densities of 2.8, 3.2, 3.6, 4.0, 4.5, 5.0, 5.6, 6.3, 7.1, and 8.0 lines per 1 mm. These ten species of original images are copied under the above-mentioned suitable copying conditions to form copy images which are then observed by means of a magnifying glass. The value of the resolution is so determined that it corresponds to the maximum number of thin lines (lines/mm) of an image wherein all the thin lines are clearly separated from each other. As the above-mentioned number is larger, it indicates a higher resolution.

Hereinbelow, the present invention will be described in further detail with reference to Examples, by which the present invention is not limited at all. In the following formulations, "parts" are parts by weight.

Example 1

Styrene/butyl acrylate/divinyl benzene copolymer (copolymerization wt. ratio: 80/19.5/0.5, weight-average molecular weight: 320,000)	100 wt.parts
Tri-iron tetraoxide (average particle size = 0.2 micron)	80 wt.parts
Nigrosin (number-average particle size = about 3 microns)	4 wt.parts
Low-molecular weight propylene-ethylene copolymer	4 wt.parts

The above ingredients were well blended in a blender and melt-kneaded at 150 °C by means of a two-axis extruder. The kneaded product was cooled, coarsely crushed by a cutter mill, finely pulverized by means of a pulverizer using jet air stream, and classified by a fixed-wall type wind-force classifier (DS-type Wind-Force Classifier, mfd. by Nippon Pneumatic Mfd. Co. Ltd.) to obtain a classified powder product. Ultra-fine powder and coarse power were simultaneously and precisely removed from the classified powder by means of a multi-division classifier utilizing a Coanda effect (Elbow Jet Classifier available from Nittetsu Kogyo K.K.), thereby to obtain black fine powder (magnetic toner) having a number-average particle size of 7.4 microns. When when thus obtained black fine powder was mixed with iron powder carrier and thereafter the triboelectric charge thereof was measured, it showed a value of +8 μC/g.

The number-basis distribution and volume-basis distribution of the thus obtained magnetic toner of positively chargeable black fine powder were measured by means of a Coulter counter Model TA-II with a 100 micron-aperture in the above-described manner. The thus obtained results are shown in the following Table 1 and Figure 5.

Table 1

Size (μm)	Number of particles	% by number (N)		% by volume (V)	
		Distribution	Accumulation	Distribution	Accumulation
2.00 - 2.52	2374	2.3	2.3	0.0	0.0
2.52 - 3.17	4351	4.2	6.6	0.4	0.4
3.17 - 4.00	9556	9.3	15.9	1.9	2.3
4.00 - 5.04	20048	19.5	35.4	8.1	10.3
5.04 - 6.35	26486	25.8	61.3	19.7	30.0
6.35 - 8.00	25653	25.0	86.3	35.1	65.1
8.00 -10.08	12200	11.9	98.2	27.2	92.3
10.08 -12.70	1815	1.8	99.9	7.2	99.5
12.70 -16.00	66	0.1	100.0	0.5	100.0
16.00 -20.20	5	0.0	100.0	0.0	100.0
20.20 -25.40	0	0.0	100.0	0.0	100.0
25.40 -32.00	0	0.0	100.0	0.0	100.0
32.00 -40.30	0	0.0	100.0	0.0	100.0
40.30 -50.80	0	0.0	100.0	0.0	100.0

Figure 1 schematically shows the classification step using the multi-division classifier, and Figure 2 shows

a sectional perspective view of the multi-division classifier.

0.5 wt. part of positively chargeable hydrophobic dry process silica (BET specific surface area: 200 m^2/g) was added to 100 wt. parts of the magnetic toner of black fine powder obtained above and mixed therewith by means of a Henschel mixer thereby to obtain a positively chargeable one-component developer comprising a magnetic toner.

The above-mentioned magnetic toner showed a particle size distribution and various characteristics as shown in Table 3 appearing hereinafter.

The thus prepared one-component developer was charged in an image forming (developing) device as shown in Fig. 3, and a developing test was conducted.

The developing conditions used in this instance is explained with reference to Figure 3. In Figure 3, the one-component developer 31 contained in a developer chamber 39 is applied in a thin layer form onto the surface of a cylindrical sleeve 33 of stainless steel as a toner-carrying means rotating in the direction of an arrow 36 by the medium of a magnetic blade 32 as a means for forming the layer of the toner. The clearance between the sleeve 33 and the blade 32 is set to about 250 microns. The sleeve 33 contains a fixed magnet 35 as a magnet means. The fixed magnet 35 produces a magnetic field of 1000 gauss in the neighborhood of the sleeve surface in the developing region where the sleeve 33 is disposed near to a photosensitive drum 34, as an electrostatic image-holding means, comprising an organic photoconductor layer carrying a negative latent image. The minimum space between the sleeve 33 and the photosensitive drum 34 rotating in the direction of an arrow 37 is set to about 300 microns by means of a spacer roller (not shown) as a means for maintaining the space. The spacer roller has a disk-like shape having a diameter larger than that of the sleeve 33, and a thickness of about 5 mm - 1 cm. Two spacer rollers are generally disposed at the both ends of the cylindrical sleeve 33, so that the center thereof corresponds to the rotation axis of the sleeve 33 and they contact the photosensitive drum 34. The spacer roller may be disposed so as to be rotatable or not.

In the development, a bias of 2000 Hz/1350 Vpp obtained by superposing an AC bias and a DC bias was applied between the photosensitive drum 34 and the sleeve by an alternating electric field-applying means 38. The layer of the one-component developer formed on the sleeve 33 had a thickness of about 75-150 microns, and the magnetic toner formed ears having a height of about 95 microns under the magnetic field due the fixed magnet 35.

By using the above-mentioned device, a negative latent image formed on the photosensitive drum 34 was developed by causing the one-component developer 31 having positive triboelectric charge to fly to the latent image. Thereafter, the resultant toner image was transferred to plain paper by using a negative corona transfer means and then fixed thereto by a hot pressure roller fixing means. Such image formation tests were successively conducted 10,000 times thereby to provide 10,000 sheets of toner images. The thus obtained results are shown in Table 4 appearing hereinafter.

As apparent from Table 4, both of the line portion and large image area portion of the letters showed a high image density. The magnetic toner of the present invention was excellent in thin-line reproducibility and resolution, and retained good image quality in the initial stage even after 10,000 sheets of image formations. Further, the copying cost per one sheet was low, whereby the magnetic toner of the present invention was excellent in economical characteristics.

Hereinbelow, the multi-division classifier and the classification step used in this instance are explained with reference to Figures 1 and 2.

Referring to Figures 1 and 2, the multi-division classifier has side walls 22, 23 and 24, and a lower wall 25. The side wall 23 and the lower wall 25 are provided with knife edge-shaped classifying wedges 17 and 18, respectively, whereby the classifying chamber is divided into three sections. At a lower portion of the side wall 22, a feed supply nozzle 16 opening into the classifying chamber is provided. A Coanda black 26 is disposed along the lower tangential line of the nozzle 16 so as to form a long elliptic arc shaped by bending the tangential line downwardly. The classifying chamber has an upper wall 27 provided with a knife edge-shaped gas-intake wedge 19 extending downwardly. Above the classifying chamber, gas-intake pipes 14 and 15 opening into the classifying chamber are provided. In the intake pipes 14 and 15, a first gas introduction control means 20 and a second gas introduction control means 21, respectively, comprising, e.g., a damper, are provided; and also static pressure gauges 28 and 29 are disposed communicatively with the pipes 14 and 15, respectively. At the bottom of the classifying chamber, exhaust pipes 11, 12 and 13 having outlets are disposed corresponding to the respective classifying sections and opening into the chamber.

Feed powder to be classified is introduced into the classifying zone through the supply nozzle 16 under reduced pressure. The feed powder thus supplied are caused to fall along curved lines 30 due to the Coanda effect given by the Coanda block 26 and the action of the streams of high-speed air, so that the feed powder is classified into coarse powder 11, black fine powder 12 having prescribed volume-average particle size and particle size distribution, and ultra-fine powder 13.

Example 2

A magnetic toner was prepared in the same manner as in Example 1 except that the amount of magnetic powder to be added thereto was changed and micropulverization and classification conditions were controlled to obtain a toner having characteristics as shown in Table 3 appearing hereinafter. The thus obtained toner was evaluated in the same manner as in Example 1.

As a result, as shown in Table 4 appearing hereinafter, clear high-quality images were stably obtained.

Example 3

A magnetic toner was prepared in the same manner as in Example 1 except that the amount of magnetic powder to be added thereto was changed and micropulverization and classification conditions were controlled to obtain a toner having characteristics as shown in Table 3 appearing hereinafter. The thus obtained toner was evaluated in the same manner as in Example 1.

As a result, as shown in Table 4 appearing hereinafter, clear high-quality images were stably obtained.

Example 4

0.5 wt. part of positively chargeable hydrophobic dry process silica and 0.3 wt. part of polyvinylidene fluoride fine powder (average primary particle size: about 0.3 micron, weight-average molecular weight (Mw): 300,000) were added to 100 wt. parts of the black fine powder obtained in Example 1, and mixed therewith by means of a Henschel mixer thereby to obtain a one-component developer.

The thus obtained developer was evaluated in the same manner as in Example 1. As a result, as shown in Table 4 appearing hereinafter, the were obtained better images excellent in image density and image quality.

Example 5

Crosslinked polyester resin (Mw = 50,000, glass transition point Tg = 60 °C)	100 wt.parts
3,5-di-t-butylsalicylic acid metal salt	1 wt.part
Tri-iron tetroxide (average particle size = 0.2 micron)	70 wt.parts
Low-molecular weight propylene-ethylene copolymer	3 wt.parts

By using the above materials, black fine powder was prepared in the same manner as in Example 1.

0.3 wt. part of negatively chargeable hydrophobic silica (BET specific surface area: 130 m^2/g) was added to 100 wt. parts of the black fine powder (magnetic toner) obtained above and mixed therewith by means of a Henschel mixer thereby to obtain a negatively chargeable one-component developer.

The above-mentioned black fine powder showed a particle size distribution, etc., as shown in Table 3 appearing hereinafter.

The thus prepared one-component developer was charged in a copying machine (NP-7550, mfd. by Canon K.K.) having an amorphous silicon photosensitive drum capable of forming a negative electrostatic latent image and image formation tests of 10,000 sheets were conducted.

As a result, as shown in Table 4 appearing hereinafter, clear high-quality images were stably obtained.

Example 6

The positively chargeable one-component developer prepared in Example 1 as charged in a digital-type copying machine (NP-9330, mfd. by Canon K.K.) having an amorphous silicon photosensitive drum and image formation tests of 10,000 sheets were conducted by developing a positive electrostatic latent image by a reversal development system.

As a result, as shown in Table 4 appearing hereinafter, the thin-line reproducibility and resolution were excellent and there were obtained clear images having a high gradational characteristic.

Example 7

Black fine powder as shown in Table 3 was prepared in a similar manner as in Example 1.

0.6 wt. part of positively chargeable hydrophobic silica was added to 100 wt. parts of the black fine powder obtained above and mixed therewith to obtain a positively chargeable one-component developer.

The thus prepared one-component developer was charged in a commercially available copying machine (NP-3525, mfd. by Canon K.K.) having a photosensitive drum comprising an organic photoconductor and image formation tests of 10,000 sheets were conducted.

The results are shown in Table 4 appearing hereinafter.

Comparative Example 1

Black fine powder (magnetic toner) as shown in Table 3 was prepared in the same manner as in Example 1, except that two fixed-wall type wind-force classifiers used in Example 1 were used for the classification instead of the combination of the fixed-wall type wind-force classifier and the multi-division classifier used in Example 1.

In the thus prepared magnetic toner of Comparative Example 1, percentage by number of the magnetic toner particles of 5 microns or smaller was smaller than the range thereof defined in the present invention, the volume-average particle size was larger than the range thereof defined in the present invention, and the value of (% by number (N))/(% by volume (V)) is larger than the range thereof defined in the present invention, whereby the conditions required in the present invention were not satisfied. The particle size distribution of magnetic toner obtained above is shown in the following Table 2 and Figure 6.

Table 2

Size (μm)	Number of particles	% by number (N)		% by volume (V)	
		Distribution	Accumulation	Distribution	Accumulation
2.00 - 2.52	992	1.4	1.4	0.0	0.0
2.52 - 3.17	1035	1.4	2.8	0.0	0.0
3.17 - 4.00	1210	1.7	4.5	0.0	0.0
4.00 - 5.04	3093	4.3	8.8	0.6	0.6
5.04 - 6.35	3189	11.4	20.3	3.2	3.8
6.35 - 8.00	15353	21.4	41.7	10.8	14.7
8.00 - 10.08	19040	26.6	68.3	21.5	36.1
10.08 - 12.70	15920	22.2	90.5	33.7	69.9
12.70 - 16.00	6161	8.6	99.1	25.8	95.7
16.00 - 20.20	584	0.8	100.0	4.3	100.0
20.20 - 25.40	25	0	100.0	0.0	100.0
25.40 - 32.00	1	0	100.0	0.0	100.0
32.00 - 40.30	0	0	100.0	0.0	100.0
40.30 - 50.80	0	0	100.0	0.0	100.0

0.5 wt. part of positively chargeable hydrophobic dry process silica was added to 100 wt. parts of the mag-

netic toner of black fine powder obtained above mixed therewith in the same manner as in Example 1 thereby to obtain a one-component developer. The thus obtained developer was subjected to image formation tests under the same conditions as in Example 1.

Referring to Figure 3, the height of ears formed in the developing region of the sleeve 33 was about 165 microns which was longer than that in Example 1. In the resultant images, the toner particles remarkably protruded from the latent image formed on the photosensitive member, the thin-line reproducibility was 135 % which was poorer than that in Example 4, and the resolution was 4.5 lines/mm. Further, after 1000 sheets of image formations, the image density in the solid black pattern decreased and the thin line reproducibility and resolution deteriorated. Moreover, the toner consumption was large.

The results are shown in Table 4 appearing hereinafter.

Comparative Example 2

Evaluation was conducted in the same manner as in Example 1 except that a toner as shown in Table 3 was used instead of the magnetic toner used in Example 1.

In the resultant images, thin lines were contaminated in several places presumably due to the aggregates of toner particles, and the resolution was 4.5 line/mm. The solid black pattern, particularly the inner portion thereof, had a lower image density than that in the line image and the edge portion of the image. Further, fog contamination in spot forms occurred, and the image quality was further deteriorated in successive copying.

Comparative Example 3

Evaluation was conducted in the same manner as in Example 1 except that a toner as shown in Table 3 was used instead of the magnetic toner used in Example 1.

The developed image formed on the drum had relatively good image quality, while it was somewhat disturbed. However, the toner image was remarkably disturbed in the transfer step, whereby transfer failure occurred and the image density decreased. Particularly, in successive copying, the image density was further decreased and the image quality was further deteriorated because poor toner particles remained and accumulated in the developing device.

Comparative Example 4

Evaluation was conducted in the same manner as in Example 1 except that a toner as shown in Table 3 was used instead of the magnetic toner used in Example 1.

In the resultant images, the image density was low and the contour was unclear and the sharpness was lacking, because the cover-up of toner particles to the edge portions of images was poor. Further, the resolution and gradational characteristic were also poor. When successive copying was conducted, the sharpness, thin-line reproducibility and resolution were further deteriorated.

Comparative Example 3

Evaluation was conducted in the same manner as in Example 1 except that a toner as shown in Table 3 was used instead of the magnetic toner used in Example 1.

In the resultant images, the image density, resolution and the thin line reproducibility were all poor. When the ears of toner particles formed on the sleeve as the toner-carrying member of the developing device were observed, they were long and sparse. As a result, when the toner particles were caused to fly to the photosensitive member, because the ears were too long, the toner particles protruded from the latent image whereby trailing and scattering of the toner occurred. Further, the image density was low because of coarse cover-up of the toner particles.

The results in Examples 1 - 7 and Comparative Examples 1 - 5 described above are inclusively shown in the following Tables 3 and 4.

Table 3-1

	Particle size distribution of toner				
	% by number of particles ≤ 5 µm	% by volume of particles ≥ 16 µm	% by number of particles of 8 - 12.7 µm	Volume-average particle size (µm)	(% by number)/(% by volume) of particles ≤ 5 µm
Example 1	35	0.0	14	7.4	3.4
2	46	0.3	11	6.5	3.3
3	20	0.5	23	8.5	5.0
4	35	0.3	14	7.4	3.6
5	40	0.5	12	7.5	3.9
6	35	0.3	14	7.4	3.6
7	57	0.2	10	5.7	2.5
Comparative Example 1	8.8	4.3	48.8	11.3	14.5
2	68	0.2	7	6.5	1.5
3	30	4	17	7.5	6.1
4	43	0.5	7	6.8	2.2
5	12	0.2	56	9.5	2.5

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Table 3-2

	True density of toner (g/cm^3)	Magnetic characteristics of toner		
		Saturation magnetization σ_s (emu/g)	Residual magnetization σ_r (emu/g)	Coercive force Hc (Öe)
Example 1	1.56	27	3.2	91
2	1.69	38	4.2	92
3	1.51	25	2.8	90
4	1.56	27	3.2	91
5	1.50	26	1.4	48
6	1.56	27	3.2	91
7	1.62	31	3.7	90
Comparative Example 1	1.43	22	2.3	90
2	1.69	36	4.4	91
3	1.47	25	1.5	65
4	1.77	43	5.0	107
5	1.43	24	1.4	49

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Table 4-1

	Initial stage			
	Dmax *1 (5 mm diameter)	Dmax *2 (solid black portion)	Thin-line reproducibility	Resolution (lines/mm)
Example 1	1.32	1.32	105 %	6.3
2	1.34	1.32	102 %	6.3
3	1.31	1.30	108 %	5.6
4	1.38	1.38	105 %	6.3
5	1.34	1.33	105 %	6.3
6	1.38	1.38	100 %	7.1
7	1.34	1.30	109 %	5.6
Comparative Example 1	1.31	1.30	135 %	4.5
2	1.34	1.23	125 %	4.5
3	1.24	1.20	115 %	5.6
4	1.23	1.20	110 %	5.6
5	1.19	1.12	135 %	4.0

*1 The image density of a copy image obtained by copying an original circular image which had a diameter of 5 mm and comprised a solid black pattern.

*2 The image density of a copy image obtained by copying an A-3 original image which comprised a solid black pattern.

Table 4-2

	After 10,000 sheets of image formations				
	Dmax (5mm diameter)	Dmax (Solid black portion)	Thin-line reproducibility	Resolution (lines/mm)	Toner consumption (g/one sheet)
Example 1	1.36	1.35	104 %	6.3	0.032
2	1.37	1.37	102 %	6.3	0.030
3	1.33	1.32	110 %	5.6	0.033
4	1.40	1.39	100 %	6.3	0.036
5	1.34	1.33	105 %	6.3	0.035
6	1.40	1.40	100 %	7.1	0.035
7	1.34	1.29	115 %	5.6	0.030
Comparative Example 1	1.31	1.25	150 %	4.0	0.055
2	1.33	1.19	140 %	4.0	0.040
3	1.20	1.03	135 %	4.0	0.039
4	1.21	1.10	125 %	4.0	0.041
5	1.15	1.04	140 %	4.0	0.053

Examples 8 - 10

Three species of magnetic toners respectively having characteristics as shown in the following Table 5 were prepared in the same manner as in Example 1, except that the amount of magnetic powder to be added

thereto was changed and micropulverization and classification conditions were controlled to obtain a toner having characteristics as shown in Table 5.

Table 5

	Particle size distribution of toner				
	% by number of particles ≤ 5 µm	% by volume of particles ≥ 16 µm	% by number of particles of 8 – 12.7 µm	volume-average particle size (µm)	(% by number)/(% by volume) of particles ≤ 5 µm
Example 8	18	0.2	20	7.7	5.6
9	58	0.5	9	5.1	4.0
10	19	0.0	17	8.5	3.9

Three species of one-component magnetic developers were prepared in the same manner as in Example 1 except that the above-mentioned magnetic toners of Examples 8 - 10 were respectively used. The thus prepared developers were respectively subjected to image formation tests in the same manner as in Example 1.

As a result, each developer showed good developing characteristics similarly as in Example 1. However, in the developer of Example 8, the thin-line reproducibility and resolution were somewhat inferior to those in Example 1. In the developer of Example 9, the stability in image quality in successive copying was somewhat inferior to that in Example 1. Further, in the developer of Example 10, the image density in the solid black portion was somewhat inferior to that in Example 1.

Figure 4 shows a graph obtained by plotting values of % by number (N)/% by volume (V) against % by number with respect to magnetic toner particles having a particle size of 5 microns or below in Examples and Comparative Examples. In Figure 4, the portion surrounded by solid lines denotes the range as defined by the present invention. The symbols "E-1" to "E-10" respectively denote the above-mentioned values obtained in Examples 1 - 10, and the symbols "C-1" to "C-5" respectively denote the above-mentioned values obtained in Comparative Examples 1 - 5.

As described hereinabove, the magnetic toners outside the range defined by the present invention were inferior to the magnetic toners according to the present invention with respect to the thin-line reproducibility resolution, image density in the solid black portion, fog and/or the toner consumption.

Example 11

A magnetic toner was prepared in the same manner as in Example 1 except that a small amount (55 wt. parts) of the magnetic material was used.

A one-component magnetic developer was prepared in the same manner as in Example 1 except that the above-prepared magnetic toner was used. The thus prepared developer was subjected to image formation tests in the same manner as in Example 1.

In the resultant image, a somewhat high degree of fog was observed as compared with that in Example 1, and the thin-line reproducibility was somewhat inferior to that in Example 1.

Example 12

A magnetic toner was prepared in the same manner as in Example 1 except that a larger amount (120 wt. parts) of the magnetic material was used.

A one-component magnetic developer was prepared in the same manner as in Example 1 except that the above-prepared magnetic toner was used. The thus prepared developer was subjected to image formation tests in the same manner as in Example 1.

In the resultant image, the image density in the solid black portion was somewhat low and the sharpness of the toner image was somewhat inferior as compared with those in Example 1.

Claims

1. A developer for developing electrostatic images, comprising a magnetic toner comprising a binder resin and magnetic powder, characterised in that:

said magnetic toner contains 17 - 60 % by number of magnetic toner particles having a particle size of 5 μm or smaller, 1 - 23 % by number of magnetic toner particles having a particle size of 8 - 12.7 μm, and 2.0 % by volume or less of magnetic toner particles having a particle size of 16 μm or larger;

said magnetic toner has a volume-average particle size of 4 - 9 μm; and

said magnetic toner particles having a particle size of 5 μm or smaller have a particle size distribution satisfying the following formula:

$$N/V = -0.04N + k,$$

wherein N denotes the percentage by number of magnetic toner particles having a particle size of 5 μm or smaller, V denotes the percentage by volume of magnetic toner particles having a particle size of 5 μm or smaller, k denotes a positive number of 4.5 - 6.5, and N denotes a positive number of 17 - 60.

2. A developer according to Claim 1, wherein the magnetic toner has a true density of 1.45 - 1.70 g/cm^3.

3. A developer according to Claim 1, wherein the magnetic toner has a true density of 1.50 - 1.65 g/cm^3.

* C L M S *

Three species of one-component magnetic developers were prepared in the same manner as in Example 1 except that the above-mentioned magnetic toners of Examples 8 - 10 were respectively used. The thus prepared developers were respectively subjected to image formation tests in the same manner as in Example 1.

As a result, each developer showed good developing characteristics similarly as in Example 1. However, in the developer of Example 8, the thin-line reproducibility and resolution were somewhat inferior to those in Example 1. In the developer of Example 9, the stability in image quality in successive copying was somewhat inferior to that in Example 1. Further, in the developer of Example 10, the image density in the solid black portion was somewhat inferior to that in Example 1.

Figure 4 shows a graph obtained by plotting values of % by number (N)/% by volume (V) against % by number with respect to magnetic toner particles having a particle size of 5 microns or below in Examples and Comparative Examples. In Figure 4, the portion surrounded by solid lines denotes the range as defined by the present invention. The symbols "E-1" to "E-10" respectively denote the above-mentioned values obtained in Examples 1 - 10, and the symbols "C-1" to "C-5" respectively denote the above-mentioned values obtained in Comparative Examples 1 - 5.

As described hereinabove, the magnetic toners outside the range defined by the present invention were inferior to the magnetic toners according to the present invention with respect to the thin-line reproducibility resolution, image density in the solid black portion, fog and/or the toner consumption.

Example 11

A magnetic toner was prepared in the same manner as in Example 1 except that a small amount (55 wt. parts) of the magnetic material was used.

A one-component magnetic developer was prepared in the same manner as in Example 1 except that the above-prepared magnetic toner was used. The thus prepared developer was subjected to image formation tests in the same manner as in Example 1.

In the resultant image, a somewhat high degree of fog was observed as compared with that in Example 1, and the thin-line reproducibility was somewhat inferior to that in Example 1.

Example 12

A magnetic toner was prepared in the same manner as in Example 1 except that a larger amount (120 wt. parts) of the magnetic material was used.

A one-component magnetic developer was prepared in the same manner as in Example 1 except that the above-prepared magnetic toner was used. The thus prepared developer was subjected to image formation tests in the same manner as in Example 1.

In the resultant image, the image density in the solid black portion was somewhat low and the sharpness of the toner image was somewhat inferior as compared with those in Example 1.

Claims

1. A developer for developing electrostatic images, comprising a magnetic toner comprising a binder resin and magnetic powder, characterised in that:

said magnetic toner contains 17 - 60 % by number of magnetic toner particles having a particle size of 5 μm or smaller, 1 - 23 % by number of magnetic toner particles having a particle size of 8 - 12.7 μm, and 2.0 % by volume or less of magnetic toner particles having a particle size of 16 μm or larger;

said magnetic toner has a volume-average particle size of 4 - 9 μm; and

said magnetic toner particles having a particle size of 5 μm or smaller have a particle size distribution satisfying the following formula:

$$N/V = -0.04N + k,$$

wherein N denotes the percentage by number of magnetic toner particles having a particle size of 5 μm or smaller, V denotes the percentage by volume of magnetic toner particles having a particle size of 5 μm or smaller, k denotes a positive number of 4.5 - 6.5, and N denotes a positive number of 17 - 60.

2. A developer according to Claim 1, wherein the magnetic toner has a true density of 1.45 - 1.70 g/cm^3.

3. A developer according to Claim 1, wherein the magnetic toner has a true density of 1.50 - 1.65 g/cm^3.

* C L M S *

4. A developer according to Claim 1, 2 or 3, wherein the magnetic toner contains 25 - 50 % by number of magnetic toner particles having a particle size of 5 μm or smaller.

5. A developer according to Claim 1, 2 or 3, wherein the magnetic toner contains 30 - 50 % by number of magnetic toner particles having a particle size of 5 μm or smaller.

6. A developer according to any preceding claim, wherein the magnetic toner contains 8 - 20 % by number of magnetic toner particles having a particle size of 8 - 12.7 μm.

7. A developer according to any preceding claim, wherein the magnetic toner particles having a particle size of 5 μm or smaller satisfy the following formula:

$$N/V = -0.04N + k,$$

wherein k denotes a number of 4.5 - 6.0, and N denotes a number of 25 - 60.

8. A developer according to any preceding claim, wherein the magnetic toner particles having a particle size of 5 μm or smaller satisfy the following formula:

$$N/V = -0.04N + k,$$

wherein k denotes a number of 4.5 - 5.5, and N denotes a number of 30 - 50.

9. A developer according to any preceding claim, wherein the magnetic toner has a volume-average particle size of 4 - 8 μm.

10. A developer according to any preceding claim, wherein the magnetic powder is present in an amount of 60 - 110 wt. parts per 100 wt. parts of a resin component, said resin component being either a resin component present in said magnetic toner in addition to said binder resin or being said binder resin when there is no additional resin component.

11. A developer according to Claim 10, wherein the magnetic powder is present in an amount of 65 100 wt. parts per 100 wt. parts of the resin component.

12. A developer according to any preceding claim, wherein the magnetic toner has a residual magnetization (σ_r) of 1 - 5 emu/g, a saturation magnetization (σ_s) of 20 - 40 emu/g and a coercive force (Hc) of 3.18 x 10^3 to 7.96 x 10^3A/m (40 - 100 Oe).

13. A developer according to any preceding claim, wherein the magnetic toner has been mixed with silica fine powder.

14. A developer according to Claim 13, wherein 0.01 - 8 wt. parts of the silica fine powder has been mixed with 100 wt. parts of the magnetic toner.

15. A developer according to Claim 13, wherein 0.1 - 5 wt. parts of the silica fine powder has been mixed with 100 wt. parts of the magnetic toner.

16. A developer according to Claim 13, 14 or 15, wherein the magnetic toner has positive chargeability and the silica fine powder has positive chargeability.

17. A developer according to Claim 13, 14 or 15, wherein the magnetic toner has negative chargeability and the silica fine powder has negative chargeability.

18. A developer according to any preceding claim, wherein the magnetic toner has been mixed with powder of a fluorine-containing polymer.

19. A developer according to Claim 18, wherein the powder of the fluorine-containing polymer is contained in an amount of 0.01 - 2.0 wt. % based on the weight of the magnetic toner.

20. A developer according to Claim 18, wherein the powder of the fluorine-containing polymer is contained in an amount of 0.02 - 1.0 wt % based on the weight of the magnetic toner.

21. A developer according to any preceding claim, wherein the magnetic toner has been mixed with silica fine powder and powder of a fluorine-containing polymer.

* C L M S *

22. A developer according to any preceding claim, wherein said binder resin comprises a crosslinked styrene copolymer or a crosslinked polyester.

23. A developer according to any preceding claim, wherein said magnetic toner includes a charge controller either incorporated in said magnetic toner particles or mixed with said magnetic toner.

24. In combination, a developer according to any preceding claim and an image forming device for developing electrostatic images on an electrostatic image-holding member, the device comprising:

a developer chamber (39) containing said developer (31);

toner-carrying means having a surface (33) for holding a toner layer thereon and for carrying the toner layer to a developing zone; the toner layer being formed from the magnetic toner particles supplied from the developer chamber (39), and said toner-carrying means being made of a non-magnetic material;

magnetic means (35) for generating a stationary magnetic field at the developing zone through the non-magnetic toner-carrying means toward the surface (34) of the electrostatic image-holding member;

means (32) for forming the layer of the magnetic toner particles of substantially uniform thickness on the surface (33) of the toner-carrying means; and

means for maintaining a space between the toner-carrying means and the electrostatic image-holding member at the developing zone within a predetermined range so as to form a clearance gap between the electrostatic image-holding member and the surface of the layer of the magnetic toner particles on said toner-carrying means.

25. The combination of Claim 24 in which said device comprises means (38) for applying an alternating electric field to the developing zone.

26. A method of developing an electrostatic image on an electrostatic image-holding member, the method comprising the steps of:

providing a developer as claimed in any one of Claims 1 to 23;

forming a layer of magnetic toner particles from said developer of substantially uniform thickness on a surface of a toner carrier, said surface being non-magnetic and said layer being sufficiently thin so that there is a clearance gap between said layer and the electrostatic image-holding member;

generating a stationary magnetic field in the region of said surface of said toner carrier; and

causing the magnetic toner to pass onto the electrostatic image-holding member to develop said image.

27. A method according to Claim 26, comprising the step of applying an alternating electric field to said toner carrier to cause said magnetic toner particles to pass onto said electrostatic image-holding member.

28. Use of a developer according to any one of Claims 1 to 23 in a process for developing images.

Patentansprüche

1. Entwickler zur Entwicklung elektrostatischer Bilder, umfassend einen magnetischen Toner, der ein Bindeharz und ein magnetisches Pulver umfaßt, dadurch gekennzeichnet, daß der magnetische Toner 17 bis 60 Zahlen% magnetische Tonerteilchen mit einer Teilchengröße von 5 µm oder weniger, 1 bis 23 Zahlen% magnetische Tonerteilchen mit einer Teilchengröße von 8 bis 12,7 µm und 2,0 Vol.-% oder weniger magnetische Tonerteilchen in einer Teilchengröße von 16 µm oder mehr enthält, worin der magnetische Toner eine volumenmittlere Teilchengröße von 4 bis 9 µm besitzt und die magnetischen Tonerteilchen mit einer Teilchengröße von 5 µm oder weniger eine Teilchengrößenverteilung besitzen, die die folgende Gleichung erfüllt:

$$N/V = -0{,}04\,N + k$$

worin N den Zahlenprozentsatz der magnetischen Tonerteilchen mit einer Teilchengröße von 5 µm oder weniger darstellt, V den Volumenprozentsatz der magnetischen Tonerteilchen mit einer Teilchengröße von 5 µm oder weniger darstellt und k eine positive Zahl zwischen 4,5 und 6,5 ist, und N eine positive Zahl zwischen 17 und 60 ist.

2. Entwickler nach Anspruch 1, worin der magnetische Toner eine wahre Dichte von 1,45 bis 1,70 g/cm³ aufweist.

* C L M S *

3. Entwickler nach Anspruch 1, worin der magnetische Toner eine wahre Dichte von 1,50 bis 1,65 g/cm³ aufweist.

4. Entwickler nach einem der Ansprüche 1, 2 oder 3, worin der magnetische Toner 25 bis 50 Zahlen% magnetische Tonerteilchen mit einer Teilchengröße von 5 µm oder weniger enthält.

5. Entwickler nach einem der Ansprüche 1, 2 oder 3, worin der magnetische Toner 30 bis 50 Zahlen% magnetische Tonerteilchen mit einer Teilchengröße von 5 µm oder weniger enthält.

6. Entwickler nach einem der Ansprüche 1, 2 oder 3, worin der magnetische Toner 8 bis 20 Zahlen% magnetische Tonerteilchen mit einer Teilchengröße von 8 bis 12,7 µm enthält.

7. Entwickler nach einem der vorhergehenden Ansprüche, worin die magnetischen Tonerteilchen mit einer Teilchengröße von 5 µm oder weniger die folgende Gleichung erfüllen:

$$N / V = -0{,}04\,N + k$$

worin k eine Zahl zwischen 4,5 und 6,0 ist und N eine Zahl zwischen 25 und 60 ist.

8. Entwickler nach einem der vorhergehenden Ansprüche, worin die magnetischen Tonerteilchen mit einer Teilchen größe von 5 µm oder weniger die folgende Gleichung erfüllen:

$$N / V = -0{,}04\,N + k$$

worin k eine Zahl zwischen 4,5 und 5,5 ist und N eine Zahl zwischen 30 und 50 ist.

9. Entwickler nach einem der vorhergehenden Ansprüche, worin der magnetische Toner eine volumenmittlere Teilchengröße von 4 bis 8 µm aufweist.

10. Entwickler nach einem der vorhergehenden Ansprüche, worin das magnetische Pulver in einer Menge von 60 bis 110 Gewichtsteilen auf 100 Gewichtsteile eines Harzbestandteils anwesend ist, wobei der Harzbestandteil entweder ein Harzbestandteil ist, der im magnetischen Toner zusätzlich zum Bindeharz vorhanden ist, oder das besagte Bindeharz selbst ist, wenn kein zusätzlicher Harzbestandteil anwesend ist.

11. Entwickler nach Anspruch 10, worin das magnetische Pulver in einer Menge von 65 bis 100 Gewichtsteilen auf 100 Gewichtsteile des Harzbestandteils anwesend ist.

12. Entwickler nach einem der vorhergehenden Ansprüche, worin der magnetische Toner eine Restmagnetisierung (σ_r) von 1 bis 5 emu/g, eine Sättigungsmagnetisierung von (σ_s) von 20 bis 40 emu/g und eine Koerzivkraft (Hc) von $3{,}18 \times 10^3$ bis $7{,}96 \times 10^3$ A/m (40 bis 100 Oe) aufweist.

13. Entwickler nach einem der vorhergehenden Ansprüche, worin der magnetische Toner mit feinem Siliciumdioxidpulver gemischt wurde.

14. Entwickler nach Anspruch 13, worin 0,01 bis 8 Gewichtsteile des feinen Siliciumdioxidpulvers mit 100 Gewichtsteilen des magnetischen Toners gemischt wurden.

15. Entwickler nach Anspruch 13, worin 0,1 bis 5 Gewichtsteile des feinen Siliciumdioxidpulvers mit 100 Gewichtsteilen des magnetischen Toners gemischt wurden.

16. Entwickler nach einem der Ansprüche 13, 14 oder 15, worin der magnetische Toner eine positive Aufladbarkeit aufweist und das feine Siliciumdioxidpulver eine positive Aufladbarkeit aufweist.

17. Entwickler nach einem der Ansprüche 13, 14 oder 15, worin der magnetische Toner eine negative Aufladbarkeit aufweist und das feine Siliciumdioxidpulver eine negative Aufladbarkeit aufweist.

18. Entwickler nach einem der vorhergehenden Ansprüche, worin der magnetische Toner mit einem Pulver aus einem fluorhaltigen Polymer gemischt wurde.

19. Entwickler nach Anspruch 18, worin das Pulver des fluorhaltigen Polymers in einer Menge von 0,01 bis 2,0 Gew.-%, bezogen auf das Gewicht des magnetischen Toners, enthalten ist.

20. Entwickler nach Anspruch 18, worin das Pulver des fluorhaltigen Polymers in einer Menge von 0,02 bis 1,0 Gew.-%, bezogen auf das Gewicht des magnetischen Toners, enthalten ist.

* C L M S *

21. Entwickler nach einem der vorhergehenden Ansprüche, worin der magnetische Toner mit Siliciumdioxidpulver und Pulver aus einem fluorhaltigen Polymer gemischt wurde.

22. Entwickler nach einem der vorhergehenden Ansprüche, worin das Bindeharz ein quervernetztes Styrolcopolymer oder einen quervernetzten Polyester umfaßt.

23. Entwickler nach einem der vorhergehenden Ansprüche, worin der magnetische Toner ein Ladungssteuermittel einschließt, das entweder in den magnetischen Tonerteilchen eingebaut ist oder mit dem magnetischen Toner gemischt wurde.

24. Kombination, bestehend aus einem Entwickler nach einem der vorhergehenden Ansprüche und einer bildgebenden Vorrichtung zur Entwicklung elektrostatischer Bilder auf einem Element zum Tragen elektrostatischer Bilder, wobei die Vorrichtung umfaßt:
    - Eine Entwicklerkammer (39), die den Entwickler (31) enthält,
    - eine tonertragende Einrichtung mit einer Oberfläche (33) zum Tragen einer Tonerschicht darauf und zum Transportieren der Tonerschicht in die Entwicklungszone, wobei die Tonerschicht aus den magnetischen Tonerteilchen gebildet ist, die aus der Entwicklerkammer (39) bereitgestellt werden, und die tonertragende Einrichtung aus nichtmagnetischem Material hergestellt ist,
    - eine magnetischen Einrichtung (35) zur Erzeugung eines stationären Magnetfeldes an der Entwicklungszone durch die nichtmagnetische, tonertragende Einrichtung hindurch in Richtung auf die Oberfläche (34) des Elementes zum Tragen der elektrostatischen Bilder,
    - eine Einrichtung (32) zur Bildung der Schicht aus magnetischen Tonerteilchen mit im wesentlichen einheitlicher Dicke auf der Oberfläche (33) der tonertragenden Einrichtung und
    - eine Einrichtung zur Aufrechterhaltung eines Raumes zwischen der tonertragenden Einrichtung und dem Element zum Tragen elektrostatischer Bilder an der Entwicklungszone innerhalb eines festgelegte Bereiches, so daß auf diese Weise ein Spalt zwischen dem Element zum Tragen elektrostatischer Bilder und der Oberfläche der Schicht aus magnetischen Tonerteilchen auf der tonertragenden Einrichtung gebildet wird.

25. Kombination nach Anspruch 24, in der die Vorrichtung eine Einrichtung (38) zum Anlegen eines elektrischen Wechselfeldes an die Entwicklungszone umfaßt.

26. Verfahren zur Entwicklung eines elektrostatischen Bildes auf einem Element zum Tragen elektrostatischer Bilder, wobei das Verfahren folgende Schritte umfaßt:
    - Bereitstellung eines Entwicklers nach einem der Ansprüche 1 bis 23,
    - Bilden einer Schicht aus magnetischen Tonerteilchen aus diesem Entwickler mit im wesentlichen einheitlicher Dicke auf der Oberfläche einer tonertragenden Einrichtung, wobei die Oberfläche nichtmagnetisch ist und die Schicht genügend dünn ist, so daß es einen Spalt zwischen dieser Schicht und dem Element zum Tragen elektrostatischer Bilder gibt,
    - Erzeugung eines stationären Magnetfeldes im Bereich der Oberfläche der tonertragenden Einrichtung und
    - Einwirkung auf den magnetischen Toner, damit er auf das Element zum Tragen elektrostatischer Bilder überwechselt, um das Bild zu entwickeln.

27. Verfahren nach Anspruch 26, umfassend den Schritt, daß ein elektrisches Wechselfeld an die tonertragende Einrichtung angelegt wird, um die magnetischen Tonerteilchen dazu zu bringen, auf das Element zum Tragen elektrostatischer Bilder zu wechseln.

28. Verwendung eines Entwicklers nach einem der Ansprüche 1 bis 23 in einem Verfahren zur Entwicklung von Bildern.

Revendications

1. Développateur pour le développement d'images électrostatiques, comportant un toner magnétique comprenant une résine formant liant et une poudre magnétique, caractérisé en ce que :

ledit toner magnétique contient 17 - 60 % en nombre de particules de toner magnétique ayant une dimension de 5 µm ou moins, 1 - 23 % en nombre de particules de toner magnétique ayant une dimension de 8 - 12,7 µm, et 2,0 % en volume ou moins de particules de toner magnétique ayant une dimension de

16 µm ou plus ;

ledit toner magnétique présente une dimension moyenne en volume de particules de 4 - 9 µm ; et

lesdites particules de toner magnétique ayant une dimension de 5 µm ou moins ont une distribution granulométrique satisfaisant la formule suivante :

$$N/V = -0{,}04N + k,$$

dans laquelle N désigne le pourcentage en nombre de particules de toner magnétique ayant une dimension de 5 µm ou moins, V désigne le pourcentage en volume de particules de toner magnétique ayant une dimension de 5 µm ou moins, k désigne un nombre positif de 4,5 - 6,5 et N désigne un nombre positif de 17 - 60.

2. Développateur selon la revendication 1, dans lequel le toner magnétique a une masse volumique réelle de 1,45 - 1,70 g/cm³.

3. Développateur selon la revendication 1, dans lequel le toner magnétique a une masse volumique réelle de 1,50 - 1,65 g/cm³.

4. Développateur selon la revendication 1, 2 ou 3, dans lequel le toner magnétique contient 25 à 50 % en nombre de particules de toner magnétique ayant une dimension de 5 µm ou moins.

5. Développateur selon la revendication 1, 2 ou 3, dans lequel le toner magnétique contient 30 - 50 % en nombre de particules de toner magnétique ayant une dimension de 5 µm ou moins.

6. Développateur selon l'une quelconque des revendications précédentes, dans lequel le toner magnétique contient 8-20 % en nombre de particules de toner magnétique ayant une dimension de 8-12,7 µm.

7. Développateur selon l'une quelconque des revendications précédentes, dans lequel les particules du toner magnétique ayant une dimension de 5 µm ou moins satisfont la formule suivante :

$$N/V = -0{,}04N + k,$$

dans laquelle k désigne un nombre de 4,5-6,0 et N désigne un nombre de 25 - 60.

8. Développateur selon l'une quelconque des revendications précédentes, dans lequel les particules de toner magnétique ayant une dimension de 5 µm ou moins satisfont la formule suivante :

$$N/V = -0{,}04N + k,$$

dans laquelle k désigne un nombre de 4,5 - 5,5 et N désigne un nombre de 30 - 50.

9. Développateur selon l'une quelconque des revendications précédentes, dans lequel le toner magnétique présente une dimension moyenne en volume de particules de 4-8 µm.

10. Développateur selon l'une quelconque des revendications précédentes, dans lequel la poudre magnétique est présente en quantité de 60 - 110 parties en poids pour 100 parties en poids d'un constituant du type résine, ledit constituant du type résine étant soit un constituant du type résine présent dans ledit toner magnétique en addition de ladite résine formant liant, soit étant ladite résine formant liant lorsqu'il n'y a pas de constituant additionnel du type résine.

11. Développateur selon la revendication 10, dans lequel la poudre magnétique est présente en quantité de 65 - 100 parties en poids pour 100 parties en poids du constituant du type résine.

12. Développateur selon l'une quelconque des revendications précédentes, dans lequel le toner magnétique possède une aimantation résiduelle (σ_r) et 1 - 5 emu/g, une aimantation de saturation (σ_s) de 20 - 40 emu/g et une force coercitive (Hc) de 3,18 x 10^3 à 7,96 x 120^3A/m (40 - 100 Oe).

13. Développateur selon l'une quelconque des revendications précédentes, dans lequel le toner magnétique a été mélangé à une fine poudre de silice.

14. Développateur selon la revendication 13, dans lequel 0,01 - 8 parties en poids de la fine poudre de silice ont été mélangées à 100 parties en poids du toner magnétique.

15. Développateur selon la revendication 13, dans lequel 0,1 - 5 parties en poids de la fine poudre de silice ont été mélangées à 100 parties en poids du toner magnétique.

16. Développateur selon la revendication 13, 14 ou 15, dans lequel le toner magnétique possède une aptitude à être chargé positivement et la fine poudre de silice possède une aptitude à être chargée positivement.

17. Développateur selon la revendication 13, 14 ou 15, dans lequel le toner magnétique possède une aptitude à être chargé négativement et la fine poudre de silice possède une aptitude à être chargée négativement.

18. Développateur selon l'une quelconque des revendications précédentes, dans lequel le toner magnétique a été mélangé à une poudre d'un polymère contenant du fluor.

19. Développateur selon la revendication 18, dans lequel la poudre du polymère contenant du fluor est contenue en quantité de 0,01 - 2,0 % en poids sur la base du poids du toner magnétique.

20. Développateur selon la revendication 18, dans lequel la poudre du polymère contenant du fluor est contenue en quantité de 0,02 - 1,0 % en poids sur la base du poids du toner magnétique.

21. Développateur selon l'une quelconque des revendications précédentes, dans lequel le toner magnétique a été mélangé à une fine poudre de silice et à une poudre d'un polymère contenant du fluor.

22. Développateur selon l'une quelconque des revendications précédentes, dans lequel ladite résine formant liant comprend un copolymère de styrène réticulé ou un polyester réticulé.

23. Développateur selon l'une quelconque des revendications précédentes, dans lequel ledit toner magnétique comprend un régulateur de charge soit incorporé dans lesdites particules de toner magnétique, soit mélangé audit toner magnétique.

24. En combinaison, un développateur selon l'une quelconque des revendications précédentes et un dispositif de formation d'images pour le développement d'images électrostatiques sur un élément portant des images électrostatiques, le dispositif comportant :

une chambre (39) à développateur contenant ledit développateur (31) ;

un moyen de transport de toner ayant une surface (33) destinée à porter une couche de toner et à transporter la couche de toner jusqu'à une zone de développement ; la couche de toner étant formée à partir des particules de toner magnétique fournies à partir de la chambre (39) à développateur, et ledit moyen de transport de toner étant formé d'une matière non magnétique ;

un moyen magnétique (35) destiné à générer un champ magnétique fixe dans la zone de développement à travers le moyen non magnétique de transport de toner vers la surface (34) de l'élément portant une image électrostatique ;

un moyen (32) destiné à former à une épaisseur sensiblement uniforme la couche des particules de toner magnétique sur la surface (33) du moyen de transport de toner ; et

des moyens destinés à maintenir dans une plage prédéterminée un espace entre le moyen de transport de toner et l'élément portant une image électrostatique, dans la zone de développement, afin de former un intervalle de dégagement entre l'élément portant une image électrostatique et la surface de la couche des particules de toner magnétique sur ledit moyen de transport de toner.

25. Combinaison selon la revendication 24, dans laquelle ledit dispositif comporte un moyen (38) destiné à appliquer un champ électrique alternatif à la zone de développement.

26. Procédé de développement d'une image électrostatique sur un élément portant une image électrostatique, le procédé comprenant les étapes qui consistent :

à utiliser un développateur selon l'une quelconque des revendications 1 à 23 ;

à former une couche de particules de toner magnétique à partir dudit développateur, d'une épaisseur sensiblement uniforme, sur une surface d'un élément de transport de toner, ladite surface étant non magnétique et ladite couche étant suffisamment mince pour qu'il existe un intervalle de dégagement entre ladite couche et l'élément portant une image électrostatique ;

à générer un champ magnétique fixe dans la zone de ladite surface dudit élément de transport de toner ; et

à faire passer le toner magnétique sur l'élément portant une image électrostatique pour développer ladite image.

27. Procédé selon la revendication 26, comprenant l'étape qui consiste à appliquer un champ électrique al-

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ternatif audit élément de transport de toner afin de faire passer lesdites particules de toner magnétique sur ledit élément portant une image électrostatique.

28. Utilisation d'un développateur selon l'une quelconque des revendications 1 à 23 dans un procédé pour développer des images.