

CARRIER FOR ELECTROPHOTOGRAPHY,
TWO COMPONENT-TYPE DEVELOPER AND IMAGE FORMING METHOD

FIELD OF THE INVENTION AND RELATED ART

5 The present invention relates to a carrier
constituting a two component-type developer for
developing an electrical or magnetic latent image in
electrophotography or electrostatic printing, a two
component-type developer containing the carrier, and
10 particularly a carrier capable of constituting a two
component-type developer provided with remarkably
improved durability, ability of providing high-quality
images and environmental characteristic, such a two
component-type developer, and an image forming method
15 using the two component-type developer.

The carrier constituting the two component-
type developer may generally be classified roughly
into an electroconductive carrier and an insulating
carrier.

20 The electroconductive carrier may generally
comprise oxidized or yet-unoxidized iron powder. The
two component-type developer comprising iron powder
carrier is accompanied with problems that the
triboelectric chargeability of the toner is liable to
25 be unstable and the resultant visible image formed by
the developer is liable to be accompanied with fog.
Further, along with continual use of the developer,

toner particles adhere onto the surface of the iron powder carrier particles (adhesion of so-called "spent toner" or toner melt-sticking) to increase the electrical resistivity of the carrier particles, so that the bias current decreases and the triboelectric charge is instabilized. As a result, the resultant toner image is liable to have a lower image density and be accompanied with increased fog. Accordingly, when a developer containing iron-powder carrier is continuously used in copying by an electrophotographic copier, the developer is deteriorated in a relatively small number of sheets of copying, so that the developer has to be exchanged in a short period. This consequently results in a high running cost.

The insulating carrier representatively comprises a core material of a ferromagnetic material, such as iron, nickel or ferrite, uniformly coated with an insulating resin. The two component-type developer using this type of carrier is advantageous in that the adhesion of toner particles onto the carrier surface is remarkably less than in the case of the electroconductive carrier, and the developer is excellent in durability and has a long service life, so that the developer is particularly suitable for a high-speed electrophotographic copying machine.

Such an insulating carrier is required to satisfy several requirements including, as

particularly important ones: appropriate charge-imparting ability, impact resistance, wear resistance, good adhesion between the core and the coating material and uniform charge distribution.

5 In view of the above-mentioned various requirements, the insulating carriers used heretofore have still left some room for improvement and are not sufficiently satisfactory as yet. For example, carriers coated with acrylic resins have been
10 disclosed in Japanese Laid-Open Patent Application (JP-A) 47-13954 and JP-A 60-208765. Particularly, JP-A 60-208767, for example, refers to a molecular weight of the coating resin and teaches that an adequate constantly controlled molecular weight will provide a
15 coated carrier having a stable chargeability. The resin coating onto a core material is largely affected by apparatus conditions and environmental conditions, particularly a humidity and, even if they are strictly controlled, it has not been sufficiently satisfactory
20 to stably coat the core material with a resin to provide sufficient chargeability and durability.

On the other hand, it has been proposed to use a coating resin having a low surface energy, such as silicone resin, in order to prevent the
25 accumulation of so-called "spent toner", such as toner melt-sticking, and provide an improved durability.

The silicone resin has low surface energy,

low surface tension and also has another advantage of high water-repellency. On the other hand, the silicone resin has a low adhesiveness so that a coating layer formed thereof is liable to be peeled off during use.

In order to solve the above problem, there have been proposed use of a resin-modified silicone resin (JP-A 55-127569), a reaction of another resin with vinylsilane previously contained in silicone resin (JP-A 56-32149), use of a mixture of trialkoxysilane and ethyl cellulose (U.S. Patent No. 3,840,464), and use of a mixture of organosilicone terpolymer and polyphenylene resin (U.S. Patent No. 3,849,127). These proposals, however, have involved problems such that a high temperature of 300 °C or higher is required for formation of the coating film, and that silicone resin and another resin have poor compatibility with each other to provide an ununiform coating layer, thus failing to exhibit expected properties.

It has been also proposed to form a coating film at a relatively low hardening temperature (JP-A 55-127569), but the resultant coating film is liable to show an insufficient adhesiveness and an insufficient toughness and is therefore liable to be worn easily. As a result, when the coated carrier is subjected to long hours of intense stirring as in a

developing device of a high-speed copying machine, the silicone resin coating layer is liable to be worn or broken to be peeled off due to impingement onto inner walls of the developing device or photosensitive member surface. Consequently, the tribo-electrification mode is changed from one between the toner and the silicone resin to one between the toner and the carrier core, the triboelectric charge of the toner is changed, thus deteriorating the image quality.

Further, in recent years, copying machines capable of providing high-resolution and high-quality image are increasingly demanded on the market, and it has been tried to use a smaller particle size of toner for realizing high-quality color images. However, a smaller particle size of toner means a larger surface area per unit weight leading to a large electric charge of toner, which is liable to lower image densities and deterioration in successive image formation performance.

For development of an electrostatic latent image held on an electrostatic latent image-bearing member, toner particles are mixed with larger carrier particles to provide a two component-type developer for electrophotography. The compositions of the toner and the carrier are selected so that the toner is charged to a prescribed polarity, e.g., opposite to

that of a charge on the latent image-bearing member, through triboelectrification therebetween. Further, as a result of the triboelectrification, the carrier is caused to carry the toner attached

5 electrostatically to the surface thereof and they are conveyed together as a developer in the developing device to supply the toner onto a latent image on the electrostatic image-bearing member.

However, when such a two component-type
10 developer is used in an electrophotographic copying apparatus for continuous copying on a large number of sheets, clear and good quality of images are formed at an initial stage, but images accompanied with noticeable fog and conspicuous edge effects and also
15 with poor gradation characteristic and clarity are liable to result after copying on several tens of thousands of sheets.

In color copying using a chromatic color toner, a continuous gradation characteristic is an
20 important factor affecting the image quality, and the occurrence of an edge effect of providing a selective enhancement of an image peripheral portion after a large number of copying remarkably impairs the gradation characteristic of an image. Further, the
25 edge effect can produce a false contrast in the neighborhood of a true contour, thus impairing the copying reproducibility including color

reproducibility in color copying.

Further, in comparison with a monochromatic copy image having an image area of 10 % or lower and comprising mostly line images as in letters, documents
5 and reports, color copy images occupy an image area of at least 20 % and frequently comprise solid images having a gradation as in photographs, catalogues, maps and paintings.

When continuous copying is performed by using
10 an original having such a large image area, copies having a high image density can be obtained at an initial stage, the toner replenishment to the two component-type developer cannot keep up with the consumption gradually, thus being liable to result in
15 a density decrease, a mixture of replenished toner and carrier in an insufficiently charged state causing fog, and a local increase or decrease in toner concentration (i.e., a toner content in the developer) on the developing sleeve leading to scratchy images
20 or ununiform image densities. This tendency is more pronounced when the toner size is made smaller.

These difficulties of insufficient development and occurrence of fog may be attributable to too low a toner content in the two component-type
25 developer (i.e., toner concentration) or a slow increase in triboelectrification between the replenished toner and the carrier in the two

component-type developer, leading to participation of a toner having an insufficiently controlled charge in development.

5 A color developer is required to show an ability of continuously providing good quality of images in continuous reproduction of an original having a large image area as an indispensable performance. Conventionally, in order to cope with problems encountered in reproduction of an original
10 having a large image area and thus causing a large toner consumption rate, an improvement in developing device has been resorted to in many cases rather than an improvement in developer per se. For example, the peripheral speed or the diameter of a developing
15 sleeve is increased so as to increase the opportunity of contact between the electrostatic latent image and the developing sleeve.

The above measures can increase the developing capacity but are accompanied with
20 difficulties, such as soiling in the apparatus due to toner scattering from the developing device and a shortening of apparatus life due to an overload on the developing device. In some cases, a larger amount of developer may be charged in a developing device in
25 order to supplement an insufficient developing ability of the developer, but this is not so desirable either because it also results in an increase in weight of



the whole apparatus, an increased production cost due to size enlargement of the apparatus and also an overload on the developing device similarly as above.

For the above reason, the improvement in both
5 toner and carrier has been examined and reported in order to provide a high image quality for a long period.

Heretofore, several developers have been proposed in order to provide improved image quality.
10 For example, JP-A 51-3324 has proposed a non-magnetic toner having a controlled particle size distribution so as to improve the image quality. The toner principally comprises particles having a size of 8 - 12 μm and is therefore relatively coarse. According
15 to our study, it is difficult for a toner having such a particle size to effect a intimate "coverage" of a latent image. Further, the toner has a rather broad particle size distribution including at most 30 % by number of particles having a size of at most 5 μm and
20 at most 5 % by number of particles of at least 20 μm . In order to form a clear image by using such a relatively coarse toner having a broad particle size distribution, it is necessary to superpose toner particles in a large thickness so as to fill gaps
25 between toner particles and provide an apparently increased image density. As a result, an increased amount of the toner is consumed in order to provide a

prescribed image.

JP-A 54-72054 has proposed a non-magnetic toner having a narrower particle size distribution. However, the toner includes particles of 8.5 - 11.0 μm as a medium size and has left a room for improvement in order to provide a high resolution.

JP-A 58-129437 has proposed a non-magnetic toner having an average particle size of 6 - 10 μm and a mode particle size of 5 - 8 μm . The toner however contains particles of at most 5 μm in a small percentage of at most 15 % by number and thus tends to provide image with insufficient sharpness.

According to our study, it has been found that toner particles of at most 5 μm principally have functions of clearly reproducing the contour of a latent image and intimately covering the whole latent image. Particularly, in the case of an electrostatic latent image on a photosensitive member, the contour (edge) of the latent image shows a higher electric field intensity than the interior due to concentration of electrical lines of force, so that the clearness or sharpness of an image is determined by the quality of toner particles gathering at the contours. According to our study, it has been found that a substantial amount of particles of 5 μm or smaller is effective in solving the problem concerning an image sharpness.

As a result, we have propose a toner

containing toner particles of at most 5 μm in a proportion of 15 - 40 % by number (JP-A 2-222966). As a result, a substantial improvement in image quality has been realized, but a further improvement in image quality has been desired.

JP-A 2-877 has proposed a toner containing toner particles of at most 5 μm in 15 - 60 % by number. The toner has actually provided stable image quality and image density. However, it has been also found difficult to stably provide images of a constant quality by an improvement in toner alone because a toner particle size distribution can change in case where an original requiring a large toner consumption, such as a photographic image, is continuously reproduced.

On the other hand, certain particle sizes and distribution thereof have been suggested in JP-A 51-3238, JP-A 58-144839 and JP-A 61-204646. Among these, JP-A 51-3238 roughly refers to a particle size distribution but does not refer to magnetic properties closely related with the developing performance and conveyability in a developing device of a developer. The carriers used in Examples all contain about 80 wt. % or more of over 250 mesh and have an average particle size of at least 60 μm .

JP-A 58-144839 simply refers to an average particle size of a carrier and does not refer to the

amount of a fine powder fraction affecting the carrier attachment onto a photosensitive member or a coarse powder fraction affecting the sharpness of a resultant image. Further, the carrier particle size
5 distribution has not been considered in view of color copying characteristics.

JP-A 61-204646 discloses a combination of a copying apparatus and an appropriate developer as an essential characteristic but does not refer to a
10 particle size distribution and magnetic properties of a carrier. Further, it has not been clarified why the developer is effective for the copying apparatus.

JP-A 49-70630 describes the magnetic force of a carrier comprising iron powder having a larger
15 specific gravity than ferrite and also a high saturation magnetization. Iron powder carrier has been frequently used heretofore but is liable to result in an increase in copying apparatus weight and an excessively large drive torque. Further, its
20 performance is liable to change depending on environmental conditions.

JP-A 58-23032 discloses a porous ferrite carrier, which is liable to cause an edge effect and have a poor continuous image forming performance, thus
25 being unsuitable as a carrier for color image formation.

Ferrite carriers containing MgO have been

disclosed in, e.g., JP-A 59-111159, JP-A 58-123551 and JP-A 55-65406. However, the particle sizes distributions of these ferrite carriers are not particularly controlled. A combination of these
5 ferrite carriers with a toner of 1 - 9 μ m would not provide a two component-type developer having satisfactory charging stability and successive image forming characteristic.

JP-A 2-33159 contains a disclosure that MgO
10 can be contained but no disclosure is made regarding a positive inclusion of MgO for improving the surface-modifying effect thereof to provide an improved durability of a resin coating layer in combination with a controlled particle size distribution.

15 Heretofore, there has been desired such a developer that it can continuously reproduce an image having a large image area in a small amount and satisfies properties peculiarly suitable for color copying, such as freeness from the edge effect even
20 after a continuous copying. Developers and carriers have been studied but most of them have been proposed for monochromatic copying, and few has been proposed as being also applicable to full color-reproduction. Further, it has been desired to provide a carrier
25 capable of continuously reproducing an almost solid image having an image area of 20 % or higher, alleviating the edge effect, and retaining a



uniformity of image density in one copy sheet.

JP-A 2-281280 has provided a carrier having improved developing performances characterized by having a narrow particle size distribution with
5 controlled amounts of fine powder and coarse powder fractions.

As described hereinbefore, however, a demand for a copying machine satisfying a high resolution and a high image quality has been increased in the market
10 and, for this purpose, a smaller particle size of toner has been tried also for accomplishing a high-quality color image formation. A smaller particle size of toner has an increased surface area per unit weight and tends to have a larger electric charge,
15 which is liable to provide a lower image density and a deterioration in continuous image formation characteristic.

In order to prevent such a lowering in image density and deterioration in continuous image forming
20 characteristic and also to provide an increase in developing performance, it has been tried to use a carrier having a further smaller particle size. Such a carrier, however, has not acquired sufficient qualities suitably copying with changes in toner
25 chargeability depending on environmental conditions and continuation of successive image formation. Accordingly, it has been difficult to accomplish the

high image density, high image quality, good fog-prevention characteristic and good carrier attachment-prevention characteristic by such a carrier.

5 SUMMARY OF THE INVENTION

 A generic object of the present invention is to provide a two component-type developer and a carrier therefore having solved the above-mentioned problems.

10 A more specific object of the present invention is to provide a two component-type developer and a carrier therefor free from a lowering in image density and formation of scratchy images even in continuous copying of a color original having a large
15 image area.

 A further object of the present invention is to provide a two component-type developer and a carrier therefor capable of providing clear images free from fog and excellent in successive image
20 forming performance.

 Another object of the present invention is to provide a two component-type developer and a carrier therefor providing a quick triboelectrification between the toner and carrier.

25 Another object of the present invention is to provide a two component-type developer and a carrier therefor with little dependence on change in

environmental conditions in triboelectrification performance.

Still another object of the present invention is to provide a two component-type developer and a carrier therefor having a good conveying performance in a developing device.

A further object of the present invention is to provide an image forming method using such a two component-type developer as described above.

According to the present invention, there is provided a carrier for electrophotography, comprising: magnetic carrier core particles and a resin coating layer coating the magnetic carrier core particles, wherein

the carrier core particles comprise a magnetic ferrite component represented by the following formula (I):



wherein A denotes a member selected from the group consisting of MgO, AgO and mixtures thereof; B denotes a member selected from the group consisting of Li₂O, MnO, CaO, SrO, Al₂O₃, SiO₂ and mixtures thereof; and x, y and z are numbers representing weight ratios and satisfying the relation of: $0.2 \leq x \leq 0.95$, $0.005 \leq y \leq 0.3$, $0 < z \leq 0.795$, and $x+y+z \leq 1$.

According to another aspect of the present invention, there is provided a two component-type

developer, comprising: a toner comprising toner particles, and the above-mentioned carrier.

According to still another aspect of the present invention, there is provided an image forming method, comprising:

circulatively conveying the above-mentioned two component-type developer comprising a toner and a carrier on a developer-carrying member, and developing, in a developing region, an electrostatic latent image held on an electrostatic image-bearing member with the toner in the two component-type developer.

These and other objects, features and advantages of the present invention will become more apparent upon a consideration of the following description of the preferred embodiments of the present invention taken in conjunction with the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a schematic illustration of an image forming apparatus suitable for performing an embodiment of the image forming method according to the invention.

Figures 2 - 5 are diagrams showing alternating electric fields used in Examples 1, 13, 14 and 16, respectively, appearing hereinafter.

Figure 6 is a partial illustration of an electrostatic image-bearing member suitably used in an embodiment of the image forming method according to the invention.

5 Figure 7 is a schematic illustration of an image forming apparatus suitable for performing another embodiment of the image forming method according to the invention.

10 DETAILED DESCRIPTION OF THE INVENTION

As a result of our study for solving the above-mentioned problems, it has been found effective to use a carrier comprising magnetic carrier core particles and a resin coating layer coating the
15 magnetic carrier core particles, wherein

the carrier core particles comprise a magnetic ferrite component represented by the following formula (I):



20 wherein A denotes a member selected from the group consisting of MgO, AgO and mixtures thereof; B denotes a member selected from the group consisting of Li_2O , MnO, CaO, SrO, Al_2O_3 , SiO_2 and mixtures thereof; and x, y and z are numbers representing weight ratios and
25 satisfying the relation of: $0.2 \leq x \leq 0.95$, $0.005 \leq y \leq 0.3$, $0 < z \leq 0.795$, and $x+y+z \leq 1$.

In the formula (I), it is further preferred



that x , y and z further satisfy: $x+y < 1$ and $z = 1-x-y$, so as to provide carrier core particles having a moderate surface roughness, an appropriate moisture content, adhesiveness to a resin and toughness. It is
5 however possible that the ferrite component can contain preferably at most 3 wt. % of another metal element in the form of a hydroxide, oxide, sulfide or aliphatic acid compound for various proposes, such as control of surface crystal grain size, prevention of
10 coalescence during calcination, and control of particle size distribution. Accordingly, $x+y+z < 1$ in the formula (I) means the case where the ferrite component contains such another optional component in an amount of preferably up to 3 wt. %. A specific
15 example of the case will be found in Example 4 appearing hereinafter.

In the above formula (I), if x is below 0.2, the carrier is liable to have a low magnetic property leading to carrier scattering and damage the surface
20 of the photosensitive member. In case where x is above 0.95, the core is liable to have a low resistivity. If y is below 0.005, it is difficult to obtain proper resistivity and magnetic properties. If y is above 0.3, it becomes difficult to form spherical
25 carrier core particles having a uniform surface. If z is 0, i.e., no B component is contained, it becomes difficult to provide a sharp particle size

distribution, resulting in ultra-fine particles which are liable to damage the photosensitive member surface and make difficult the carrier production due to severe coalescence during the calcination. If z
5 exceeds 0.795, the core is caused to have low magnetic properties leading to carrier scattering.

In the above formula (I), it is further preferred that x, y and z satisfying the following conditions::

10 $0.4 \leq x \leq 0.9, 0.01 \leq y \leq 0.25, 0.001 \leq z \leq 0.2.$

Among the B components of Li_2O , MnO , CaO , Al_2O_3 and SiO_2 , it is preferred to use MnO , CaO , SiO_2 and Al_2O_3 because of little decrease in resistivity under a high-voltage application, and particularly MnO
15 and CaO in view of good compatibility with a replenished toner.

The carrier core particles comprising the ferrite component represented by the above formula (I) are coated with a layer of resin, which may preferably
20 comprise a reactive resin containing a specific curing agent.

Heretofore, it has been proposed to use a modified silicone resin in order to provide an increased adhesiveness with the carrier core
25 particles. The modification may be with alkyd, epoxy, acryl, polyester, phenol, melamine or urethane. However, such a modified silicone resin is caused to

have an increased surface energy and is liable to cause toner sticking, so that it is not sufficiently satisfactory in respect of successive image forming characteristic of the resultant developer.

5 It has been proposed to use various additives so as to increase the adhesiveness while retaining a low surface energy (JP-A 2-33159).

 These additives are reacted with a silicone resin or by itself to impart an adhesiveness and a
10 toughness. The modified silicone resin disclosed by JP-A 2-33159 actually provides a coating resin having an improved durability but does not provide a sufficiently satisfactory adhesiveness with the carrier core particles when it is formed as a thin
15 coating layer onto the surface of the carrier core particles. A further improvement is therefore desired.

 As a result of further study of ours, it has been found possible to provide a long-life carrier
20 having high performances inclusive of good adhesiveness and chargeability if magnetic carrier core particles containing a metal oxide having a solubility of 0.5 - 10 mg/100 ml, preferably 0.5 - 2 mg/100 ml, in water at 25 °C are coated with a
25 reactive silicone resin, preferably one containing a curing agent represented by a formula (III) appearing hereinafter, preferably an aminosilane coupling agent,

through an appropriate degree of reaction between some moisture contained in the carrier core particles and remaining reactive group in the silicone resin.

JP-A 2-33159 also discloses a silicone resin
5 containing a curing agent represented by the formula (III) appearing hereinafter, but the above-described method is different therefrom in that a metal oxide having a specific solubility is caused to be contained in a specific amount in the magnetic carrier core
10 particles and is reacted with such a reactive silicone resin. As a result, it is possible to provide a carrier with an enhanced strength between the carrier core particles and the resin coating layer.

The magnetic carrier core particles suitably
15 used in the present invention may comprise MgO having a solubility of 0.62 mg/100 ml or Ag₂O having a solubility of 1.74 mg/100 ml, respectively in water at 25 °C. It is further preferred to use ferrite particles containing 0.5 - 30 wt. % (as oxide) of MgO
20 in view of a stability of resistivity, surface uniformization, easiness of spherization, and an appropriate moisture content of the ferrite particles.

The coated carrier according to the present invention may also be characterized by a specific
25 surface property and a particle size distribution.

More specifically, as a result of our study, a two component-type developer providing high image



qualities inclusive of high image density, good highlight reproducibility and good thin-line reproducibility can be realized by using a carrier having specific particle size distribution and surface
5 property.

The carrier (particularly, core particles thereof) according to the present invention may be characterized a a uniformly small particle size carrier having a small average particle size and
10 controlled contents of fine and coarse powder fractions and having a certain degree of surface unevenness. Accordingly, even when the core particles are coated with a resin having a small free energy, the resultant coated carrier retains a good toner-
15 conveying performance and is provided with a quick triboelectrification characteristic.

The carrier may preferably have a 50 %-particle size (volume-basis median particle size, i.e., a particle size at which a cumulative particle
20 size fraction (from the smallest measurable particle size) reaches 50 % by volume) of 15 - 60 μm , preferably 20 - 45 μm , and contains 1 - 20 wt. %, desirably 2 - 15 wt. %, more preferably 4 - 12 wt. %, of carrier particles of below 22 μm , including 0.01 -
25 3 wt. %, preferably 0.01 - 2 wt. %, more preferably 0.01 - 1 wt. %, of carrier particles of below 16 μm .

If the content of the fine powder fraction

(below 22 μm) exceeds the above-mentioned upper limit, the carrier core particles cannot be stably coated with a resin, and the resultant carrier is liable to cause carrier attachment and prevent smooth charging of the toner. If the carrier particles of below 22 μm is below 1 wt. %, only sparse magnetic brush can be formed to provide a slow initial charging rate of the toner, thus causing toner scattering and fog.

Carrier particles of 62 μm or larger are closely related with the sharpness of the resultant images and may preferably be contained in 2 - 20 wt. %. Above 20 wt. %, the toner-conveying performance of the carrier is lowered and the toner scattering onto non-image parts is increased to lower the image resolution and the highlight reproducibility. Below 2 wt. %, the flowability of the resultant two component-type developer is lowered to cause localization of the developer in the developing device, so that it becomes difficult to form stable images.

The carrier according to the present invention may preferably have a specific area ratio S_1/S_2 of 1.2 - 2.0, more preferably 1.3 - 1.8, further preferably 1.4 - 1.7, wherein S_1 represents a specific surface area measured by the air permeation method (described in detail hereinafter) and S_2 denotes a specific surface area calculated by the following formula (II):

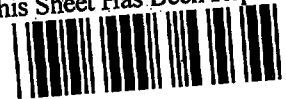
$$S_2 = [6/(\rho \times D_{50})] \times 10^4 \quad (II),$$

wherein ρ denotes a density and D_{50} denotes a 50 %-particle size, respectively, of a sample carrier.

If the ratio S_1/S_2 is below 1.2, the carrier
5 surface becomes smooth and this means a lower
adhesiveness of the resin coating layer onto the
carrier core particles, resulting in toner scattering,
fog or image irregularity. If the ratio S_1/S_2 exceeds
2.0, the carrier surface becomes excessively uneven,
10 thus being liable to provide an ununiform resin
coating layer on the carrier core particles. As a
result, the uniformity of charging is impaired, thus
being liable to result in fog, toner scattering, and
carrier attachment.

15 In order to enhance the effect of the present
invention, the carrier may preferably have an apparent
density of 1.2 - 3.2 g/cm³, more preferably 1.5 - 2.8
g/cm³. If the apparent density is below the above
described range, the carrier attachment is liable to
20 occur. Above the above-described range, the
circulatability of the resultant two component-type
developer becomes worse, the toner scattering is
liable to occur, and the image quality degradation is
accelerated.

25 In order to promote the effect of the present
invention, the carrier may preferably show a current
value (as measured by a method described hereinafter)

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of 20 - 300 μ A, more preferably 30 - 250 μ A, further preferably 40 - 200 μ A.

If the current value is below 20 μ A, the charge migration on the carrier surface may not be effectively performed and the carrier is caused to have a lower charge-imparting ability to the toner, thus being liable cause fog and toner scattering. Above 300 μ A, the carrier attachment onto the photosensitive member and the leakage of a bias voltage are liable to occur, thus being liable to result in image defects.

The magnetic performances of a carrier are affected by a magnet roller contained in a developing sleeve and, in turn, greatly affect the developing performance and the conveyability of the two component-type developer.

In an embodiment of the image forming method according to the present invention, a developing sleeve (developer-carrying member) containing a magnet roller therein is rotated while the magnetic roller is fixed, thereby circulatively conveying a two component-type developer comprising the magnetic carrier and an insulating color toner to develop an electrostatic latent image held on the electrostatic image-bearing member. In this instance, preferred conditions may include (1) the magnet roller having 5 magnetic poles including a repulsive magnetic pole,



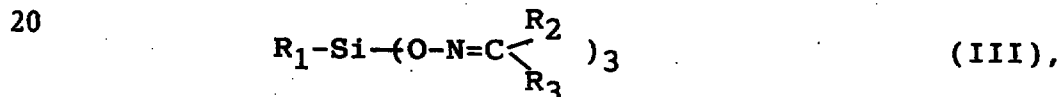
- (2) a magnetic flux of 50 - 1200 gauss in the developing region, and (3) a saturation magnetization of the carrier of 20 - 70 Am²/kg, so as to provide excellent image uniformity and gradation
- 5 reproducibility in color image formation.

If the carrier has a saturation magnetization exceeding 70 Am²/kg (under an applied magnetic field of 3000 oersted), the resultant brush or ear compose of the carrier and the toner on the developing sleeve

10 opposite an electrostatic latent image on the photosensitive member becomes tightly packed, thus providing a lower reproducibility of gradation and halftone. Below 20 Am²/kg, it becomes difficult to well hold the toner and the carrier on the developing

15 sleeve, thus being liable to cause carrier attachment and toner scattering.

The curing agent contained in the reactive particle size may suitably be an oxime-type curing agent represented by the following formula (III):



wherein R₂ denotes a substituent selected from the group consisting of CH₃, C₂H₅ and  each capable of having a substituent; and R₂ and R₃ independently

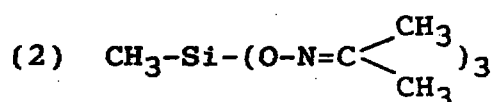
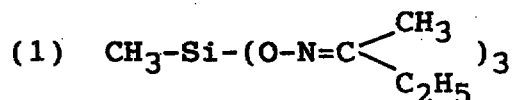
25 denote CH₃ and C₂H₅ each capable of having a substituent. Thus, such an oxime-type silane coupling agent is suitable in view of an appropriate degree of

control of remaining reactive groups in the silicone resin, storage stability and inexpensiveness.

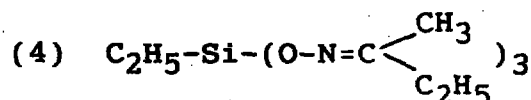
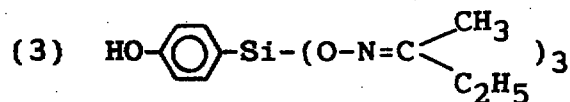
As coupling agents having a high reactivity, there have been known acetic acid-type (acetoxysilane) and acetone-type (propenoxysilane). By using these coupling agents, however, it is somewhat difficult to set reaction conditions for effecting a stable reaction between the carrier core particles and the silicone resin to leave some reactive groups so that these coupling agents are less advantageous in view of the production stability.

Specifically preferred examples of the curing agent may include those represented by the following formulae (1) - (4):

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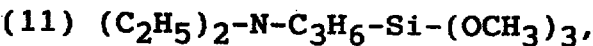
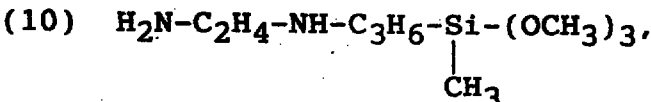
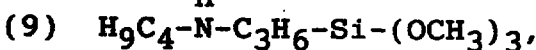
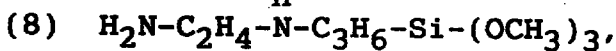
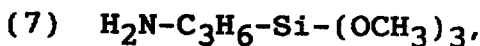
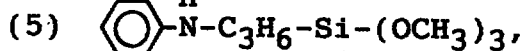
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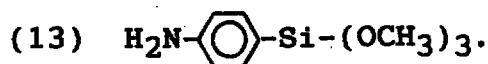


The above-mentioned curing agent may preferably be added in a proportion of 0.1 - 10 wt. parts, more preferably 0.5 - 5 wt. parts, per 100 wt. parts of the siloxane resin (solid matter). Below 0.1

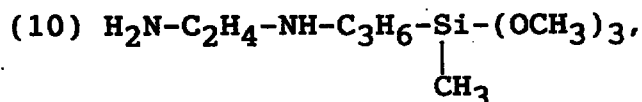
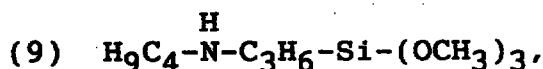
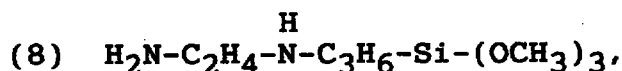
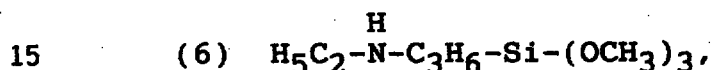
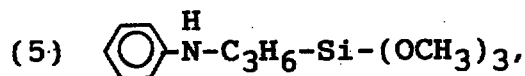
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These aminosilane coupling agents may be used singly or in combination of two or more species (or in combination with the above-mentioned oxime-type coupling agent). Among the above, aminosilane coupling agents including a nitrogen atom having one hydrogen atom bonded thereto (i.e., an imino group) as represented by those shown below are particularly suitable in view of mutual solubility, reactivity and stability.



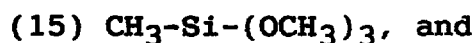
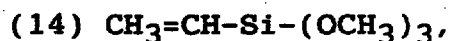
These aminosilane coupling agents may preferably be added in a proportion of 0.1 - 8 wt. parts, more preferably 0.3 - 5 wt. parts, per 100 wt. parts of the siloxane resin (solid matter). Below 0.1 wt. part, a sufficient effect of addition cannot be

attained. In excess of 8 wt. parts, a sufficient reaction may not be effected thus being liable to lower the coating layer strength.

Another class of the coupling agent
5 additionally usable in the present invention may include those represented by the following formula (IV):



wherein R denotes a substituent selected from the
10 group consisting of vinyl, methacryl, epoxy, amino, mercapto and derivatives of these; X denotes a halogen or alkoxy group; and a is an integer of 1 - 3. These coupling agents may be used in combination with the above-mentioned oxime-type silane coupling agent or
15 aminosilane coupling agent. Specific examples of this class of coupling agents may include those represented by the following formulae (14) - (16):



The magnetic carrier core particles may be coated with a resin according to various methods, including a method wherein a coating resin composition is dissolved in an appropriate solvent and, into the
25 resultant solution, the carrier core particles are dipped and taken up therefrom, followed by solvent removal, drying and baking at an elevated temperature;



a method wherein the carrier core particles are fluidized in a fluidizing system and a solution of the coating resin composition is sprayed thereonto for coating, followed by drying and baking at an elevated temperature; and a method wherein the carrier core particles are simply blended with powder or an aqueous emulsion of the coating resin composition.

In a preferred method, a mixture solvent formed by adding 0.1 - 5 wt. parts, preferably 0.3 - 3 wt. parts, of water to a solvent containing at least 5 wt. %, preferably at least 20 wt. %, of a polar solvent, such as ketone or alcohol, may be used so as to intimately attach a coating resin, such as a reactive silicone size, onto the carrier core particles. In case where the water is below 0.1 wt. part, the hydrolysis of the reactive silicone resin is not sufficiently effected so that it is difficult to form a thin and uniform coating film onto the surface of the carrier core particles. In excess of 5 wt. parts, the reaction control becomes difficult, thus providing a rather low coating strength.

In the present invention, the carrier and a toner are blended to prepare a two component-type developer in a mixing ratio which preferably provides a toner concentration in the developer of 1 - 12 wt. %, more preferably 2 - 9 wt. %, so as to provide generally good results. If the toner concentration is

below 1 wt. %, the resultant image density is lowered. In excess of 12 wt. %, fog and toner scattering in the apparatus are liable to occur, thus shortening the life of the developer.

5 A first preferred mode of the toner blended with the carrier to provide a two component-type developer according to the present invention may comprise toner particles and an external additive of surface-treated inorganic fine particles preferably
10 having a weight-average particle size of 0.001 - 0.2 μm . The toner may have a weight-average particle size of 1 - 9 μm . (Incidentally, a toner including toner particles and an external additive may be subjected to a particle size measurement. However, the weight-
15 average particle size measurement. However, the weight-average particle size of the toner is generally governed by the toner particles, since the external additive has a particle size which is generally below the lower limit of the toner particle size
20 measurement.)

 The inorganic fine powder as an external additive may for example comprise alumina, titanium oxide or silica. Among these, alumina or titanium oxide fine particles may preferably be used so as to
25 further stabilize the toner chargeability.

 It is further preferred to hydrophobize (i.e., impart hydrophobicity to) the inorganic fine powder in

order to reduce the dependency of the toner chargeability on environmental conditions, such as temperature and humidity, and also to prevent the isolation thereof from the surface of the toner particles. Examples of the hydrophobizing agent may include coupling agents, such as silane coupling agents, titanium coupling agents and aluminum coupling agents; and oils, such as silicone oil, fluorine-containing oils and various modified oils. Among the above-mentioned hydrophobizing agents, the coupling agent is particularly preferred in view of the stabilization of toner chargeability and the flowability-imparting effect.

Consequently, the external additive particularly preferably used in the present invention may comprise alumina or titanium oxide fine particles surface-treated with a coupling agent while being hydrolyzed in view of the stabilization of the toner chargeability and the fluidity imparting effect.

The hydrophobized inorganic fine powder may preferably have a hydrophobicity of 20 - 80 %, more preferably 40 - 80 %. If the hydrophobicity below 20 %, the chargeability is liable to be remarkably lowered when the toner is left standing for a long period in a high-humidity environment, so that a charging promotion mechanism may be required in the apparatus, thus complicating the apparatus. If the

hydrophobicity exceeds 80 %, the charging control of the inorganic fine powder per se becomes difficult, thus resulting in a toner charge-up (i.e., an excessive toner charge) in a low-humidity environment.

5

The hydrophobized inorganic fine powder may preferably have a weight-average particle size of 0.001 - 0.2 μm , more preferably 0.005 - 0.15 μm in view of the flowability-imparting effect and the prevention of isolation from the toner surface.

10

If the weight-average particle size is below 0.001 μm , the inorganic fine powder is liable to be embedded at the surface of the toner particles, thus rather lowering the successive image forming characteristic due to the toner deterioration. In excess of 0.2 μm , an improved toner flowability cannot be attained, thus being liable to result in an ununiform toner charge leading to toner scattering and fog.

15

The hydrophobized inorganic fine powder may preferably show a light transmittance (as measured according to a method described hereinafter) of at least 40 % at wavelength of 400 nm.

20

The inorganic fine powder, even though having a small primary particle size, is not necessarily present in the form of primary particles but can be present in the form of secondary particles when it is actually contained in the toner. Accordingly, even if

25

the primary particle size is sufficiently small, the inorganic fine powder can provide a lower transmittance if it has a large effective particle size as a result of behavior as secondary particles.

5 On the other hand, an inorganic fine powder having a higher optical transmittance at a lower limit wavelength in the visible region of 400 nm shows a smaller secondary particle size, thus providing excellent performances in respects of flowability-
10 imparting ability and clearness of projected images in the case of a color toner. The wavelength of 400 nm is a boundary between the ultra violet and visible regions. Further, particles having a particle size which is equal to or shorter than the wavelength of an
15 objective light are known to substantially transmit the objective light, so that light having a longer wavelength shows a larger transmittance and has a lower value as a reference light. This is why the light having a wavelength of 400 nm is used as a
20 reference light.

The toner used in the present invention may preferably have a weight-average particle size of 1 - 9 μm , more preferably 2 - 8 μm , so as to provide a good harmonization of high image quality and high
25 successive image forming performance.

If the weight-average particle size is below 1 μm , the mixability with the carrier is lowered to

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result in defects, such as toner scattering and fog. In excess of 9 μm , the accomplishment of a high image quality is hindered due to a lowering in minute dot-reproducibility or scattering at the time of transfer.

5 The toner used in the present invention may contain a colorant which may be a known dye and/or pigment, examples of which may include: Phthalocyanine Blue, Indanthrene Blue, Peacock Blue, Permanent Red, Lake Red, Rhodamine Lake, Hansa Yellow, Permanent
10 Yellow, and Benzidine Yellow. The colorant may be added in an amount of 12 wt. parts or less, more preferably 0.5 - 9 wt. parts, per 100 wt. parts of the binder resin, so as to provide a good sensitivity to transmittance of an OHP film.

15 The toner used in the present invention can contain are additive within an extent of not impairing the toner characteristic. Examples of such an additive may include: a lubricant, such as
polytetrafluoroethylene, zinc stearate, or
20 polyvinylidene fluoride; a fixing aid, such as low-molecular weight polyethylene or low-molecular weight polypropylene; and organic resin particles.

 The toner may be produced through various processes including a process wherein starting
25 ingredients are melt-kneaded in a hot kneading means, such as hot rollers, a kneader or an extruder, and the kneaded and cooled product is mechanically pulverized

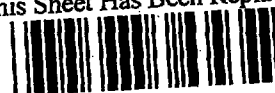


and classified; a process wherein toner materials, such as a colorant, are dispersed in a binder resin solution and then the resultant dispersion are spray-dried; and a process wherein prescribed materials such as a colorant are dispersed in a polymerizable monomer providing a polymer constituting the binder resin to provide a polymerizable mixture, and the resultant polymerizable mixture is dispersed in suspension or emulsion to be polymerized.

10 The binder constituting the toner may comprise various resins, examples of which may include: polystyrene; styrene-copolymers, such as, styrene-butadiene copolymer, styrene-acrylic copolymer; polyethylene, ethylene copolymers, such as
15 ethylene-vinyl acetate copolymer; and ethylene-vinyl alcohol copolymer; phenolic resins, epoxy resins, ally phthalate resin, polyamide resins, polyester resin, and maleic acid resin.

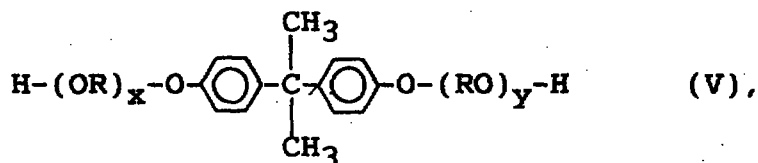
Any of these resins produced through any
20 production processes may be used.

The present invention is most suitably applied to a toner obtained from a polyester resin having a high negative chargeability. A polyester resin has an excellent fixability, is suitable for a
25 color toner but, on the other hand, is liable to be charged excessively because of a strong negative chargeability. However, this difficulty is alleviated



when combined with the carrier according to the present invention.

It is particularly preferred to use a polyester resin formed by condensation copolymerization between a diol component comprising a bisphenol derivative represented by the following formula (V) or a substituted derivative thereof and a carboxylic acid component comprising a carboxylic acid having two or more carboxylic groups or an anhydride thereof, such as fumaric acid, maleic acid, maleic anhydride, phthalic acid, terephthalic acid, trimellitic acid and pyromellitic acid:



wherein R denotes an ethylene or propylene group, x and y are independently a positive integer of at least 1 with the proviso that the average of x+y is in the range of 2 - 10. This type of polyester resin is preferred because of a sharp melting characteristic.

Thus, a second preferred mode of toner used in the present invention may a weight-average particle size of 1 - 9 μm , comprise toner particles containing a binder resin comprising a polyester resin and have an acid value of 1 - 20 mgKOH/g, preferably 2 - 18 mgKOH/g, further preferably 3 - 15 mgKOH/g.

More specifically, if the above-described

toner having an acid value of 1 - 20 mgKOH/g is used in combination with the carrier of the present invention comprising the above-mentioned specific ferrite component coated with a resin coating layer, the charging stability is improved to allow quick charging, thereby providing a two component-type developer which is free from fog or toner scattering for a long period even when an original having a high image area ratio is used.

10 In case where the acid value is below 1 mgKOH/g, the initial charging speed is lowered, thus being liable to result in severer fog. On the other hand, if the acid value exceeds 20 mgKOH/g, the chargeability in a high humidity environment is liable to be lowered, thus resulting in fog and toner scattering.

In order to provide a toner having an acid value in the range of 1 - 20 mgKOH/g, the acid component for providing the binder resin may preferably contain 0.1 - 20 mol. %, more preferably 0.1 - 10 mol. %, of polyvalent carboxylic acid having at least three functional groups. It is further preferred that the toner comprising a polyester resin as a binder resin may preferably have a glass transition temperature (T_g) in the range of 45 - 70 °C and a temperature giving an apparent viscosity of 10^5 poises (T_m) in the range of 80 - 120 °C. A preferred

class of the polyester resin is the above-described polyester resin formed from the bisphenol represented by the formula (V).

The polyester resin can be used in mixture
5 with another resin, examples of which may include those enumerated in the first preferred mode of toner used in the present invention.

The toner particles may be blended with external additives, as desired, examples of which may
10 include those enumerated in the first preferred mode of toner used in the present invention.

Now, an embodiment of the image forming method according to the present invention using a two component-type developer as described above will now
15 be described.

In the image forming method according to the present invention, a two component-type developer comprising a toner and a carrier is circulatively conveyed on a developer-carrying member and, in a
20 developing region, an electrostatic latent image held on an electrostatic image-bearing member is developed with the toner in the two component-type developer carried on the developer carrying member.

In the image forming method according to the
25 present invention, it is preferred to effect the development under application of a developing bias in the developing region.

A particularly preferred developing bias voltage will now be described. More specifically, in the present invention, it is preferred to apply a developing bias comprising a succession of voltages including a first voltage directing a toner from the image-bearing member toward the developer-carrying member, a second voltage directing the toner from the developer carrying member toward the image-bearing member and a third voltage intermediate between the first and second voltages. It is further preferred that a period (T_1) for applying the first voltage and the second voltage is set to be shorter than a period (T_2) for applying the third voltage so as to cause an rearrangement of the toner on the image-bearing member for faithful development of the latent image.

More specifically, the first voltage (i.e., one forming an electric field for directing the toner from the image-bearing member toward the developer-carrying member) and the second voltage (i.e., one forming an electric field for directing the toner from the developer-carrying member toward the image-bearing member) for at least one cycle (once each), and then the third voltage (for establishing an electric field for directing the toner from the developer-carrying member toward the image-bearing member at an image part on the image-bearing member and for directing the toner from the image-bearing member toward the

developer-carrying member) is applied for a prescribed period, thereby to develop the latent image on the image-bearing member with the toner in the two component-type developer. In this instance, the time
5 (T_2) for applying the third voltage is preferably set to be longer than the total time (T_1) for applying the first and second voltages.

The above-mentioned application of the first to third voltages may be performed simply by a
10 sequence of applying an alternating electric field (applying the first and second voltages) and turning off the alternating electric field (applying the third voltage). This sequence may be repeated periodically.

15 The application of the first to third voltages is effective for preventing carrier attachment. The mechanism thereof has not been fully clarified as yet but may be reasoned as follows.

According to the application of a
20 conventional continuous sine waveform or alternating rectangular waveform, when the electric field is intensified in order to accomplish a high image quality and density, the toner and the carrier integrally move reciprocally between the image-bearing
25 member and the developer-carrying member, whereby the image-bearing member is intensely rubbed with the carrier to cause carrier attachment. This tendency is

conspicuous when much fine powder carrier fraction is contained.

On the other hand, when the above-mentioned specific alternating electric field is applied, the toner or carrier causes a reciprocal movement such that it does not complete the reciprocation between the developer-carrying member and the image-bearing member within one cycle of the alternating electric field. As a result, during the application of the third voltage thereafter, in case where a potential difference V_{cont} between the surface potential of the image-bearing member and the DC component of the developing bias (third voltage) satisfies $V_{cont} < 0$, V_{cont} functions to direct the carrier from the developer-carrying member toward the image-bearing member, but the movement of the carrier causing carrier attachment in this case can be prevented by adequate control of the magnetic properties of the carrier and the magnetic flux in the developing region exerted by the magnet roller. On the other hand, in case of $V_{cont} > 0$, V_{cont} and the magnetic field force both function to pull the carrier toward the developer-carrying member. As a result, the carrier attachment (onto the image-bearing member) may be effectively prevented.

A preferred form of the electrostatic image-bearing member suitably used in an embodiment of the

image forming method according to the present invention will now be described with reference to Figure 6.

Referring to Figure 6, an electrostatic
5 latent image-bearing member 1 comprises a
photosensitive layer 43 and a protective layer 44
disposed on an electroconductive support 41. At least
the protective layer 44 contains fluorine-containing
resin particles so as to reduce a surface frictional
10 resistance of the image-bearing member 1. The
protective layer 44 may preferably be mechanically
abraded to provide a ten point-average surface
roughness Rz according to JIS B061 (hereinafter simply
called "average surface roughness") of 0.01 - 1.5 μm .

15 If the average surface roughness is within
the above range, the friction between a cleaning blade
50 and the image-bearing member 1 is sufficiently
small and, even on repetitive use, no image defects
appear thereby. Further, an excellent highlight
20 reproducibility can be attained.

The content of the fluorine-containing resin
particles added for effectively lowering the surface
frictional coefficient of the image-bearing member 1
may be 5 - 40 wt. %, preferably 10 - 40 wt. %, of the
25 total weight of the protective layer 44. The
protective layer may preferably have a thickness of
0.05 - 8.0 μm , more preferably 0.1 - 6.0 μm .

In case where the photosensitive layer 43 also contains the fluorine-containing resin particles, the content of the particles may be reduced as the photosensitive layer 43 is thicker than the protective layer 44. More specifically, the content in the photosensitive layer may preferably be at most 10 wt. %, more preferably at most 7 wt. %.

Even if the content of the fluorine-containing resin particles in the photosensitive layer is reduced, remarkable decreases in sensitivity and uniformity of images can occur due to light scattering in case where the total thickness of the photosensitive layer 43 is large and particularly when photocarrier are principally generated at a support side of the photosensitive layer 43. Too small a thickness of the photosensitive layer 43 can cause a decrease in sensitivity and a decrease in chargeability due to an electric capacity increase of the photosensitive layer 43. Further, even in case where no such particles are contained in the photosensitive layer, an extremely large photosensitive layer thickness is not desirable. This is because the protective layer 44 containing the particles disposed on the photosensitive layer 43 functions as a light-scattering layer. Particularly, in case where photocarriers are generated in a support side of the photosensitive layer, the influence of the

light scattering is increased if the site of photocarrier generation is remoter from the light scattering layer, i.e., if the photosensitive layer is thicker, to provide an increased light path length after the scattering.

Accordingly, the total thickness of the photosensitive layer 43 and the protective layer 44 may preferably be 10 - 35 μm , more preferably 15 - 30 μm . A smaller content of the fine particles in the photosensitive layer 43 is preferred. Accordingly, the average content of the fine particles in the photosensitive layer 43 and the protective layer 44 may preferably be at most 17.5 wt. % based on the total weight of these layers.

The fluorine-containing resin particles used in the image-bearing may comprise one or more species selected from polytetrafluoroethylene, polychlorotrifluoroethylene, polyvinylidene fluoride, polydichlorodifluoroethylene, tetrafluoroethylene-perfluoroalkyl vinyl ether copolymer, tetrafluoroethylene, tetrafluoroethylene-hexafluoropropylene copolymer, tetrafluoroethylene-ethylene copolymer and tetrafluoroethylene-hexafluoropropylene-perfluoroalkyl vinyl ether copolymer. Commercially available fluorine-containing resin particles can be used as they are. The fluorine-containing resin may have a molecular weight of 0.3×10^4 - 5×10^6 . The particle size may be

0.01 - 10 μm , preferably 0.05 - 2.0 μm .

The photosensitive layer 43 may contain organic photoconductive substances inclusive of charge generation substance and charge transportation substance.

Examples of the charge generation substance may include: phthalocyanine pigments, polycyclic quinone pigments, trisazo pigments, disazo pigments, azo pigments, perylene pigments, indigo pigments, quinacridone pigments, azulenium pigments, squallium dyes, thiopyryllium dyes, xanthene dyes, quinoneimine dyes, triphenylmethane dyes, styryl dyes, selenium, selenium-tellurium alloy, amorphous silicon, and cadmium sulfide.

Examples of the charge transportation substance may include; pyrene compounds, N-alkylcarbazole compounds, hydrazone compounds, N,N-dialkylaniline compounds, diphenylamine compounds, triphenylamine compounds, triphenylmethane compounds, pyrazoline compounds, styryl compounds, stilbene compounds, polynitro compounds, polycyano compounds, and pendant polymers formed by fixing these compounds on polymers.

In many cases, the fluorine-containing resin particles, the charge generation substance, and the charge transportation substance are dispersed or contained in the respective film-forming binder

resins. Examples of the binder resins may include: polyester, polyurethane, polyacrylate, polyethylene, polystyrene, polybutadiene, polycarbonate, polyamide, polypropylene, polyimide, phenolic resin, acrylic resin, silicone resin, epoxy resin, urea resin, allyl resin, alkyd resin, polyamide-imide, nylon, polysulfone, polyallyl ether, polyacetal and butyral resin.

The electroconductive support may comprise metals, such as iron, copper, gold, silver, aluminum, zinc, titanium, lead, nickel, tin, antimony and indium; alloys of these metals; or oxide of these metals; carbons, and electroconductive polymers. The support may have a shape of drum or a tube or pillar; a belt, or a sheet. The electroconductive material may be molded as it is, applied as a coating, vapor-deposited, or worked by etching or plasma treatment. The coating may be formed on a support of a metal or alloy as described above, paper or plastic.

The photosensitive layer 43 may comprise a single layer or a laminate layer structure. The laminate layer structure may comprise at least a charge generation layer 43a and a charge transport layer 43b. The charge generation layer 43a or the charge transport layer 43b (as shown in Figure 6) may be disposed closer to the electroconductive support. Depending on whether either one of these is adopted,

the charging polarity and the polarity of toner charge are changed. The charge generation layer 43a may preferably have a thickness of 0.001 - 6 μm , more preferably 0.01 - 2 μm . The charge generation substance may comprise 10 - 100 wt. %, preferably 50 - 100 wt. %, thereof of a charge generation substance. The charge transport layer 43b may have a thickness which is equal to a subtraction of the charge generation layer thickness from the above-mentioned photosensitive layer thickness. The charge transport layer may preferably contain the charge transportation substance in 20 - 80 wt. %, more preferably 30 - 70 wt. %.

It is possible to dispose an undercoating layer 42 between the electroconductive support 41 and the photosensitive layer 43. The undercoating layer 42 may have a function of charge injection control or function as an adhesive layer. The undercoating layer 42 may principally comprise a binder resin but can further contain a metal or alloy, or an oxide of these, a salt, or a surfactant. The binder resin may comprise a resin selected from those resins for the photosensitive layer 43. The undercoating layer may have a thickness of 0.05 - 7 μm , preferably 0.1 - 2 μm .

The protective layer may be disposed on the photosensitive layer as described above and may

preferably comprise at least resin particles containing a high concentration of fluorine atoms and a binder resin.

The image-bearing member may be produced
5 through various processes including vapor deposition and/or coating. By the coating, it is possible to form various compositions of films in a widely varying thickness. Examples of the coating method may include those using bar coater or knife coater, dipping, spray
10 coating, beam coating, electrostatic coating, roller coating, attritor and powder coating.

The coating composition for providing the protective layer may be formed by dispersing the fluorine-containing resin particles in a mixture of a
15 binder and a solvent. The dispersion may be performed by using a ball mill, ultrasonic disperser, a paint shaker, a red devil, or a sand mill. Similar dispersion methods may be adopted for dispersion of electroconductive powder and pigments inclusive of a
20 pigment as a charge generation substance.

An image forming apparatus suitably used for practicing an embodiment of the image forming method according to the present invention will now be described with reference to Figure 1.

25 Referring to Figure 1, an image forming apparatus includes a photosensitive drum 1 as an electrostatic image-bearing member, and a developing

device 4 which in turn includes a developing vessel
16. The interior of the developing vessel 16 is
divided by a partitioning wall into a developing
chamber (first chamber) R_1 and a stirring chamber
5 (second chamber) R_2 , above which a toner storage
chamber R_3 is formed. In the developing chamber R_1
and the stirring chamber R_2 , a developer 19 is stored
and, in the toner storage chamber R_3 , a replenishing
toner (non-magnetic toner) 18 is contained. The toner
10 storage chamber R_3 is provided with a replenishing
hole 20, through which the replenishing toner 18 is
dropped and supplied in an amount corresponding to a
consumed amount.

Inside the developing chamber, a conveying
15 screw 13 is provided and rotated to convey the
developer 19 in the developing chamber R_1 along a
longitudinal direction of developer sleeve 11.
Similarly, in the stirring chamber R_2 , a conveying
screw 14 is disposed and rotated to convey the toner
20 dropped through the replenishing hole 20 in a
direction parallel to the longitudinal direction of
the developing sleeve.

The developer 19 is a two component-type
developer comprising a non-magnetic toner and a
25 magnetic carrier. Adjacent the photosensitive drum 1,
the developing vessel 16 is provided with an opening,
through which the developing sleeve 11 is projected so

as to form a gap from the photosensitive drum 1. The developing sleeve 11 comprises a non-magnetic material and is provided with a bias application means 30.

A magnetic roller 12 as a magnetic field
5 generating means is disposed inside the developing sleeve 11 and provided with 5 magnetic poles including a developing pole S_2 , a magnetic pole N_2 disposed downstream of S_1 , and magnetic poles N_3 , S_1 and N_1 for conveying the developer 19. The magnet 12 is disposed
10 within the developing sleeve 11 so that the developing pole S_2 is opposite the photosensitive drum 1. The developing pole S_2 forms a magnetic field in the vicinity of the developing region between the developing sleeve 11 and the photosensitive drum 1,
15 and a magnetic brush is formed by the magnetic field.

A regulating blade 15 is disposed above the developing sleeve 11 so as to regulate the layer thickness of the developer 19 on the developing sleeve 11. The regulating blade 15 comprises a non-magnetic
20 material, such as aluminum or SUS 316 and is disposed to have an end which is spaced from the developing sleeve 11 by 300 - 1000 μm , preferably 400 - 900 μm . If the spacing is below 300 μm , the magnetic carrier is liable to plug the spacing to cause an irregularity
25 in the developer layer formed and further fail to form a developer coating layer required for good development, thus resulting in developed images which

are thin in density and with much irregularity. In order to prevent irregular coating (or so-called blade plugging) caused by unnecessary particles possibly commingling within developer, it is preferred to have a spacing of at least 400 μm . If the spacing is larger than 1000 μm , the developer amount supplied onto the developing sleeve 11 is increased, thus failing to provide a specifically regulated developer layer thickness and resulting in much magnetic carrier attachment onto the photosensitive drum 1. The circulation and regulation by the non-magnetic blade 15 of the developer become insufficient, thus providing a toner having insufficient triboelectric charge and resulting in fog.

The angle θ_1 may be set at -5 degrees to +35 degrees, preferably 0 to 25 degrees. If $\theta_1 < -5$ degrees, the developer thin layer formed by magnetic force, image force and agglomerating force acting on the developer is liable to be sparse and irregular. If $\theta > 35$ degrees, the developer coating amount is increased and it becomes difficult to obtain a prescribed developer coating amount.

Even if the sleeve 11 is rotated in the arrow direction, the movement of the magnetic carrier particle layer becomes gradually slower as it leaves away from the sleeve surface due to a balance between a constraint by gravity and the conveying force

exerted by movement of the sleeve. Some can fall under the action of the gravity.

Accordingly, by appropriately selecting the position of the magnetic poles N_1 and N_2 , and also
5 the flowability and magnetic properties of the magnetic carrier particles, the magnetic carrier particles closer to the sleeve are preferentially conveyed toward the magnetic pole N_1 to form a moving layer. According to the movement of the magnetic
10 carrier particles, the developer is conveyed accompanying the rotation of the developing sleeve to the developing region where the developer is used for development. An upstream toner scattering-preventing member 21 and a downstream toner scattering-preventing
15 member 22 are further provided to prevent toner scattering.

Another embodiment of an image forming apparatus, particularly a developing apparatus, usable in the image forming method according to the present
20 invention is illustrated in Figure 7.

Referring to Figure 7, the developing apparatus includes a developer container 102 having a developer chamber 145 in which a non-magnetic developing sleeve (developer-carrying member) 121
25 having a specific surface shape is disposed opposite to an electrostatic latent image-bearing member 101 rotated in an arrow a direction. In the developing

sleeve 121, a magnetic roller 102 as a magnetic field-generating means is disposed immovably and provided with magnetic poles S_1 , N_1 , S_2 , N_2 and N_3 in this order in an arrow b direction from the pole S_1
5 disposed almost at the highest position.

The developing chamber 145 contains a two-component-type developer 141 comprising a mixture of a non-magnetic toner 140 and a magnetic carrier 143.

The developer 141 is introduced into a
10 stirring chamber 142 equipped with a partitioning wall 148 having an upper opening end through one opening (not shown) of the wall 148 at one end of the developing chamber 145 in the developer container 102. Into the stirring chamber 142, the non-magnetic toner
15 140 is replenished from a toner chamber 147 and the developer 141 conveyed toward the other end of the stirring chamber 142 while being mixed with a first developer stirring and conveying means 150. The developer 141 conveyed to the other end of the
20 stirring chamber 142 is returned to the developing chamber 145 through the other opening (not shown) of the partitioning wall 148 and stirred and conveyed by a second developer stirring and conveying means 151 in the developing chamber 145 and a third developer
25 stirring and conveying means 152 disposed at an upper part in the developing chamber 145 and conveying the developer in direction opposite to the conveying

direction of the conveying means 151, whereby the developer is supplied to the developing sleeve 121.

The developer 141 supplied to the developing sleeve 121 magnetically constrained under the action of a magnetic force exerted by the magnet roller 122 and carried on the developing sleeve 121. The developer 141 is formed into a thin layer under the regulation of a developer regulating blade 123 disposed confronting almost the highest position of the developing sleeve 21 and conveyed along with the rotation of the developing sleeve 21 in the arrow b direction to a developing zone 110 confronting the electrostatic latent image-bearing member 101, where the developer is used for developing an electrostatic latent image on the latent image-bearing member 101. The developer 141 not consumed for development is recovered into the developer container 102 along with the rotation of the developing sleeve 121. An upstream toner scattering-preventing member 103 and a downstream toner scattering-preventing member 104 are further provided to prevent toner scattering.

In the developer container 102, the residual developer magnetically constrained on the developing sleeve 121 is peeled off from the developing sleeve 121 by a repulsive magnetic field acting between poles N_2 and N_3 of the same polarity. In order to prevent scattering of the toner at the time when the developer

141 stands up to form ears along magnetic lines of force caused by the pole N_2 , an elastic sealing member 131 is fixedly disposed at a lower part of the developer container 102 so that its one end contacts the developer 141.

We have further studied about the image density, highlight reproducibility and thin-line reproducibility in a color image forming method. As a result, it has been found that excellent performances can be accomplished regarding the above items when a toner having a specific particle size distribution as described hereinbelow is used in an image forming method including a developing step by application of the above-mentioned specific alternating electric field.

The toner may preferably comprise toner particles and an external additive, and the toner particles have a weight-average particle size of 3 - 7 μm , include more than 40 % by number of particles of at most 5.04 μm , 10 - 70 % by number of particles of at most 4 μm , 2 - 20 % by volume of particles of at least 8 μm , and 0 - 6 % by volume of particles of at least 10.08 μm .

The toner having the above-mentioned particle size distribution can faithfully develop a latent image formed on a photosensitive member, can show an excellent reproducibility of minute dot images

inclusive of digital images, and can provide images excellent in gradation characteristic of highlight portion and resolution. Further, high-quality images are retained even when continuous image formation of copying or printing out is performed, and high-density
5 images can be reproduced at a smaller toner consumption than conventional non-magnetic toners. Thus, the toner is advantageous from the view points of economy and size reduction of copiers or printers.

10 However, even if a toner having a potentially excellent image reproducibility can fail to exhibit its excellent performance under application of conventional continuous sine wave or alternating rectangular waveform, because a sufficient electric
15 field is not applied for a latent image having a small developing (voltage) contrast, such as highlight images, to which an increased proportion of toner does not reach the image-bearing member under application of such a continuous alternating electric field. In
20 other words, under such bias application conditions, a substantial portion of toner causes a mere vibrational movement and does not reach the image-bearing member.

 However, good highlight images free from roughness can be obtained if the above-mentioned
25 intermittent alternating developing electric field is applied. In this case, the toner similarly causes a vibrational movement and does not reach the image-

bearing member by application of one cycle of the alternating electric field. However, during the application of the third voltage (i.e., the period of non-application of the alternating electric field), in case where a potential difference V_{cont} between the surface potential and the DC component of the developing bias satisfies $V_{cont} < 0$, V_{cont} functions to direct the toner toward the developer-carrying member to localize the toner on the developer-carrying member side and, in case of $V_{cont} > 0$ reversely, V_{cont} functions to direct the toner toward the image-bearing member depending on the image-bearing member depending on the latent image potential difference on the image-bearing member, so that the toner is localized on the image-bearing member side in an amount corresponding to the latent image potential. On further application of the alternating electric field, the toner having reached the image-bearing member side oscillate thereat to be concentrated at the latent image portion. As a result, the dot shape is uniformly reproduced to provide images free from irregularity.

For the reason described above, if a latent image is developed under application of the intermittent alternating bias electric field, the lacking of dot images can be obviated even in a highlight latent image. Further as the toner repetitively oscillates on the image-bearing member,

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the toner is concentrated at the latent image part to faithfully reproduce individual dots. Further, while using a two component-type developer, the contact of the magnetic brush onto the image-bearing member is
5 suppressed to provide uniform halftone images.

Various parameters characterizing the present invention are based on values measured in the following manners.

(1) Magnetic properties of carrier

10 The apparatus used in a commercially available magnetization tester ("Model BHU-60", available from Riken Sokutei K.K.). Ca. 1.0 g of a sample is weighed and packed in a cell measuring 7 mm in diameter and 10 mm in height, and the cell is set
15 in the apparatus. The sample in the cell is then supplied with a magnetic field which is gradually increased up to a maximum value of 3,000 oersted. Then, the magnetic field is gradually decreased. A B-H hysteresis curve during the process is drawn on a
20 recording paper. The saturation magnetization, residual magnetization and coercive force of the sample are obtained from the hysteresis curve.

(2) Particle size distribution of carrier

The apparatus used is a micro-track particle
25 size analyzer ("SRA-type", available from Nikkiso K.K.), and the measurement range is set to 0.7 - 125 μ m. From the resultant volume-basis particle size

distribution, a 50 % particle size (D_{50}) is obtained.

(3) Current value of carrier

800 g of a carrier sample is weighed and exposed for at least 15 min. to an environment (room
5 temperature: 22 - 25 °C, humidity: 50 - 54 %). A counter electrode is disposed opposite to and 1 mm spaced apart from an electroconductive sleeve containing a magnet roller and provided with an ear-regulating blade. The carrier is magnetically
10 attracted between the sleeve and counter electrode. The magnet roller in the sleeve is rotated so that a magnetic brush of the carrier with ears standing on the sleeve contacts the counter electrode. Then, a DC voltage of 500 volts is applied between the sleeve and
15 the counter electrode to measure a voltage decrease between both ends of resistors of 1 M.ohm and 10 k.ohm connected in series. A current value is calculated from the value.

(4) Toner particle size (weight-average particle
20 size)

The average particle size and particle size distribution of a toner may be measured by a Coulter counter (e.g., "Model TA-II" or "Coulter Multisizer", available from Coulter Electronics Inc.). Herein, we
25 have used Coulter Multisizer, to which an interface (available from Nikkaki K.K.) for providing a number-basis distribution and a volume-basis distribution,

and a personal computer PC 9801 (available from NEC K.K.) are connected.

For measurement, a 1 %-NaCl aqueous solution as an electrolyte solution is prepared by using a reagent-grade sodium chloride. Into 100 to 150 ml of the electrolyte 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 electrolyte 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 by using the above-mentioned Coulter Multisizer with a 100 micron-aperture to obtain a number-basis distribution and a volume basis distribution for particles having a particle size of 2 μm or larger. From these distributions, it is possible to obtain a volume-average particle size (D_v , by using a central value for each channel as a representative value for the channel) and a weight-average particle size (D_4) based on the volume-basis distribution, a length-average particle size (D_1) based on the number-basis distribution, volume-basis contents of particle size fractions ($\geq 8.00 \mu\text{m}$ and $\leq 3.17 \mu\text{m}$) and number-absis contacts of particle size fractions ($\leq 5 \mu\text{m}$ and $\leq 3.17 \mu\text{m}$).

(5) Weight-average particle size of external additive (inorganic fine powder)

The measurement is performed by using a micro-track particle size analyzer ("Model 8230 UPA",
5 available from Nikkiso K.K.) in the following manner.

20 ml of ethanol is placed in a 50 cc-glass beaker. A sample is added so as to provide a Reflected Power indication of 200 mV, and dispersion is performed for 3 min. by an ultrasonic wave
10 generator ("UD 200", available from Tomy Seiko K.K.). The sample dispersion liquid is taken in 6 ml and subjected to three times of measurement at 22 °C to obtain a volume-basis particle size distribution, from which a weight-average particle size is calculated.

15 (6) Hydrophobicity of inorganic fine powder

A methanol titration test is performed.

0.2 g of a sample inorganic fine powder is added to 50 ml of water in a 250 cc-Erlenmeyer flask. While the content in the flask is continuously stirred
20 with a magnetic stirrer, methanol is gradually added to the flask until all the inorganic fine powder is wetted. The terminal point is detected by observing all the inorganic fine powder is suspended in the liquid. The hydrophobicity is determined as a
25 methanol content (%) in the methanol-water mixture at the terminal point.

(7) Light transmittance

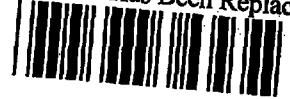
	Sample	0.10 g
	Alkyd resin	13.20 g
	("Beckozole 1323-6-EL", mfd. by Dainippon Ink K.K.)	
5	Melamine resin	3.30 g
	("Super Beckamine J-820-60", mfd. by Dai Nippon Ink K.K.)	
	Thinner	3.50 g
	("Aramic Thinner", mfd. by Kansai Paint K.K.)	
10	Glass medium	50.00 g

The above formulation is placed in a 150 cc-glass bottle and subjected to dispersion for 1 hour by a paint conditioner (mfd. by Red Devil Co.). After
15 the dispersion, the composition is applied on a PET film by a doctor blade 2 mm spaced from the PET film, followed by baking at 120 °C for 10 min. The thus-coated sheet is subject to measurement of transmittance in a range of 320 - 800 nm by a
20 transmittance meter ("U-BEST 50", mfd. by Nippon Bunko K.K.).

(8) Specific surface area S_1 (air permeation method)

Measurement is performed by using a specific surface area meter ("Model SS-100", mfd. by Shimazu
25 Seisakusho K.K.) in the following manner.

- 1) A variable-voltage power supply to a powder tester for sample powder packing is turned on and



adjusted to 100 V.

2) A changeover switch for the powder tester is set to a tap position and the timer is set for 1 min. (50 times $\pm$ 1 time/1 min.).

5 3) A sieve plate is inserted into a plastic-made sample tube and a sheet of filter paper is placed thereon, and a sample is placed thereon up to a 1/3 position of the sample tube.

4) The sample tube is set on a tap stand of the
10 powder tester, and a tapping start button is pressed (tapping for 1 min.).

5) Into the tapped sample tube, an additional amount of the sample is placed up to a 2/3 position of the sample tube.

15 6) Tapping is performed similarly as 4) above.

7) A supplemental tube is inserted to the top of the sample tube, and an additional amount of the sample is added so as to form a pile of the sample.

8) Tapping is performed similarly as the above 4)
20 or 6).

9) The tapped sample tube is taken out of the tap stand, the supplemental tube is pulled out, and an excessive amount of the sample is cut by a spatula.

10) Water is poured into a metering pipe for a
25 specific surface area up to an S mark.

11) The sample tube is connected with the metering pipe (after the sample packing, grease is

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applied onto the ground joint face).

12) A cock for the lower effluent port is opened, and a stopwatch is started when the water level passes a 0 (zero) mark of the metering pipe (the effluent water is received by a beaker).

13) A time required for the water level to descent down to a 20 cc-mark is measured.

14) The sample tube is taken out and the sample is weighed.

15) The specific surface area $SW (= S_1)$ of the sample is calculated from the following equation:

$$SW = \frac{14}{\rho} \sqrt{\frac{\Delta P A T}{\eta L Q} \cdot \frac{\varepsilon^3}{(1-\varepsilon)^2}}$$

15

$$\varepsilon = 1 - \frac{W}{\rho A L}$$

SW: specific surface area of a powder sample
[cm²/g]

20 e: void ratio of a packed sample layer

ρ : density of the powder sample [g/cm³]

η : viscosity coefficient of fluid (air)
[g/cm.sec]

L: thickness of the sample layer [cm]

25 Q: amount of fluid having passed the sample layer [cc]

ΔP : pressure different between both ends of the

sample layer [cc]

A: sectional area of the sample layer [cm^2]

t: time in which the Q (20) cc of fluid (air)
has passed through the sample layer [sec]

5 W: sample weight [g]

(9) Carrier density ρ

An apparatus used in "Aqupic 1330" (available from Shimazu Seisakusho K.K.). A sample carrier is packed into a 10 cm^3 -measurement cell up to ca. 80 %
10 thereof while lightly tapping the cell. The sample cell is dried in a vacuum drier at 40°C , weighed and inserted into an apparatus main body. Then, the sample is subjected to 10 cycles of packing under a pressure of 134, 45 kPa and purging and then 5 times
15 of measurement at a packing pressure of 134.45 kPa and an equilibrium pressure of 0.0345 kPa. An average value is taken as a carrier density.

(10) Acid value

2 - 10 g of a sample resin is weighed into a
20 200 to 300 ml-Erlenmeyer flask, and ca. 50 ml of a methanol/toluene (= 30/70) mixture solvent is added thereto to dissolve the resin. If the solubility is low, a small amount of acetone can be added. The sample solution is titrated with a preliminarily
25 standardized N/10-potassium hydroxide/alcohol solution with a mixture indicator of 0.1 % Bromo Thymol Blue and Phenol Red. The acid value is calculated from the

consumed amount of the KOH solution as follows.

Acid value = KOH (ml) x N x 56.1/sample weight,
wherein N denotes the factor of the N/10-KOH solution
used.

5 (11) Glass transition temperature Tg

A differential scanning calorimeter ("DSC-7",
mfd. by Perkin-Elmer Corp.) is used.

A sample is accurately weighed in an amount
of 5 - 20 g, preferably ca. 10 g. The weighed sample
10 is placed in an aluminum pan and subjected to
temperature raising at a rate of 10 °C/min in a
temperature range of 30 - 200 °C in a normal
temperature - normal humidity environment to obtain a
differential thermal curve. In the temperature
15 raising stage, a main absorption peak appears in the
range of 40 - 100 °C. A median line is drawn between
base lines before and after the appearance of the main
absorption peak. The glass transition temperature Tg
of the sample is determined as the temperature at an
20 intersection of the median line and the differential
thermal curve.

As described above, according to the two
component-type developer of the present invention
containing the carrier formed by coating magnetic
25 carrier core particles comprising a specific ferrite
component with a resin coating layer, it is possible
to obviate difficulties, such as a decrease in image

density and fog even in continuous reproduction of a color original having a large image area. Further, a quick increase in triboelectric charge in the initial stage is accomplished, and fog-free, clear images can
5 be retained even after a continuous image formation on a large number of sheets. Further, the triboelectric chargeability is little affected by a change in environmental conditions. Further, a good conveyability in the developing device is
10 accomplished.

Hereinbelow, the present invention will be described more specifically based on Examples wherein "part(s)" means "part(s) by weight".

15 [Production Examples 1 - 3 of Magnetic Carrier Core Particles]

20 parts of MgO (solubility: 0.62 mg/100 ml), 20 parts of MnO and 60 parts of Fe₂O₃ were respectively formed into fine particles and mixed with
20 each other together with water to be formed into particles. Then, the particles were calcined at 1100 °C and subjected to particle size adjustment to provide Ferrite carrier core particles (σ_s (saturation magnetization) = 58 Am²/kg) A, B and C having average
25 particle sizes (Dav.) of 35.7 μ m, 25.6 μ m and 61.3 μ m, respectively.

[Production Example 4 of Magnetic Carrier Core

Particles]

Ferrite carrier core particle D ($\sigma_s = 60$
Am²/kg) having an average particle size of 36.3 μ m was
prepared in the same manner as in Production Example 1
5 except for the use of 15 parts of MgO, 10 parts of
NiO, 3 parts of Al₂O₃, and 72 parts of Fe₂O₃.
[Production Example 5 of Magnetic Carrier Core
Particles]

Ferrite carrier core particles E ($\sigma_s = 65$
10 Am²/kg) having an average particle size of 39.3 μ m was
prepared in the same manner as in Production Example 1
except for the use of 3 parts of Ag₂O (solubility:
1.74 mg/100 ml) 27 parts of MnO and 70 parts of Fe₂O₃.
[Production Example 6 of Magnetic Carrier Core
15 Particles]

Ferrite carrier core particle F ($\sigma_s = 57$
Am²/kg) having an average particle size of 36.0 μ m was
prepared in the same manner as in Production Example 1
except for the use of 20 parts of BaO (solubility: ≥ 1
20 g/100 ml), 20 parts of ZnO, and 60 parts of Fe₂O₃.
[Production Example 7 of Magnetic Carrier Core
Particles]

Ferrite carrier core particles G ($\sigma_s = 55$
Am²/kg) having an average particle size of 36.8 μ m was
25 prepared in the same manner as in Production Example 1
except for the use of 5 parts of K₂O (solubility: ≥ 1
g/100 ml), 20 parts of NiO and 73 parts of Fe₂O₃.

[Production Example 8 of Magnetic Carrier Core
Particles]

Ferrite carrier core particle H ($\sigma_s = 47$
 Am^2/kg) having an average particle size of $37.5 \mu\text{m}$ was
5 prepared in the same manner as in Production Example 1
except for the use of 35 parts of MgO (solubility:
0.62 mg/100 ml), 5 parts of MnO, and 60 parts of
 Fe_2O_3 .

[Production Example 9 of Magnetic Carrier Core
10 Particles]

Ferrite carrier core particles I ($\sigma_s = 63$
 Am^2/kg) having an average particle size of $35.5 \mu\text{m}$ was
prepared in the same manner as in Production Example 1
except for the use of 0.002 parts of MgO (solubility:
15 0.62 mg/100 ml) 25 parts of MnO and 74.998 parts of
 Fe_2O_3 .

[Production Example 10 of Magnetic Carrier Core
Particles]

Ferrite carrier core particle J ($\sigma_s = 15$
20 Am^2/kg) having an average particle size of $35.8 \mu\text{m}$ was
prepared in the same manner as in Production Example 1
except for the use of 10 parts of MgO (solubility =
0.62 mg/100 ml), 80 parts of MnO, and 10 parts of
 Fe_2O_3 .

25 [Production Example 11 of Magnetic Carrier Core
Particles]

Production of ferrite carrier core particles

was tried in the same manner as in Production Example 1 except for the use of 25 parts of MgO (solubility: 0.62 mg/100 ml) and 75 parts of Fe_2O_3 . However, adequate carrier particles could not be produced due to severe coalescence of the particles.

[Production Example 12 of Magnetic Carrier Core Particles]

Ferrite carrier core particle K ($\sigma_s = 20 \text{ Am}^2/\text{kg}$) having an average particle size of $36.3 \mu\text{m}$ was prepared in the same manner as in Production Example 1 except for the use of 20 parts of MgO (solubility: 0.62 mg/100 ml), 65 parts of MnO, and 15 parts of Fe_2O_3 .

[Production Example 13 of Magnetic Carrier Core Particles]

Ferrite carrier core particles L ($\sigma_s = 70 \text{ Am}^2/\text{kg}$) having an average particle size of $38.5 \mu\text{m}$ was prepared in the same manner as in Production Example 1 except for the use of 3 parts of MgO (solubility: 0.62 mg/100 ml), 1 part of MnO and 96 parts of Fe_2O_3 .

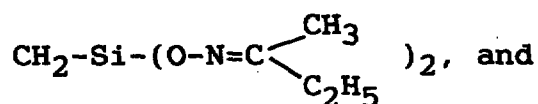
(Carrier Production Examples 1 - 7)

20 parts of toluene, 20 parts of butanol, 20 parts of water and 40 parts of ice were added into a four-necked flask and under stirring, 40 parts of a mixture of $\text{CH}_3\text{SiCl}_3/(\text{CH}_3)_2\text{SiCl}_2$ (= 15/10 by mol) was added thereto, followed further by 30 min. of stirring and 1 hour of condensation reaction at 60°C . Then,

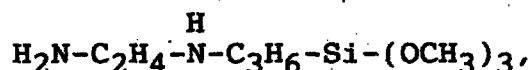
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the resultant siloxane was washed sufficiently with water and dissolved in a toluene-methyl ethyl ketone-butanol mixture solvent to prepare a silicone varnish with a solid matter content of 10 %.

- 5 To 100 parts of the silicone varnish were added 2.0 parts of deionized water, 2.0 parts of the following curing agent



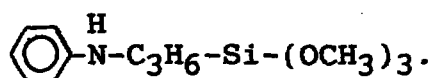
- 10 3.0 parts of the following aminosilane coupling agent



respectively based on the siloxane solid matter content, to prepare Carrier Coating liquid I.

- 15 The above-prepared Ferrite carrier core particles A - G were respectively coated with Coating liquid I thus-prepared so as to provide a resin coating rate of 1.0 wt. %, by using a coater ("Spira Coater", mfd. by Okada Seiko K.K.), thereby to obtain
- 20 Coated Carriers 1 - 7.
(Carrier Production Example 8)

- Coated Carrier 8 was prepared in the same manner as in Carrier Production Example 1 except for replacing the aminosilane coupling agent with the
- 25 following aminosilane coupling agent to prepare Coating liquid II and using Coating liquid II instead of Coating liquid I:

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(Carrier Production Example 9)

Coated Carrier 9 was prepared in the same
5 manner as in Carrier Production Example 1 except for
omitting the curing agent to prepare Coating liquid
III and using Coating liquid III instead of Coating
liquid I.

(Carrier Production Example 10)

10 Coated Carrier 10 was prepared in the same
manner as in Carrier Production Example 1 except for
omitting the siloxane and the aminosilane coupling
agent (i.e., using only the aminosilane coupling
agent) to prepare Coating liquid IV and using Coating
15 liquid IV instead of Coating liquid I.

(Carrier Production Examples 11 - 15)

Coated Carriers 11 - 15 were was prepared in
the same manner as in Carrier Production Examples 1 -
7 except for replacing Ferrite carrier core particles
20 A - G with Ferrite carrier core particles H - L.

Table 1 below shows characterization data of
Coated Carriers 1 - 15 thus prepared.

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Table 1

Carrier	Core	D ₅₀ (μm)	+88 μm (%)	+62 μm (%)	-22 μm (%)	-16 μm (%)	S ₁ (cm ² /g)	S ₂ (cm ² /g)	S ₁ /S ₂	ρ _{ap} (g/cm ²)	Core elements	Coating	Current value (μA)
1	A	35.8	0.8	8.0	7.4	0	540	364	1.48	2.2	Mg-Mn-Fe	I	120
2	B	26.0	0	1.0	14.2	0	780	502	1.55	2.0	Mg-Mn-Fe	I	140
3	C	61.3	7.6	30.3	1.6	0	270	213	1.27	2.5	Mg-Mn-Fe	I	90
4	D	36.5	0.8	8.4	7.5	0	590	355	1.66	2.3	Mg-Ni-Al-Fe	I	110
5	E	39.5	1.2	8.8	5.4	0	455	330	1.38	2.4	Ag-Mn-Fe	I	100
6	F	36.2	0.8	8.2	8.0	0.3	510	360	1.42	2.4	Ba-Zn-Fe	I	120
7	G	37.0	0.9	10.2	7.5	0.1	495	353	1.40	2.3	K-Ni-Fe	I	150
8	A	35.9	0.8	8.0	7.4	0	545	364	1.50	2.2	Mg-Mn-Fe	II	70
9	A	35.6	0.7	8.0	7.5	0	540	364	1.48	2.2	Mg-Mn-Fe	III	80
10	A	36.1	0.9	8.1	7.3	0	535	363	1.47	2.2	Mg-Mn-Fe	IV	100
11	H	37.5	1.0	8.5	7.0	0.3	490	345	1.42	2.2	Mg-Mn-Fe	I	110
12	I	35.5	0.8	7.9	7.3	0	545	364	1.50	2.3	Mg-Mn-Fe	I	130
13	J	35.8	0.8	8.2	7.1	0.3	543	364	1.49	2.4	Mg-Mn-Fe	I	150
14	K	36.3	0.9	8.5	6.8	0.5	515	354	1.45	2.3	Mg-Mn-Fe	I	150
15	L	38.5	1.3	9.2	6.5	0	495	339	1.46	2.2	Mg-Mn-Fe	I	220

ρ_{ap}: apparent density

D₅₀: represents a 50 %-particle size of a coated carrier

(Toner Production Example 1)

	Polyester resin	100 parts
	(condensation product of propoxidized bisphenol with fumaric acid and 5 trimellitic acid)	
	Phthalocyanine pigment	4 "
	Di-tert-butylsalicylic acid metal complex	4 "

The above ingredients were sufficiently
preliminarily blended with each other by a Henschel
10 mixer and melt-kneaded through a twin-screw extruder
kneader. After cooling, the kneaded product was
coarsely crushed into ca. 1 - 2 μm and finely
pulverized by an air jet pulverizer, followed by
classification to obtain blue powder (toner particles)
15 having a weight-average particle size (D_4) of 5.8 μm .

100 parts of the above powder was blended by
a Henschel mixer with 1.5 parts of hydrophobic
anatase-type titanium oxide fine powder ($D_4 = 0.05 \mu\text{m}$,
hydrophobicity (H_{MeOH}) = 55 %, transmittance (T_p) = 70
20 %) hydrophobized through treatment of 100 parts of
anatase-type titanium oxide fine powder with 20 parts
of $n\text{-C}_4\text{H}_9\text{-Si-(OCH}_3)_3$ in aqueous medium, thereby to
obtain Cyan Toner a.

(Toner Production Example 2)

25 Cyan Toner b was prepared in the same manner
as in Toner Production Example 1 except for using
hydrophobic titanium oxide fine powder ($D_4 = 0.0008$

μm , $H_{\text{MeOH}} = 50 \%$ and $T_p = 70 \%$) prepared by hydrophobizing anatase-type titanium oxide fine powder in the form of a hydrate before calcination.

(Toner Production Example 3)

5 Cyan Toner c was prepared in the same manner as in Toner Production Example 1 except for using 2.0 parts of hydrophobic titanium oxide fine powder ($D_4 = 0.04 \mu\text{m}$, $H_{\text{MeOH}} = 70 \%$ and $T_p = 20 \%$) prepared by using rutile-type titanium oxide fine powder (for pigment
10 use) instead of the anatase-type titanium oxide fine powder.

(Toner Production Example 4)

 Cyan Toner d was prepared in the same manner as in Toner Production Example 1 except for using
15 hydrophobic titanium oxide fine powder ($D_4 = 0.05 \mu\text{m}$, $H_{\text{MeOH}} = 65 \%$ and $T_p = 65 \%$) prepared by further treating the hydrophobized anatase-type titanium oxide fine powder with dimethylsilicone oil (100 cp).

(Toner Production Example 5)

20 Cyan Toner e was prepared in the same manner as in Toner Production Example 1 except for using hydrophobic silica fine powder ($D_4 = 0.02 \mu\text{m}$, $H_{\text{MeOH}} = 90 \%$ and $T_p = 34 \%$) prepared by through treatment with dimethylsilicone oil (100 cp) in gaseous phase,
25 instead of the anatase-type titanium oxide.

Example 1

A two component-type developer (toner

concentration (C_{toner}) = 7 wt. %) was prepared by blending the above-prepared Cyan Toner a and Carrier 1, and subjected to continuous image formation by using a color copying machine ("CLC 700", mfd. by Canon K.K.) using an intermittent alternating electric field shown in Figure 2 under a developing contrast of 300 volts for reproducing an original having an image area ratio of 25 %. The continuous image formation was performed on 10000 sheets for each of normal temperature/normal humidity (23 °C/65 %) conditions, high temperature/high humidity (30 °C/80 %RH) conditions and normal temperature/low humidity (20 °C/10 %RH) conditions. The results are shown in Table 2 appearing hereinafter. As shown in Table 2, the two component-type developer showed little change in performance during the continuous image formation and good performances inclusive of substantially no scattering even after 10000 sheets of image formation.

Example 2

A two component-type developer (C_{toner} = 9 %) was prepared in a similar manner as in Example 1 except for using Carrier 2 instead of Carrier 1 and the above-mentioned toner concentration. The developer was evaluated in the same manner as in Example 1. The results are also shown in Table 2.

Example 3

A two component-type developer (C_{toner} = 5 %)



was prepared in a similar manner as in Example 1 except for using Carrier 3 instead of Carrier 1 and the above-mentioned toner concentration. The developer was evaluated in the same manner as in

5 Example 1. The results are also shown in Table 2.

Examples 4 - 7

Two component-type developers were prepared in a similar manner as in Example 1 except for using Carriers 4, 5, 8 and 10 instead of Carrier 1 in

10 manners as shown in Table 2. The developers were evaluated in the same manner as in Example 1. The results are also shown in Table 2.

Comparative Examples 1 - 3

Two component-type developers were prepared in a similar manner as in Example 1 except for using Carriers 6, 7 and 9 instead of Carrier 1 in manners

15 shown in Table 2. The developers were evaluated in the same manner as in Example 1. The results are also shown in Table 2.

20 Comparative Examples 4 - 9

Two component-type developers were prepared in a similar manner as in Example 1 except for using Carriers 11 - 15 instead of Carrier 1 in manners shown in Table 2. The developers were evaluated in the same

25 manner as in Example 1. The results are also shown in Table 2.



Table 2

Ex. or Comp. Ex.	Carrier	Toner	C _{toner} (%)	Image density	Fog (%)	Durability (spent toner)	30°C/80% toner scattering	20°C/10% solid image uniformity
Ex. 1	1	a	7	1.6 - 1.7	~1.2	⊙	⊙	⊙
" 2	2	a	9	1.7 - 1.8	~1.3	⊙	⊙	⊙
" 3	3	a	5	1.5 - 1.6	~1.5	⊙	Δ	○
" 4	4	a	7	1.6 - 1.7	~1.3	⊙	⊙	○
" 5	5	a	7	1.6 - 1.7	~1.3	⊙	○	⊙
Comp. Ex. 1	6	a	7	1.7 - 1.8	~2.0	Δ	Δ	○
" 2	7	a	7	1.7 - 1.9	~2.0	Δ	Δ	Δ
Ex. 6	8	a	7	1.6 - 1.7	~1.3	⊙	⊙	⊙
Comp. Ex. 3	9	a	7	1.6 - 1.9	~2.0	Δ	Δ	○
Ex. 7	10	a	7	1.7 - 1.8	~1.3	⊙	○	⊙
Comp. Ex. 4	11	a	7	1.8 - 2.0	~2.0	Δ	x	○
" 5	12	a	7	1.5 - 1.7	~2.0	Δ	Δ	x
" 6	13	a	7	1.5 - 1.8	~2.3	x	Δ	x
" 7	14	a	7	1.5 - 1.7	~2.5	x	x	x
" 8	15	a	7	1.2 - 1.4	~2.0	Δ	Δ	x

The manner of performance evaluation and the evaluation standards are supplemented at the end of this specification.



(Carrier Production Examples 17 and 18)

Coated Carriers 17 and 18 was prepared in the same manner as in Carrier Production Example 1 except for changing the amount of water added at the time of producing Coating liquid to 0 part and 7 parts, respectively.

Example 8

A two component-type developer was prepared and evaluated in the same manner as in Example 1 except for the use of Carrier 17. As a result, a slight fog of 1.5 % was caused in continuous image formation under 20 °C/10 %RH, while that was a practically acceptable level. The inferior performance might be attributable to insufficient resin coating due to non-use of the water.

Example 9

A two component-type developer was prepared and evaluated in the same manner as in Example 1 except for the use of Carrier 18. As a result, a slight toner scattering was observed when the toner concentration was close to the upper limit of the control range under 30 °C/80 %RH, while that was a practically acceptable level. The result might be attributable to the use of too much water causing an excessive self-crosslinking of the resin to result in a somewhat lower adhesion with the carrier core particles.

Example 10

A two component-type developer was prepared and evaluated in the same manner as in Example 1 except for using Toner b instead of Toner a. As a
5 result, the image qualities at the initial stage were good but the uniformity of a solid image was slightly lowered and the fog was somewhat increased to 1.6 % under 20 °C/10 %RH.

Example 11

10 A two component-type developer was prepared and evaluated in the same manner as in Example 1 except for using Toner c instead of Toner a. As a result, toner scattering slightly occurred and fog was increased to 1.7 % under 30 °C/80 %RH.

15 Example 12

A two component-type developer was prepared and evaluated in the same manner as in Example 1 except for using Toner d instead of Toner a. As a
20 result, fog was at a good level of 0.9 %. The uniformity of a solid image was slightly lowered under 20 °C/10 %RH, but the performances were generally good.

Example 13

A two component-type developer was prepared
25 and evaluated in the same manner as in Example 1 except for using Toner e instead of Toner a. As a result, the uniformity of a solid image was slightly

lowered under 20 °C/10 %RH, and the fog was somewhat increased to 1.5 % under 30 °C/80 %RH. The performances were, however, generally good.

Example 14

5 The two component-type developer comprising Toner a and Carrier 1 used in Example 1 was subjected to continuous image formation by using an image forming apparatus shown in Figure 1 and equipped with a developing sleeve containing a 5-pole magnet roller
10 including a developing principal magnetic pole of 960 gauss under application of an intermittent alternating electric field shown in Figure 4 providing developing conditions of $V_{cont} = 230$ volts, $V_{back} = -930$ volts under environmental conditions of 23 °C/60 %RH.

15 As a result, even after image formation on 10000 sheets, the fog was at a good level of 1.0 %, and the uniformity of solid image was good under 20 °C/10 %RH. Thus, very good performances were attained.

20 Example 15

 An image forming test was performed in the same manner as in Example 14 except for using an alternating electric field shown in Figure 3.

 As a result, the solid uniformity was
25 somewhat lowered and the fog was somewhat increased to 1.4 % under 20 °C/10 %RH. The performances were, however, generally good.

Example 16

An image forming test was performed in the same manner as in Example 14 except for using an alternating electric field shown in Figure 5.

5 As a result, the solid uniformity was somewhat lowered under 20 °C/10 %RH. The performances were, however, generally good.

[Production Example 16 of Magnetic Carrier Core Particles]

10 20 parts of MgO (solubility: 0.62 mg/100 ml), 20 parts of MnO and 60 parts of Fe₂O₃ were respectively formed into fine particles and mixed with each other together with water to be formed into particles. Then the particles were calcined at 1100
15 °C and subjected to particle size adjustment to provide Ferrite carrier core particles M (σ_s (saturation magnetization) = 58 Am²/kg) having average particle sizes (Dav.) of 35.7 μm.

[Production Example 17 of Magnetic Carrier Core
20 Particles]

Ferrite carrier core particle N (σ_s = 60 Am²/kg) having an average particle size of 38.3 μm was prepared in the same manner as in Production Example 16 except for the use of 15 parts of MgO, 15 parts of
25 MnO, 3 parts of SiO₂ and 67 parts of Fe₂O₃, and calcination at 1300 °C.

[Production Example 18 of Magnetic Carrier Core

Particles]

Ferrite carrier core particles O ($\sigma_s = 57$
Am²/kg) having an average particle size of 40.5 μ m was
prepared in the same manner as in Production Example
5 16 except for the use of 3 parts of MgO, 5 parts of
Li₂O and 92 parts of Fe₂O₃.

[Production Example 19 of Magnetic Carrier Core
Particles]

Ferrite carrier core particle P ($\sigma_s = 57$
10 Am²/kg) having an average particle size of 43.2 μ m was
prepared in the same manner as in Production Example
16 except for the use of 20 parts of MgO, 5 parts of
Al₂O₃, and 75 parts of Fe₂O₃.

(Carrier Production Examples 16 - 19)

15 Coated Carriers 16 - 19 were prepared in the
same manner as in Carrier Production Examples 1 - 7
except for replacing Ferrite carrier core particles A
- G with Ferrite carrier core particles M - P and
changing the resin coating rate with Coating liquid I
20 to 0.5 wt. %.

(Carrier Production Example 20)

Coated Carrier 20 was prepared in the same
manner as in Carrier Production Example 16 except for
using Coating liquid V prepared by mixing 50 parts of
25 styrene 2-ethylhexyl acrylate/methyl methacrylate (= 50/20/30) copolymer and 50 parts vinylidene
fluoride/tetrafluoroethylene (= 50/50) copolymer, and

dissolving the mixture in a toluene/methyl ethyl ketone mixture solvent.

Table 3 below shows characterizing data of Coated Carriers 16 - 20 thus prepared.

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Table 3

Carrier	Core	D ₅₀ (μm)	+88 μm (%)	+62 μm (%)	-22 μm (%)	-16 μm (%)	S ₁ (cm^2/g)	S ₂ (cm^2/g)	S ₁ /S ₂	ρ_{ap} (g/cm^2)	Core elements	Coating	Current value (μA)
16	M	35.8	0.8	8.0	7.4	0	540	364	1.48	2.2	Mg-Mn-Fe	I	120
17	N	38.3	1.0	8.3	6.5	0	510	340	1.50	2.3	Mg-Mn-Si-Fe	I	60
18	O	40.5	1.3	9.0	5.8	0	480	322	1.49	2.3	Mg-Li-Fe	I	42
19	P	43.2	1.4	10.0	4.2	0	450	302	1.49	2.2	Mg-Al-Fe	I	70
20	M	36.0	0.9	8.2	7.0	0	530	362	1.46	2.2	Mg-Mn-Fe	V	110

 ρ_{ap} : apparent densityD₅₀: represents a 50 %-particle size of a coated carrierTHIS SHEET HAS BEEN
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[Polyester resin Synthesis Example 1]

	Polyoxypropylene(2,2)-2,2-	
	bis(4-hydroxyphenyl)propane	45 mol.%
	Polyoxyethylene(2)-2,2-bis(4-	
5	hydroxyphenyl)propane	6 "
	Fumaric acid	47 "
	Trimellitic anhydride	2 "

The above ingredients were subjected to polycondensation with dibutyltin oxide as the catalyst under nitrogen stream at 200 °C. The reaction was terminated at a point of providing a softening point (according to ASTM E28-51T) of 92 °C to provide Polyester resin (I), which showed an acid value (AV) of 9.5 mgKOH/g and a glass transition temperature (Tg) of 57.2 °C.

[Polyester resin Synthesis Example 2]

	Polyoxypropylene(2,2)-2,2-	
	bis(4-hydroxyphenyl)propane	45 mol.%
	Polyoxyethylene(2)-2,2-bis(4-	
20	hydroxyphenyl)propane	4 "
	Fumaric acid	40 "
	Terephthalic acid	10 "
	Trimellitic anhydride	1 "

The above ingredients were subjected to polycondensation with dibutyltin oxide as the catalyst under nitrogen stream at 200 °C. The reaction was terminated at a point of providing a softening point

of 91 °C to provide Polyester resin (II), which showed an acid value (AV) of 22.0 mgKOH/g and a glass transition temperature (Tg) of 55.3 °C.

[Polyester resin Synthesis Example 3]

5	Polyoxypropylene(2,2)-2,2-	
	bis(4-hydroxyphenyl)propane	45 mol.%
	Polyoxyethylene(2)-2,2-bis(4-	
	hydroxyphenyl)propane	10 "
	Fumaric acid	43 "
10	1,2,5-Hexanetricarboxylic acid	2 "

The above ingredients were subjected to polycondensation with dibutyltin oxide as the catalyst under nitrogen stream at 200 °C. The reaction was terminated at a point of providing a softening point of 95 °C to provide Polyester resin (III), which showed an acid value (AV) of 0.8 mgKOH/g and a glass transition temperature (Tg) of 58.1 °C.

[Polyester resin Synthesis Example 4]

	Polyoxypropylene(2,2)-2,2-	
20	bis(4-hydroxyphenyl)propane	49 mol.%
	Terephthalic acid	49 "
	2,5,7-Naphthalenetricarboxylic acid	2 "

The above ingredients were subjected to polycondensation with dibutyltin oxide as the catalyst under nitrogen stream at 200 °C. The reaction was terminated at a point of providing a softening point of 92 °C to provide Polyester resin (IV), which showed

an acid value (AV) of 17.1 mgKOH/g and a glass transition temperature (Tg) of 57 °C.

[Polyester resin Synthesis Example 5]

Polyoxypropylene(2,2)-2,2-

5	bis(4-hydroxyphenyl)propane	45 mol.%
	Fumaric acid	45 "
	1,2,7,8-Octanetetracarboxylic acid	2 "

The above ingredients were subjected to polycondensation with dibutyltin oxide as the catalyst under nitrogen stream at 200 °C. The reaction was terminated at a point of providing a softening point of 95 °C to provide Polyester resin (V), which showed an acid value (AV) of 2.2 mgKOH/g and a glass transition temperature (Tg) of 59 °C.

15 [Polyester resin Synthesis Example 6]

Polyoxypropylene(2,2)-2,2-

	bis(4-hydroxyphenyl)propane	50 mol.%
	Terephthalic acid	49.5 "
	Trimellitic anhydride	0.5 "

20 The above ingredients were subjected to polycondensation with dibutyltin oxide as the catalyst under nitrogen stream at 200 °C. The reaction was terminated at a point of providing a softening point of 103 °C to provide Polyester resin (VI), which showed an acid value (AV) of 8.7 mgKOH/g and a glass transition temperature (Tg) of 61 °C.

25 (Toner Production Example 7)

Polyester resin (I)	100 parts
Phthalocyanine pigment	4 "
Di-tert-butylsalicylic acid metal complex	4 "

The above ingredients were sufficiently
5 preliminarily blended with each other by a Henschel
mixer and melt-kneaded through a twin-screw extruder
kneader. After cooling, the kneaded product was
coarsely crushed into ca. 1 - 2 mm and finely
pulverized by an air jet pulverizer, followed by
10 classification to obtain blue powder (toner particles)
having a weight-average particle size (D_4) of 5.8 μm .

100 parts of the above powder was blended by
a Henschel mixer with 1.5 parts of hydrophobic alumina
fine powder ($D_4 = 0.02 \mu\text{m}$, hydrophobicity (H_{MeOH}) = 65
15 %) hydrophobized through treatment with 20 parts of
iso- $\text{C}_4\text{H}_9\text{-Si-(OCH}_3)_3$ in aqueous medium, thereby to
obtain Cyan Toner f.

The toner showed an acid value (AV) of 9.5
mgKOH/g, $T_m = 90^\circ\text{C}$ and $T_g = 55^\circ\text{C}$.

20 (Toner Production Example 8)

Cyan Toner g was prepared in the same manner
as in Toner Production Example 7 except for using
hydrophobic titanium oxide fine powder ($D_4 = 0.03 \mu\text{m}$,
 $H_{\text{MeOH}} = 60 \%$) prepared by hydrophobizing titanium
25 oxide fine powder with n- $\text{C}_4\text{H}_9\text{-Si-(OH)}_3$.

Toner g showed the same AV, T_m and T_g as
Toner f.

(Toner Production Examples 9 - 13)

Toners h - 1 were prepared in the same manner as in Toner Production Example 7 except for using Polyester resins (II) - (VI) instead of Polyester resin (I).

Characterizing data of Toners f - 1 are summarized in the following Table 4.

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Table 4

Toner	Polyester	Additive	D ₄ (μm)	Acid value (KOHmg/g)	T _m (°C)	T _g (°C)
f	(I)	Al ₂ O ₃	5.8	9.5	90	55
g	(I)	TiO ₂	5.8	9.5	90	55
h	(II)	Al ₂ O ₃	6.1	22.0	88	54
i	(III)	Al ₂ O ₃	5.6	0.8	93	56
j	(IV)	Al ₂ O ₃	6.0	17.1	91	56
k	(V)	Al ₂ O ₃	5.8	2.2	93	57
l	(VI)	Al ₂ O ₃	5.9	8.7	100	60

Example 17

A two component-type developer (toner concentration (C_{toner}) = 7 wt. %) was prepared by blending the above-prepared Cyan Toner f and Carrier 16, and subjected to continuous image formation by using a color copying machine ("CLC 700", mfd. by Canon K.K.) including an image-bearing member (I) having a protective layer containing 30 wt. % of fluorine-containing resin particles and using an intermittent alternating electric field shown in Figure 4 under a developing contrast of 300 volts for reproducing an original having an image area ratio of 25 %. The continuous image formation was performed on 10000 sheets for each of normal temperature/normal humidity (23 °C/65 %) conditions, high temperature/high humidity (30 °C/80 %RH) conditions and normal temperature/low humidity (20 °C/10 %RH) conditions. The results are shown in Table 5 appearing hereinafter.

Examples 18 - 22

Two component-type developers were prepared in the same manner as in Example 17 except for using Cyan Toners g - k instead of Cyan toner f. The resultant developers were evaluated in the same manner as in Example 17. The results are also shown in Table 5.

The developers of Examples 19 and 20

containing Toner h having a high acid value and Toner j having a low acid value showed somewhat inferior toner scattering than those of Examples 17 and 18 but were at a level of practically no problem.

5 Example 23

A two component-type developer was prepared and evaluated in the same manner as in Example 17 except for using Toner l instead of Toner f. The resultant images showed a lower gloss and a somewhat
10 lower image density, but generally good performances were exhibited as shown in Table 5.

Examples 24 - 26

Two component-type developers were prepared and evaluated in the same manner as in Example 17
15 except for using Carriers 17 - 19 instead of Carrier 16. Generally good performances were exhibited as shown in Table 5.

Example 27

A two component-type developer was prepared
20 and evaluated in the same manner as in Example 17 except for using Carrier 20 instead of Carrier 16. The successive image forming characteristic was somewhat inferior since the coating resin was not of the silicone-type, but generally good performances
25 were exhibited as shown in Table 5.

Examples 28 - 30

The image forming test was performed in the

same manner as in Example 17 except that the image-bearing member (I) was replaced by image-bearing members (II) - (IV) having protective layers containing 20 %, 6 % and 0 %, respectively, of the
5 fluorine-containing resin particles. The results are also shown in Table 5. As the content of the fluorine-containing resin particles was decreased, the uniformity of the solid image part became somewhat inferior but it was at a level of practically no
10 problem.

Examples 31 and 32

The image forming test was performed in the same manner as in Example 17 except that the alternating electric field was changed from the one
15 shown in Figure 4 to those shown in Figures 5 and 2, respectively. Good results as shown in Table 5 were attained.

Examples 33

The image forming test was performed in the same manner as in Example 17 except that a continuous
20 alternating electric field as shown in Figure 3 was used. As a result, the image density was somewhat lowered and the solid image uniformity was also somewhat lowered. However, they were at a level of
25 practically no problem.

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Table 5

Example	Carrier	Toner	C _{toner} (%)	Image- bearing number	Electric field	Image density	Fog (%)	Durability (spent toner)	30°C/80% toner scattering	20°C/10% solid image uniformity
17	16	f	7	I	Fig.3	1.6-1.7	1.2	○	○	○
18	16	g	7	I	"	1.7-1.8	1.2	○	○	○
19	16	h	7	I	"	1.6-1.8	1.5	○	△	○
20	16	i	7	I	"	1.6-1.7	1.5	○	△	△
21	16	j	7	I	"	1.6-1.7	1.3	○	○	○
22	16	k	7	I	"	1.5-1.7	1.3	○	○	○
23	16	<u>l</u>	7	I	"	1.5-1.6	1.2	○	○	○
8	17	f	7	I	"	1.6-1.7	1.3	○	○	○
9	18	f	7	I	"	1.6-1.7	1.2	○	○	○
10	19	f	7	I	"	1.6-1.7	1.3	○	○	○
11	20	f	7	I	"	1.6-1.8	1.3	○	○	○
12	16	f	7	II	"	1.6-1.7	1.2	○	○	○
13	16	f	7	III	"	1.5-1.6	1.1	○	○	○
14	16	f	7	IV	"	1.5-1.6	1.1	○	○	△
15	16	f	7	I	Fig.4	1.6-1.7	1.2	○	○	○
16	16	f	7	I	Fig.5	1.6-1.7	1.3	○	○	○
17	16	f	7	I	Fig.6	1.4-1.5	1.5	○	○	△

The manner of performance evaluation and the evaluation standards are supplemented at the end of this specification.

Some items of performance evaluation shown in Tables 2 and 5 were performed in the following manner.

[Image density]

Image density (I.D.) was evaluated by a
5 reflective densitometer ("RD-918", mfd. by Macbeth Co.) and indicated according to the following standard.

- ⊙ (excellent): I.D. = 1.6 - 1.7
- o (good): >1.7 - 1.8 or 1.45 - <1.6
- 10 Δ (fair): >1.8 - 1.9 or 1.3 - <1.45
- x (poor): >1.9 or <1.3

[Fog]

Fog was evaluated by measurement of the reflectance by using a reflectometer ("MODEL TC-6DS",
15 mfd. by Tokyo Denshoku K.K.) and an amber filler for cyan toner images. Fog was calculated by the following equation.

Fog (%) = reflectance on standard paper (%) -
reflectance at a non-image portion on a recorded
20 sample sheet (%).

A smaller value means less fog, and the evaluation standard is as follows:

- ⊙: 0 - 1.2 %
- o: >1.2 % - 1.6 %
- 25 Δ: >1.6 % - 1.9 %
- x: >1.9 %

[Durability (spent toner)]

The carriers after the continuous image formation were observed through a scanning electron microscope at a magnification of 2000.

5 ⊙: No spent toner (toner melt-sticking) was observed. No charge decrease was observed.

 ○: Slight spent toner observed. No charge decrease.

 △: Noticeable spent toner observed at concavities, but little decrease in charge.

10 x: Spent toner observed on the entirety. A substantial charge decrease.

[Toner scattering]

 Toner scattering was evaluated by checking the degree of soiling with toner on the outer surfaces
15 of the upstream toner scattering-preventing member (21 in Figure 1 and 103 in Figure 7) and the downstream toner scattering-preventing member (22 in Figure 1 and 104 in Figure 7) of the developing device, and on the members other than the developing device in the image
20 forming apparatus. Evaluation results are indicated according to the following standard:

 ⊙: No soiling was recognized at all.

 ○: Slight soiling was recognized on the water surface of the upstream toner scattering-preventing
25 member but not on the downstream toner scattering preventing member.

 △: Soiling was recognized on the outer surfaces

of the upstream and downstream toner scattering-preventing members, but no soiling was observed on the members other than the developing device.

x: Soiling was observed on the members other
5 than the developing device.

[Uniformity of solid images]

Solid image formed on CLC-SK paper (standard paper for "CLC" copier) was observed with respect to the occurrence of irregularity after standing.

10 ⊙: No problem at all after standing for 1 week.

 o: No problem after standing for 3 days.

 Δ: No problem after standing overnight.

 x: Irregularity observed after standing
overnight.

15 [Softening temperature (T_m)]

A flow tester ("Model CFT-500", mfd. by Shimazu Seisakusho K.K.) was used. Ca. 1 g of a sample having passed 60 mesh was weighed and compressed for 1 min. under a pressure of 100 kg/cm².

20 The compressed sample was subjected to measurement in the flow tester under conditions shown below and under normal temperature/normal humidity conditions (ca. 20 - 30 °C/30 - 70 %RH) to obtain a temperature-apparent viscosity curve. From a
25 smoothened curve, a temperature ($= T_{1/2}$) at a time when half a volume of the sample was flown out was measured and taken as a softening temperature (T_m).

	RATE TEMP	6.0 DEG (%) / M
	SET TEMP	50.0 DEG (°C)
	MAX TEMP	180.0 DEG
	INTERVAL	3.0 DEG
5	PREHEAT	300.0 SEC
	LOAD	20.0 KGF (kg)
	DIE (DIA)	1.0 MM (mm)
	DIE (LENG)	1.0 MM
	PLUNGER	1.0 CM ² (cm ²)

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WHAT IS CLAIMED IS:

1. A carrier for electrophotography, comprising:
magnetic carrier core particles and a resin coating
layer coating the magnetic carrier core particles,

5 wherein

the carrier core particles comprise a
magnetic ferrite component represented by the
following formula (I):



10 wherein A denotes a member selected from the group
consisting of MgO, AgO and mixtures thereof; B denotes
a member selected from the group consisting of Li_2O ,
MnO, CaO, SrO, Al_2O_3 , SiO_2 and mixtures thereof; and
x, y and z are numbers representing weight ratios and
15 satisfying the relation of: $0.2 \leq x \leq 0.95$, $0.005 \leq y$
 ≤ 0.3 , $0 < z \leq 0.795$, and $x+y+z \leq 1$.

2. The carrier according to Claim 1, wherein x,
y and z in the formula (I) further satisfying the
20 conditions of:

$$x+y < 1 \text{ and } z = 1-x-y.$$

3. The carrier according to Claim 1, wherein
said carrier core particles contains 0.5 - 30 wt. % of
25 MgO calculated as its oxide form.

4. The carrier according to Claim 2, wherein



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said carrier core particles contains 0.5 - 30 wt. % of MgO calculated as its oxide form.

5. The carrier according to Claim 1, wherein the
5 component B in the formula (I) is selected from the group consisting of MnO, CaO, SiO₂, Al₂O₃ and mixtures thereof.

6. The carrier according to Claim 1, wherein
10 the component B in the formula (I) is selected from the group consisting of MnO, CaO, and mixtures thereof.

7. The carrier according to Claim 1, wherein the
15 carrier has a 50 %-particle size of 15 - 60 μ m, and contain 1 - 20 wt. % of carrier particles of below 22 μ m, 0.01 - 3 wt. % of carrier particles of below 16 μ m, 2 - 20 wt. % of carrier particles of at least 62 μ m, and at most 3 wt. % of carrier particles of at
20 least 88 μ m.

8. The carrier according to Claim 2, wherein the carrier has a 50 %-particle size of 15 - 60 μ m, and contain 1 - 20 wt. % of carrier particles of below 22
25 μ m, 0.01 - 3 wt. % of carrier particles of below 16 μ m, 2 - 20 wt. % of carrier particles of at least 62 μ m, and at most 3 wt. % of carrier particles of at



least 88 μm .

9. The carrier according to Claim 1, wherein the carrier has a specific area ratio S_1/S_2 of 1.2 - 2.0, wherein S_1 represents a specific surface area measured by the air permeation method and S_2 denotes a specific surface area calculated by the following formula (II):

$$S_2 = [6/(\rho \times D_{50})] \times 10^4 \quad (\text{II}),$$

- wherein ρ denotes a density and D_{50} denotes a 50 %- particle size, respectively, of the carrier.

10. The carrier according to Claim 9, wherein the carrier has an S_1/S_2 ratio of 1.3 - 1.8.

11. The carrier according to Claim 1, wherein the carrier has an apparent density of 1.2 - 3.2 g/cm^3 .

12. The carrier according to Claim 1, wherein the carrier has an apparent density of 1.5 - 2.8 g/cm^3 .

13. The carrier according to Claim 1, wherein the carrier has a current value of 20 - 300 μA .

14. The carrier according to Claim 1, wherein the carrier has a current value of 20 - 250 μA .

15. The carrier according to Claim 1, wherein the



resin coating layer comprises a reactive silicone resin containing a curing agent represented by the following formula (III):



wherein R_2 denotes a substituent selected from the group consisting of CH_3 , C_2H_5 and  each capable of having a substituent; and R_2 and R_3 independently denote CH_3 and C_2H_5 each capable of having a substituent.

16. The carrier according to Claim 2, wherein the resin coating layer comprises a reactive silicone resin containing a curing agent represented by the following formula (III):



wherein R_2 denotes a substituent selected from the group consisting of CH_3 , C_2H_5 and  each capable of having a substituent; and R_2 and R_3 independently denote CH_3 and C_2H_5 each capable of having a substituent.

17. The carrier according to Claim 1, wherein the resin coating layer comprises a reactive silicone resin containing an aminosilane coupling agent.

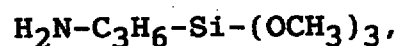
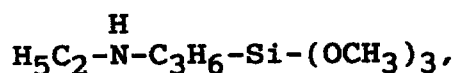
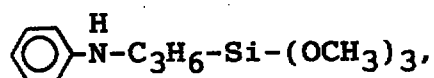
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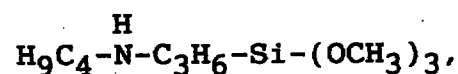
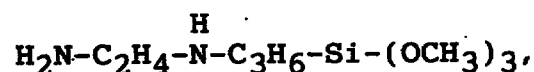
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18. The carrier according to Claim 17, wherein the amino silane coupling agent is a member selected from the group consisting of:

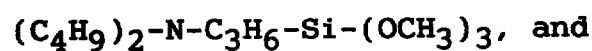
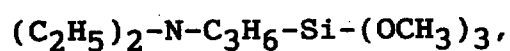
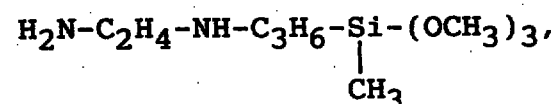
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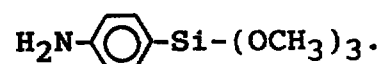
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19. The carrier according to Claim 17, wherein the reactive silicone resin contain 0.1 - 8 wt. parts of the aminosilane coupling agent per 100 wt. parts of siloxane solid matter.

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20. The carrier according to Claim 17, wherein the reactive silicone resin contains 0.3 - 5 wt. parts of the aminosilane coupling agent per 100 wt. parts of siloxane solid matter.

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21. The carrier according to Claim 17, wherein the reactive silicone resin further contains a coupling agent represented by the following formula (IV):

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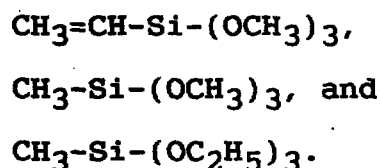


wherein R denotes a substituent selected from the group consisting of vinyl, methacryl, epoxy, amino, mercapto and derivatives of these; X denotes a halogen or alkoxy group; and a is an integer of 1 - 3.

15

22. The carrier according to Claim 21, wherein the coupling agent is a member selected from the groups consisting of:

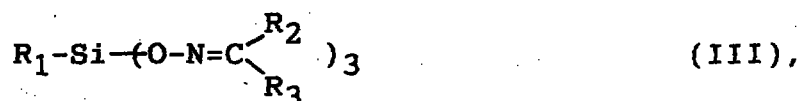
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23. The carrier according to Claim 1, wherein the resin coating layer comprises a reactive silicone resin containing:

a curing agent represented by the following formula (III):

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wherein R_2 denotes a substituent selected from the group consisting of CH_3 , C_2H_5 and  each capable of having a substituent; and R_2 and R_3 independently denote CH_3 and C_2H_5 each capable of having a substituent;

an aminosilane coupling agent; and

a coupling agent represented by the following formula (IV):



wherein R denotes a substituent selected from the group consisting of vinyl, methacryl, epoxy, amino, mercapto and derivatives of these; X denotes a halogen or alkoxy group; and a is an integer of 1 - 3.

24. A two component-type developer, comprising: a toner comprising toner particles, and a carrier comprising magnetic carrier core particles and a resin coating layer coating the magnetic carrier core particles, wherein

the carrier core particles comprise a magnetic ferrite component represented by the following formula (I):



wherein A denotes a member selected from the group consisting of MgO , AgO and mixtures thereof; B denotes

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a member selected from the group consisting of Li_2O ,
MnO, CaO, SrO, Al_2O_3 , SiO_2 and mixtures thereof; and
x, y and z are numbers representing weight ratios and
satisfying the relation of: $0.2 \leq x \leq 0.95$, $0.005 \leq y$
5 ≤ 0.3 , $0 < z \leq 0.795$, and $x+y+z \leq 1$.

25. The developer according to Claim 24, wherein
x, y and z in the formula (I) further
satisfying the condition of $x+y < 1$ and $z = 1-x-y$;
10 the toner comprises toner particles and an
external addition;
the toner has a weight-average particle size
of 1 - 9 μm ; and
the external additive surface treated
15 inorganic fine particles having a weight-average
particle size of 0.001 - 0.2 μm .

26. The developer according to Claim 2, wherein
x, y and z in the formula (I) further satisfy the
20 conditions of:

$$x+y < 1 \text{ and } z = 1-x-y.$$

27. The developer according to Claim 24, wherein
said carrier core particles contains 0.5 - 30 wt. % of
25 MgO calculated as its oxide form.

28. The developer according to Claim 25, wherein



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said carrier core particles contains 0.5 - 30 wt. % of MgO calculated as its oxide form.

29. The developer according to Claim 24, wherein
5 the component B in the formula (I) is selected from the group consisting of MnO, CaO, SiO₂, Al₂O₃ and mixtures thereof.

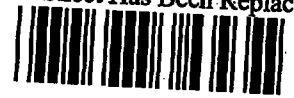
30. The developer according to Claim 24, wherein
10 the component B in the formula (I) is selected from the group consisting of MnO, CaO, and mixtures thereof.

31. The developer according to Claim 24, wherein
15 the carrier has a 50 %-particle size of 15 - 60 μ m, and contain 1 - 20 wt. % of carrier particles of below 22 μ m, 0.01 - 3 wt. % of carrier particles of below 16 μ m, 2 - 20 wt. % of carrier particles of at least 62 μ m, and at most 3 wt. % of carrier particles of at
20 least 88 μ m.

32. The developer according to Claim 25, wherein
the carrier has a 50 %-particle size of 15 - 60 μ m, and contain 1 - 20 wt. % of carrier particles of below
25 22 μ m, 0.01 - 3 wt. % of carrier particles of below 16 μ m, 2 - 20 wt. % of carrier particles of at least 62 μ m, and at most 3 wt. % of carrier particles of at



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least 88 μm .

33. The developer according to Claim 24, wherein the carrier has a specific area ratio S_1/S_2 of 1.2 - 2.0, wherein S_1 represents a specific surface area measured by the air permeation method and S_2 denotes a specific surface area calculated by the following formula (II):

$$S_2 = [6/(\rho \times D_{50})] \times 10^4 \quad (\text{II}),$$

wherein ρ denotes a density and D_{50} denotes a 50 %-average particle size, respectively, of the carrier.

34. The developer according to Claim 33, wherein the carrier has an S_1/S_2 ratio of 1.3 - 1.8.

35. The developer according to Claim 24, wherein the carrier has an apparent density of 1.2 - 3.2 g/cm^3 .

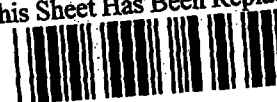
36. The developer according to Claim 24, wherein the carrier has an apparent density of 1.5 - 2.8 g/cm^3 .

37. The developer according to Claim 24, wherein the carrier has a current value of 20 - 300 μA .

38. The developer according to Claim 24, wherein



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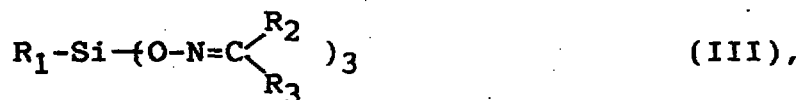
the carrier has a current value of 20 - 250 μ A.

39. The developer according to Claim 24, wherein the resin coating layer comprises a reactive silicone resin containing a curing agent represented by the following formula (III):



wherein R_2 denotes a substituent selected from the group consisting of CH_3 , C_2H_5 and  each capable of having a substituent; and R_2 and R_3 independently denote CH_3 and C_2H_5 each capable of having a substituent.

40. The developer according to Claim 25, wherein the resin coating layer comprises a reactive silicone resin containing a curing agent represented by the following formula (III):



wherein R_2 denotes a substituent selected from the group consisting of CH_3 , C_2H_5 and  each capable of having a substituent; and R_2 and R_3 independently denote CH_3 and C_2H_5 each capable of having a substituent.

41. The developer according to Claim 24, wherein



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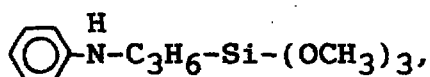
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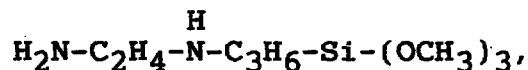
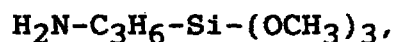
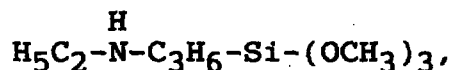
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the resin coating layer comprises a reactive silicone resin containing an aminosilane coupling agent.

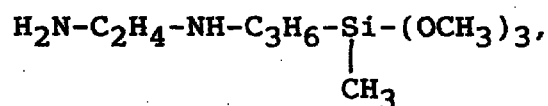
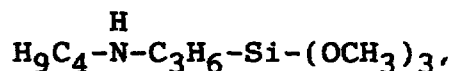
42. The developer according to Claim 41, wherein
5 the amino silane coupling agent is a member selected from the group consisting of:



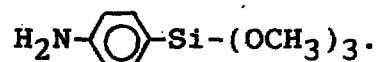
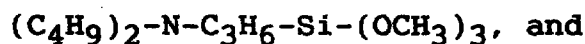
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43. The developer according to Claim 41, wherein
the reactive silicone resin contains 0.1 - 8 wt. parts



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of the aminosilane coupling agent per 100 wt. parts of siloxane solid matter.

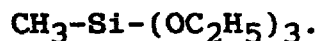
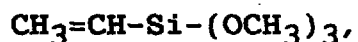
44. The developer according to Claim 41, wherein
5 the reactive silicone resin contain 0.3 - 5 wt. parts of the aminosilane coupling agent per 100 wt. parts of siloxane solid matter.

45. The developer according to Claim 41, wherein
10 the reactive silicone resin further contains a coupling agent represented by the following formula (IV):



wherein R denotes a substituent selected from the
15 group consisting of vinyl, methacryl, epoxy, amino, mercapto and derivatives of these; X denotes a halogen or alkoxy group; and a is an integer of 1 - 3.

46. The developer according to Claim 45, wherein
20 the coupling agent is a member selected from the groups consisting of:



25

47. The developer according to Claim 24, wherein the resin coating layer comprises a reactive silicone



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resin containing:

a curing agent represented by the following formula (III):



wherein R_2 denotes a substituent selected from the group consisting of CH_3 , C_2H_5 and  each capable of having a substituent; and R_2 and R_3 independently denote CH_3 and C_2H_5 each capable of having a substituent;

an aminosilane coupling agent; and

a coupling agent represented by the following formula (IV):



wherein R denotes a substituent selected from the group consisting of vinyl, methacryl, epoxy, amino, mercapto and derivatives of these; X denotes a halogen or alkoxy group; and a is an integer of 1 - 3.

48. The developer according to Claim 24, wherein the toner has a weight-average particle size of 1 - 9 μm .

49. The developer according to Claim 24, wherein the toner comprises toner particles, and an external additive comprising hydrophobic inorganic fine particles.



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50. The developer according to Claim 49, wherein the hydrophobic inorganic fine particles comprise at least one member selected from the group consisting of alumina fine particles, titanium oxide fine particles
5 and silica fine particles.

51. The developer according to Claim 49, wherein the hydrophobic inorganic fine particles have a hydrophobicity of 20 - 80 %.

10

52. The developer according to Claim 49, wherein the hydrophobic inorganic fine particles have a weight-average particle size of 0.001 - 0.2 μm .

15

53. The developer according to Claim 49, wherein the hydrophobic inorganic fine particles have an optical transmittance of at least 40 % at a wavelength of 400 nm.

20

54. The developer according to Claim 24, wherein the toner particles comprise a binder resin and a colorant, and the binder resin comprises a polyester resin.

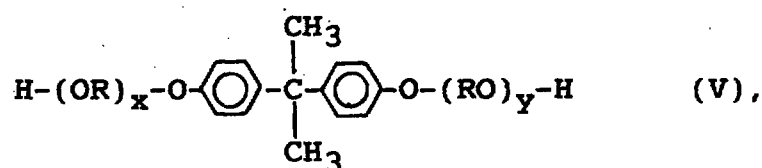
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55. The developer according to Claim 54, wherein the polyester resin comprises a condensation copolymer of an etherified bisphenol and a polycarboxylic acid



having at least two functional groups.

56. The developer according to Claim 55, wherein the etherified bisphenol comprises a compound represented by the following formula (V):



wherein R denotes an ethylene or propylene group, x and y are independently a positive integer of at least 1 with the proviso that the average of x+y is in the range of 2 - 10.

57. The developer according to Claim 54, wherein the binder resin has an acid value of 1 - 20 mgKOH/g.

58. The developer according to Claim 55, wherein said polycarboxylic acid includes 0.1 - 20 mol. % of a polycarboxylic acid component having at least three functional groups.

59. The developer according to Claim 54, wherein the toner particles have a glass transition temperature (T_g) of 45 - 47 °C.

60. The developer according to Claim 54, wherein the toner particles have a temperature providing an



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apparent viscosity of 10^5 poises (Tm) in the range of
80 - 120 °C.

61. An image forming method, comprising:

5 circulatively conveying a two component-type
developer comprising a toner and a carrier on a
developer-carrying member, and

 developing, in a developing region, an
electrostatic latent image held on an electrostatic
10 image-bearing member with the toner in the two
component-type developer, wherein

 the toner comprises toner particles, and the
carrier comprises magnetic carrier core particles and
a resin coating layer coating the magnetic carrier
15 core particles, wherein

 the carrier core particles comprise a
magnetic ferrite component represented by the
following formula (I):



20 wherein A denotes a member selected from the group
consisting of MgO, AgO and mixtures thereof; B denotes
a member selected from the group consisting of Li_2O ,
MnO, CaO, SrO, Al_2O_3 , SiO_2 and mixtures thereof; and
x, y and z are numbers representing weight ratios and
25 satisfying the relation of: $0.2 \leq x \leq 0.95$, $0.005 \leq y$
 ≤ 0.3 , $0 < z \leq 0.795$, and $x+y+z \leq 1$.



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62. The method according to Claim 61, wherein the electrostatic latent image is developed with the toner in the two component-type developer under application of a developing bias comprising a succession of
5 voltages including a first voltage directing a toner from the image bearing member toward the developer-carrying member, a second voltage directing the toner from the developer carrying member toward the image-bearing member and a third voltage intermediate
10 between the first and second voltages, respectively, to the developer-carrying member.

63. The method according to Claim 62, wherein a period (T_1) for applying the first voltage and the
15 second voltage is set to be shorter than a period (T_2) for applying the third voltage.

64. The method according to Claim 61, wherein said electrostatic latent image-holding member
20 comprises a photosensitive layer and a protective layer coating the photosensitive layer; the protective layer containing fluorine-containing resin particles.

65. The method according to Claim 61, wherein
25 said protective layer has a ten point average surface roughness (R_z) of 0.01 - 1.5 μm .



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66. The method according to Claim 61, wherein the two component-type developer comprises a developer according to any of Claims 25 - 59.

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ABSTRACT OF THE DISCLOSURE

A carrier for electrophotography is constituted by magnetic carrier core particles and a resin coating layer coating the magnetic carrier core particles. The carrier core particles contain a magnetic ferrite component represented by the following formula (I):



wherein A denotes a member selected from the group consisting of MgO, AgO and mixtures thereof; B denotes a member selected from the group consisting of Li_2O , MnO, CaO, SrO, Al_2O_3 , SiO_2 and mixtures thereof; and x, y and z are numbers representing weight ratios and satisfying the relation of: $0.2 \leq x \leq 0.95$, $0.005 \leq y \leq 0.3$, $0 < z \leq 0.795$, and $x+y+z \leq 1$. The coated carrier particles thus formed exhibit excellent performances in continuous image formation.

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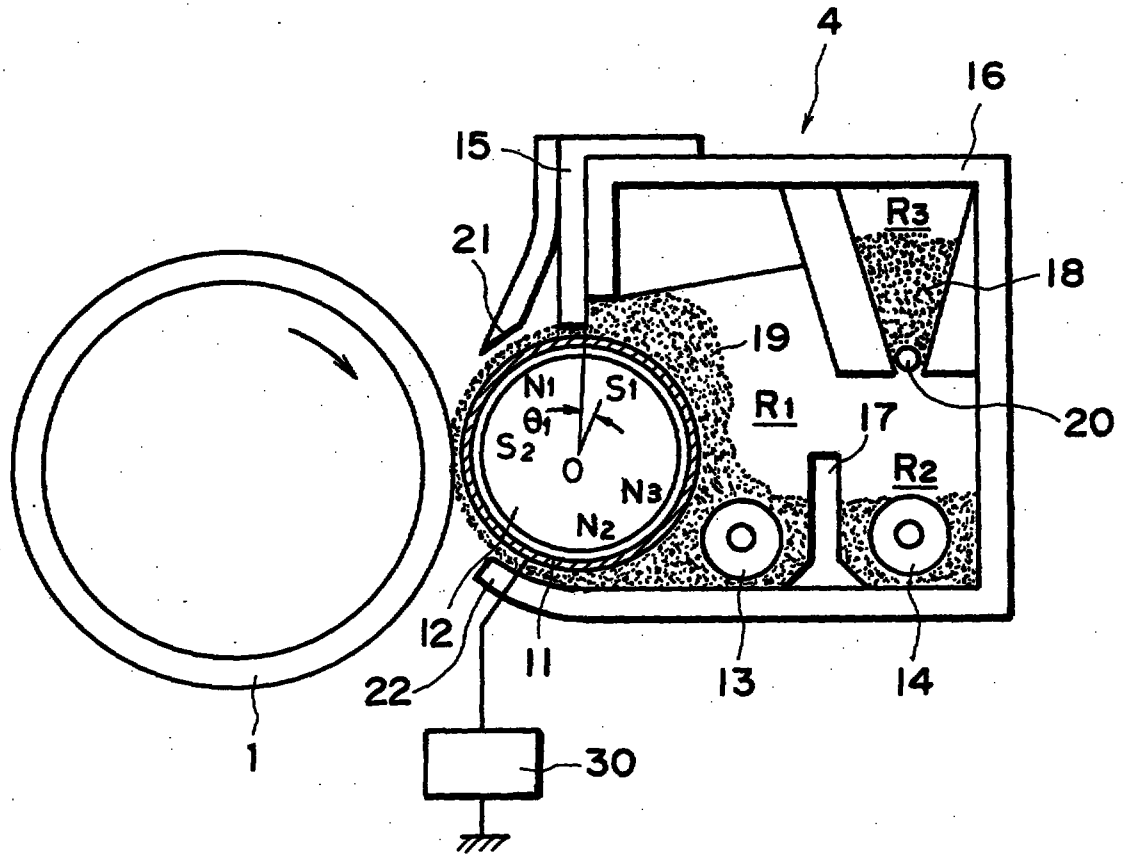
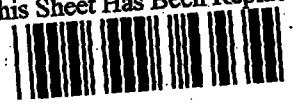


FIG. 1

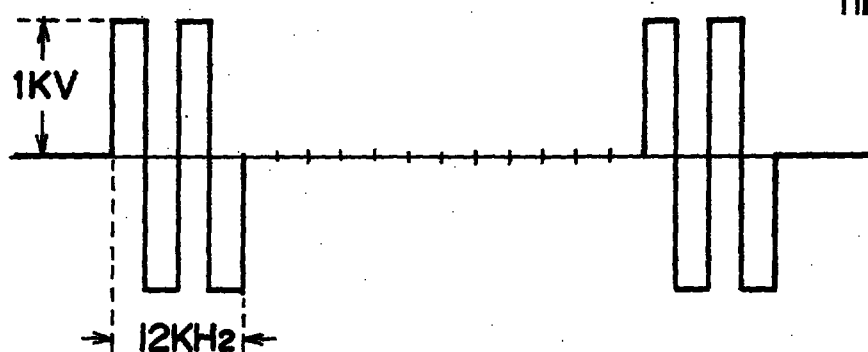


FIG. 2

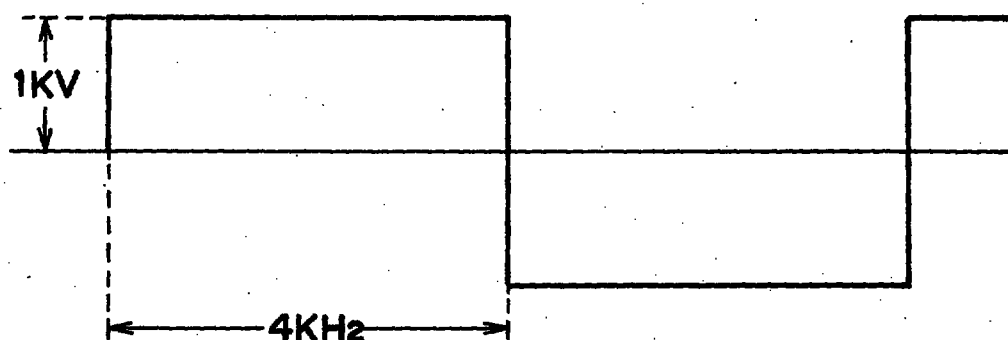


FIG. 3

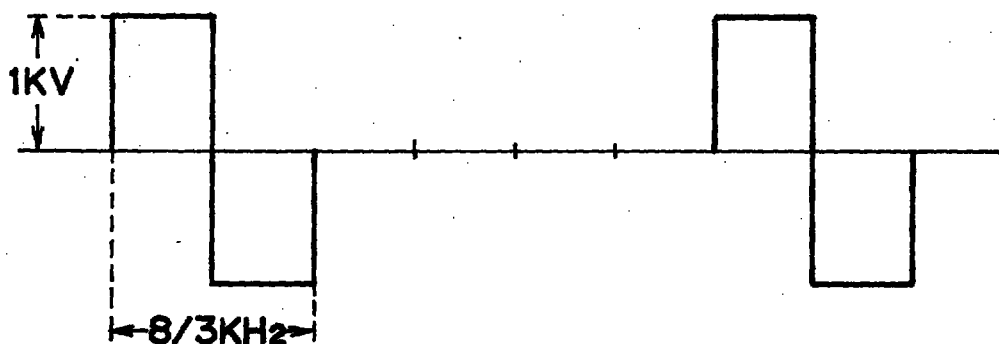


FIG. 4

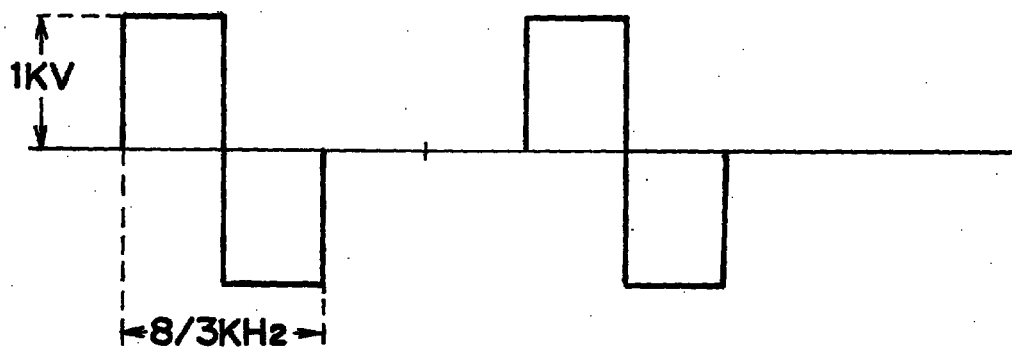


FIG. 5



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Table 1

Carrier	Core	D ₅₀ (μ m)	+88 μ m (%)	+62 μ m (%)	-22 μ m (%)	-16 μ m (%)	S ₁ (cm ² /g)	S ₂ (cm ² /g)	S ₁ /S ₂	ρ_{ap} (g/cm ²)	Core elements	Coating	Current value (μ A)
1	A	35.8	0.8	8.0	7.4	0	540	364	1.48	2.2	Mg-Mn-Fe	I	120
2	B	26.0	0	1.0	14.2	0	780	502	1.55	2.0	Mg-Mn-Fe	I	140
3	C	61.3	7.6	30.3	1.6	0	270	213	1.27	2.5	Mg-Mn-Fe	I	90
4	D	36.5	0.8	8.4	7.5	0	590	355	1.66	2.3	Mg-Ni-Al-Fe	I	110
5	E	39.5	1.2	8.8	5.4	0	455	330	1.38	2.4	Ag-Mn-Fe	I	100
6	F	36.2	0.8	8.2	8.0	0.3	510	360	1.42	2.4	Ba-Zn-Fe	I	120
7	G	37.0	0.9	10.2	7.5	0.1	495	353	1.40	2.3	K-Ni-Fe	I	150
8	A	35.9	0.8	8.0	7.4	0	545	364	1.50	2.2	Mg-Mn-Fe	II	70
9	A	35.6	0.7	8.0	7.5	0	540	364	1.48	2.2	Mg-Mn-Fe	III	80
10	A	36.1	0.9	8.1	7.3	0	535	363	1.47	2.2	Mg-Mn-Fe	IV	100
11	H	37.5	1.0	8.5	7.0	0.3	490	345	1.42	2.2	Mg-Mn-Fe	I	110
12	I	35.5	0.8	7.9	7.3	0	545	364	1.50	2.3	Mg-Mn-Fe	I	130
13	J	35.8	0.8	8.2	7.1	0.3	543	364	1.49	2.4	Mg-Mn-Fe	I	150
14	K	36.3	0.9	8.5	6.8	0.5	515	354	1.45	2.3	Mg-Mn-Fe	I	150
15	L	38.5	1.3	9.2	6.5	0	495	339	1.46	2.2	Mg-Mn-Fe	I	220

 ρ_{ap} : apparent densityD₅₀: represents a 50 % particle size of a coated carrier

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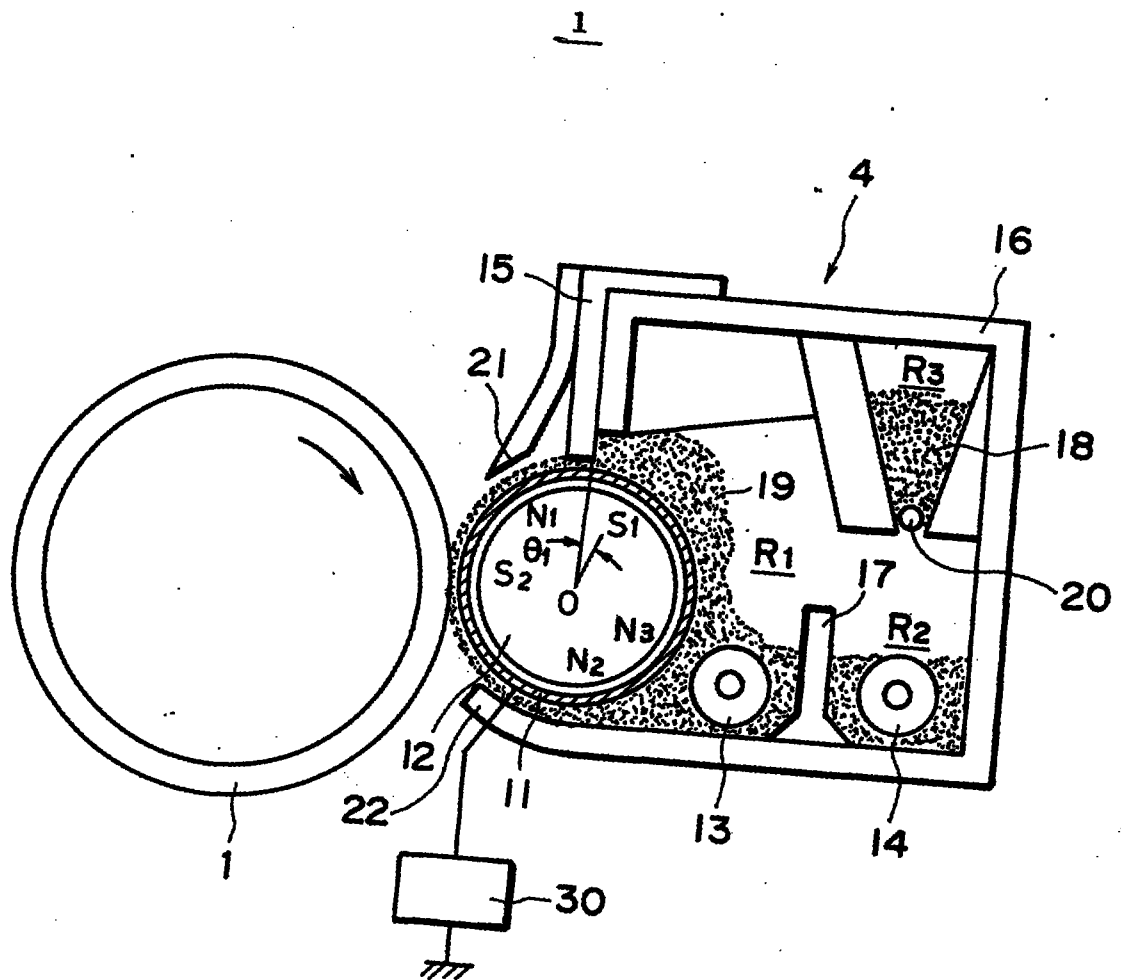
Table 3

Carrier	Core	D ₅₀ (μm)	+88 μm (%)	+62 μm (%)	-22 μm (%)	-16 μm (%)	S1 (cm^2/g)	S2 (cm^2/g)	S1/S2	ρ_{ap} (g/cm^2)	Core elements	Coating	Current value (μA)
16	M	35.8	0.8	8.0	7.4	0	540	364	1.48	2.2	Mg-Mn-Fe	I	120
17	N	38.3	1.0	8.3	6.5	0	510	340	1.50	2.3	Mg-Mn-Si-Fe	I	60
18	O	40.5	1.3	9.0	5.8	0	480	322	1.49	2.3	Mg-Ii-Fe	I	42
19	P	43.2	1.4	10.0	4.2	0	450	302	1.49	2.2	Mg-Al-Fe	I	70
20	M	36.0	0.9	8.2	7.0	0	530	362	1.46	2.2	Mg-Mn-Fe	V	110

 ρ_{ap} : apparent densityD₅₀: represents a 50 %-particle size of a coated carrier

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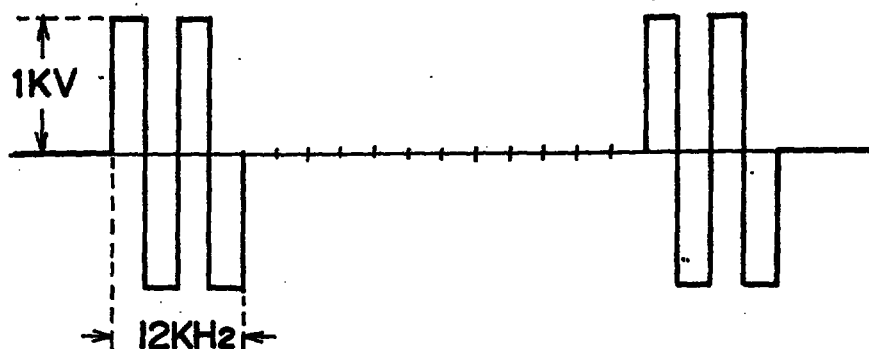


FIG. 2

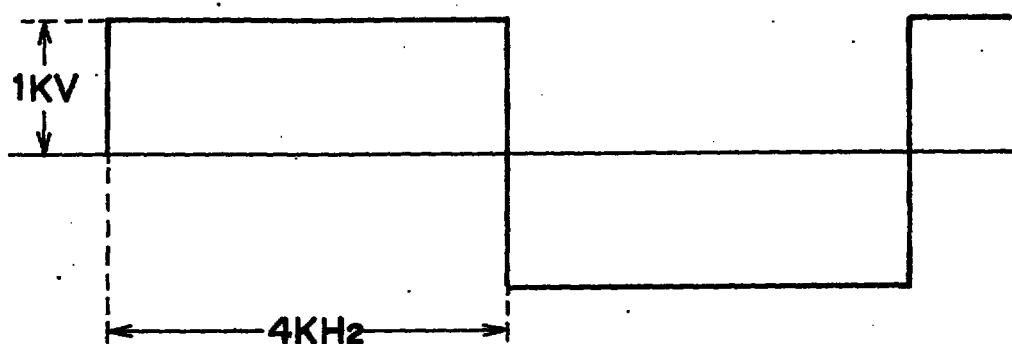


FIG. 3

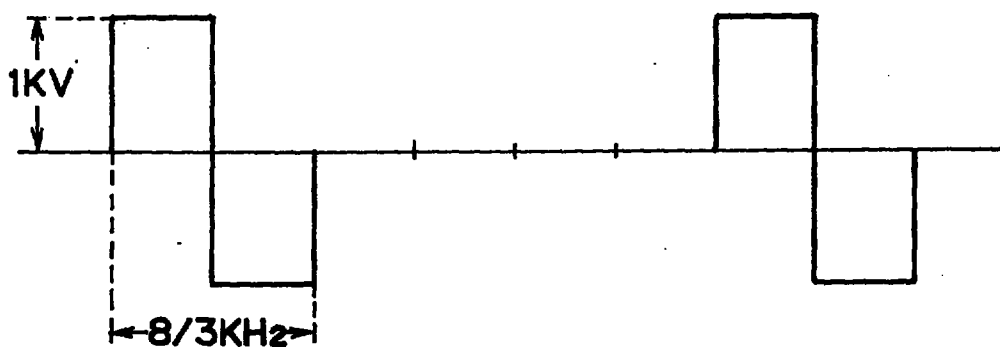


FIG. 4

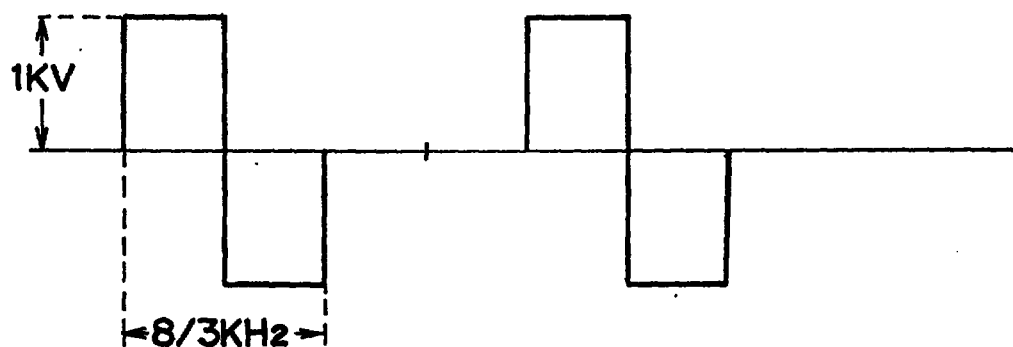


FIG. 5

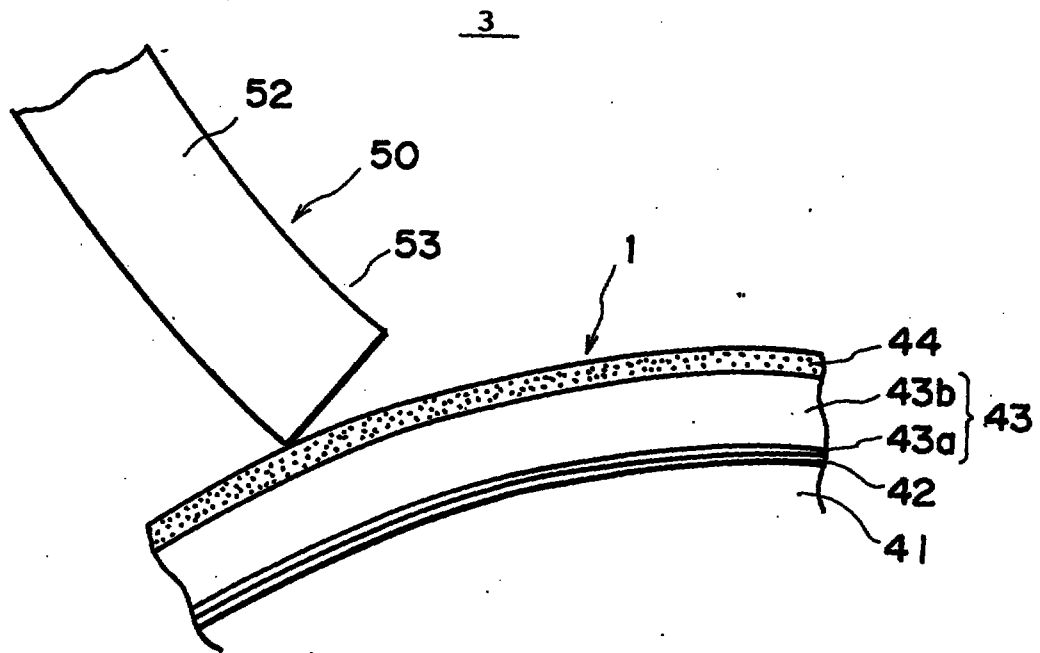


FIG. 6

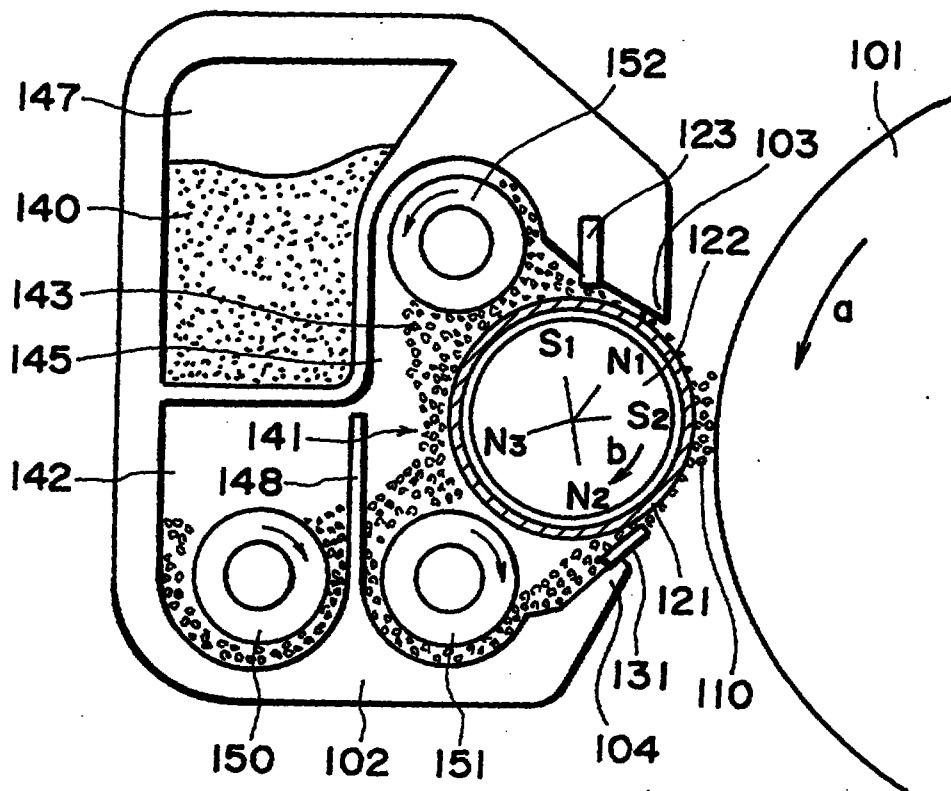


FIG. 7



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CARRIER FOR ELECTROPHOTOGRAPHY,TWO COMPONENT-TYPE DEVELOPER AND IMAGE FORMING METHODABSTRACT OF THE DISCLOSURE

A carrier for electrophotography is constituted by magnetic carrier core particles and a resin coating layer coating the magnetic carrier core particles. The carrier core particles contain a magnetic ferrite component represented by the following formula (I):



wherein A denotes a member selected from the group consisting of MgO, AgO and mixtures thereof; B denotes a member selected from the group consisting of Li_2O , MnO, CaO, SrO, Al_2O_3 , SiO_2 and mixtures thereof; and x, y and z are numbers representing weight ratios and satisfying the relation of: $0.2 \leq x \leq 0.95$, $0.005 \leq y \leq 0.3$, $0 < z \leq 0.795$, and $x+y+z \leq 1$. The coated carrier particles thus formed exhibit excellent performances in continuous image formation.

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CARRIER FOR ELECTROPHOTOGRAPHY

TWO COMPONENT-TYPE DEVELOPER AND IMAGE FORMING METHOD

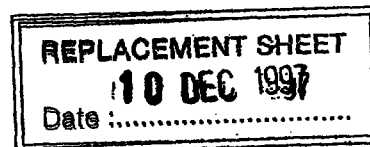
ABSTRACT OF THE DISCLOSURE

A carrier for electrophotography is constituted by magnetic carrier core particles and a resin coating layer coating the magnetic carrier core particles. The carrier core particles contain a magnetic ferrite component represented by the following formula (I):



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Figure 1



the whole apparatus, an increased production cost due to size enlargement of the apparatus and also an overload on the developing device similarly as above.

For the above reason, the improvement in both
5 toner and carrier has been examined and reported in order to provide a high image quality for a long period.

Heretofore, several developers have been proposed in order to provide improved image quality.
10 For example, JP-A 51-3244 has proposed a non-magnetic toner having a controlled particle size distribution so as to improve the image quality. The toner principally comprises particles having a size of 8 - 12 μm and is therefore relatively coarse. According
15 to our study, it is difficult for a toner having such a particle size to effect a intimate "coverage" of a latent image. Further, the toner has a rather broad particle size distribution including at most 30 % by number of particles having a size of at most 5 μm and
20 at most 5 % by number of particles of at least 20 μm . In order to form a clear image by using such a relatively coarse toner having a broad particle size distribution, it is necessary to superpose toner particles in a large thickness so as to fill gaps
25 between toner particles and provide an apparently increased image density. As a result, an increased amount of the toner is consumed in order to provide a



uniformity of image density in one copy sheet.

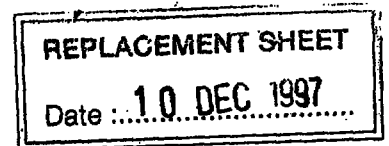
JP-A 2-281280 has provided a carrier having improved developing performances characterized by having a narrow particle size distribution with
5 controlled amounts of fine powder and coarse powder fractions.

As described hereinbefore, however, a demand for a copying machine satisfying a high resolution and a high image quality has been increased in the market
10 and, for this purpose, a smaller particle size of toner has been tried also for accomplishing a high-quality color image formation. A smaller particle size of toner has an increased surface area per unit weight and tends to have a larger electric charge,
15 which is liable to provide a lower image density and a deterioration in continuous image formation characteristic.

In order to prevent such a lowering in image density and deterioration in continuous image forming
20 characteristic and also to provide an increase in developing performance, it has been tried to use a carrier having a further smaller particle size. Such a carrier, however, has not acquired sufficient qualities suitably coping with changes in toner
25 chargeability depending on environmental conditions and continuation of successive image formation. Accordingly, it has been difficult to accomplish the

that x , y and z further satisfy: $x+y < 1$ and $z = 1-x-y$, so as to provide carrier core particles having a moderate surface roughness, an appropriate moisture content, adhesiveness to a resin and toughness. It is
5 however possible that the ferrite component can contain preferably at most 3 wt. % of another metal element in the form of a hydroxide, oxide, sulfide or aliphatic acid compound for various proposes, such as control of surface crystal grain size, prevention of
10 coalescence during calcination, and control of particle size distribution. Accordingly, $x+y+z < 1$ in the formula (I) means the case where the ferrite component contains such another optional component in an amount of preferably up to 10 wt.%. A specific
15 example of the case will be found in Example 4 appearing hereinafter.

In the above formula (I), if x is below 0.2, the carrier is liable to have a low magnetic property leading to carrier scattering and damage the surface
20 of the photosensitive member. In case where x is above 0.95, the core is liable to have a low resistivity. If y is below 0.005, it is difficult to obtain proper resistivity and magnetic properties. If y is above 0.3, it becomes difficult to form spherical
25 carrier core particles having a uniform surface. If z is 0, i.e., no B component is contained, it becomes difficult to provide a sharp particle size



qualities inclusive of high image density, good highlight reproducibility and good thin-line reproducibility can be realized by using a carrier having specific particle size distribution and surface
5 property.

The carrier (particularly, core particles thereof) according to the present invention may be characterized by a uniformly small particle size carrier having a small average particle size and
10 controlled contents of fine and coarse powder fractions and having a certain degree of surface unevenness. Accordingly, even when the core particles are coated with a resin having a small free energy, the resultant coated carrier retains a good toner-
15 conveying performance and is provided with a quick triboelectrification characteristic.

The carrier may preferably have a 50 %-particle size (volume-basis median particle size, i.e., a particle size at which a cumulative particle
20 size fraction (from the smallest measurable particle size) reaches 50 % by volume) of 15 - 60 μm , preferably 20 - 45 μm , and contains 1 - 20 wt. %, desirably 2 - 15 wt. %, more preferably 4 - 12 wt. %, of carrier particles of below 22 μm , including 0.01 -
25 3 wt. %, preferably 0.01 - 2 wt. %, more preferably 0.01 - 1 wt. %, of carrier particles of below 16 μm .

If the content of the fine powder fraction

of 20 - 300 μ A, more preferably 30 - 250 μ A, further preferably 40 - 200 μ A.

If the current value is below 20 μ A, the charge migration on the carrier surface may not be effectively performed and the carrier is caused to have a lower charge-imparting ability to the toner, thus being liable to cause fog and toner scattering.

Above 300 μ A, the carrier attachment onto the photosensitive member and the leakage of a bias voltage are liable to occur, thus being liable to result in image defects.

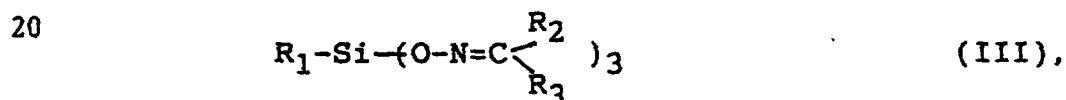
The magnetic performances of a carrier are affected by a magnet roller contained in a developing sleeve and, in turn, greatly affect the developing performance and the conveyability of the two component-type developer.

In an embodiment of the image forming method according to the present invention, a developing sleeve (developer-carrying member) containing a magnet roller therein is rotated while the magnetic roller is fixed, thereby circulatively conveying a two component-type developer comprising the magnetic carrier and an insulating color toner to develop an electrostatic latent image held on the electrostatic image-bearing member. In this instance, preferred conditions may include (1) the magnet roller having 5 magnetic poles including a repulsive magnetic pole,

(2) a magnetic flux of 50 - 1200 gauss in the developing region, and (3) a saturation magnetization of the carrier of 20 - 70 Am²/kg, so as to provide excellent image uniformity and gradation reproducibility in color image formation.

If the carrier has a saturation magnetization exceeding 70 Am²/kg (under an applied magnetic field of 3000 oersted), the resultant brush or ear composed of the carrier and the toner on the developing sleeve opposite an electrostatic latent image on the photosensitive member becomes tightly packed, thus providing a lower reproducibility of gradation and halftone. Below 20 Am²/kg, it becomes difficult to well hold the toner and the carrier on the developing sleeve, thus being liable to cause carrier attachment and toner scattering.

The curing agent contained in the reactive particle size may suitably be an oxime-type curing agent represented by the following formula (III):



wherein R₁ denotes a substituent selected from the group consisting of CH₃, C₂H₅ and  each capable of having a substituent; and R₂ and R₃ independently denote CH₃ and C₂H₅ each capable of having a substituent. Thus, such an oxime-type silane coupling agent is suitable in view of an appropriate degree of

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a method wherein the carrier core particles are fluidized in a fluidizing system and a solution of the coating resin composition is sprayed thereonto for coating, followed by drying and baking at an elevated temperature; and a method wherein the carrier core particles are simply blended with powder or an aqueous emulsion of the coating resin composition.

In a preferred method, a mixture solvent formed by adding 0.1 - 5 wt. parts, preferably 0.3 - 3 wt. parts, of water to a solvent containing at least 5 wt. %, preferably at least 20 wt. %, of a polar solvent, such as ketone or alcohol, may be used so as to intimately attach a coating resin, such as a reactive silicone resin, onto the carrier core particles. In case where the water is below 0.1 wt. part, the hydrolysis of the reactive silicone resin is not sufficiently effected so that it is difficult to form a thin and uniform coating film onto the surface of the carrier core particles. In excess of 5 wt. parts, the reaction control becomes difficult, thus providing a rather low coating strength.

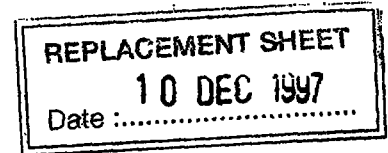
In the present invention, the carrier and a toner are blended to prepare a two component-type developer in a mixing ratio which preferably provides a toner concentration in the developer of 1 - 12 wt. %, more preferably 2 - 9 wt. %, so as to provide generally good results. If the toner concentration is

result in defects, such as toner scattering and fog. In excess of 9 μ m, the accomplishment of a high image quality is hindered due to a lowering in minute dot-reproducibility or scattering at the time of transfer.

5 The toner used in the present invention may contain a colorant which may be a known dye and/or pigment, examples of which may include: Phthalocyanine Blue, Indanthrene Blue, Peacock Blue, Permanent Red, Lake Red, Rhodamine Lake, Hansa Yellow, Permanent
10 Yellow, and Benzidine Yellow. The colorant may be added in an amount of 12 wt. parts or less, more preferably 0.5 - 9 wt. parts, per 100 wt. parts of the binder resin, so as to provide a good sensitivity to transmittance of an OHP film.

15 The toner used in the present invention can contain an additive within an extent of not impairing the toner characteristic. Examples of such an additive may include: a lubricant, such as polytetrafluoroethylene, zinc stearate, or
20 polyvinylidene fluoride; a fixing aid, such as low-molecular weight polyethylene or low-molecular weight polypropylene; and organic resin particles.

 The toner may be produced through various processes including a process wherein starting
25 ingredients are melt-kneaded in a hot kneading means, such as hot rollers, a kneader or an extruder, and the kneaded and cooled product is mechanically pulverized



and classified; a process wherein toner materials, such as a colorant, are dispersed in a binder resin solution and then the resultant dispersion are spray-dried; and a process wherein prescribed materials such as a colorant are dispersed in a polymerizable monomer providing a polymer constituting the binder resin to provide a polymerizable mixture, and the resultant polymerizable mixture is dispersed in suspension or emulsion to be polymerized.

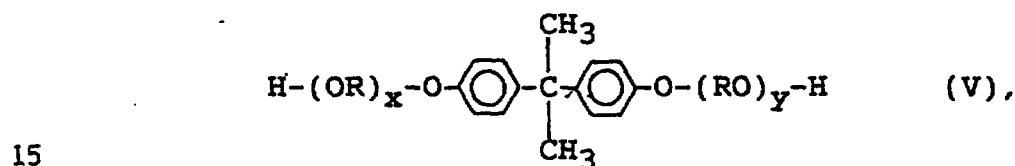
10 The binder constituting the toner may comprise various resins, examples of which may include: polystyrene; styrene-copolymers, such as, styrene-butadiene copolymer, styrene-acrylic copolymer; polyethylene, ethylene copolymers, such as
15 ethylene-vinyl acetate copolymer; and ethylene-vinyl alcohol copolymer; phenolic resins, epoxy resins, ally phthalate resin, polyamide resins, polyester resin, and maleic acid resin.

 Any of these resins produced through any
20 production processes may be used.

 The present invention is most suitably applied to a toner obtained from a polyester resin having a high negative chargeability. A polyester resin has an excellent fixability, is suitable for a
25 color toner but, on the other hand, is liable to be charged excessively because of a strong negative chargeability. However, this difficulty is alleviated

when combined with the carrier according to the present invention.

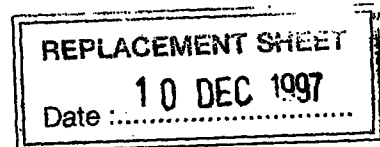
It is particularly preferred to use a polyester resin formed by condensation
 5 copolymerization between a diol component comprising a bisphenol derivative represented by the following formula (V) or a substituted derivative thereof and a carboxylic acid component comprising a carboxylic acid having two or more carboxylic groups or an anhydride
 10 thereof, such as fumaric acid, maleic acid, maleic anhydride, phthalic acid, terephthalic acid, trimellitic acid and pyromellitic acid:



wherein R denotes an ethylene or propylene group, x and y are independently a positive integer of at least 1 with the proviso that the average of x+y is in the range of 2 - 10. This type of polyester resin is
 20 preferred because of a sharp melting characteristic.

Thus, a second preferred mode of toner used in the present invention may have a weight-average particle size of 1 - 9 μm , comprise toner particles containing a binder resin comprising a polyester resin and have
 25 an acid value of 1 - 20 mgKOH/g, preferably 2 - 18 mgKOH/g, further preferably 3 - 15 mgKOH/g.

More specifically, if the above-described



the toner is concentrated at the latent image part to faithfully reproduce individual dots. Further, while using a two component-type developer, the contact of the magnetic brush onto the image-bearing member is
5 suppressed to provide uniform halftone images.

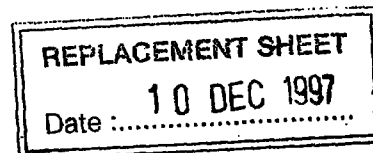
Various parameters characterizing the present invention are based on values measured in the following manners.

(1) Magnetic properties of carrier

10 The apparatus used is a commercially available magnetization tester ("Model BHU-60", available from Riken Sokutei K.K.). Ca. 1.0 g of a sample is weighed and packed in a cell measuring 7 mm in diameter and 10 mm in height, and the cell is set
15 in the apparatus. The sample in the cell is then supplied with a magnetic field which is gradually increased up to a maximum value of 3,000 oersted. Then, the magnetic field is gradually decreased. A B-H hysteresis curve during the process is drawn on a
20 recording paper. The saturation magnetization, residual magnetization and coercive force of the sample are obtained from the hysteresis curve.

(2) Particle size distribution of carrier

The apparatus used is a micro-track particle
25 size analyzer ("SRA-type", available from Nikkiso K.K.), and the measurement range is set to 0.7 - 125 μ m. From the resultant volume-basis particle size



adjusted to 100 V.

2) A changeover switch for the powder tester is set to a tap position and the timer is set for 1 min. (50 times $\pm$ 1 time/1 min.).

5 3) A sieve plate is inserted into a plastic-made sample tube and a sheet of filter paper is placed thereon, and a sample is placed thereon up to a 1/3 position of the sample tube.

10 4) The sample tube is set on a tap stand of the powder tester, and a tapping start button is pressed (tapping for 1 min.).

5) Into the tapped sample tube, an additional amount of the sample is placed up to a 2/3 position of the sample tube.

15 6) Tapping is performed similarly as 4) above.

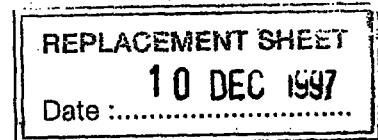
7) A supplemental tube is inserted to the top of the sample tube, and an additional amount of the sample is added so as to form a pile of the sample.

20 8) Tapping is performed similarly as the above 4) or 6).

9) The tapped sample tube is taken out of the tap stand, the supplemental tube is pulled out, and an excessive amount of the sample is cut by a spatula.

25 10) Water is poured into a metering pipe for a specific surface area up to an S mark.

11) The sample tube is connected with the metering pipe (after the sample packing, grease is



applied onto the ground joint face).

12) A cock for the lower effluent port is opened, and a stopwatch is started when the water level passes a 0 (zero) mark of the metering pipe (the effluent
5 water is received by a beaker).

13) A time required for the water level to descent down to a 20 cc-mark is measured.

14) The sample tube is taken out and the sample is weighed.

10 15) The specific surface area SW (= S₁) of the sample is calculated from the following equation:

$$SW = \frac{14}{\rho} \sqrt{\frac{\Delta P A T}{\eta L Q} \cdot \frac{\varepsilon^3}{(1 - \varepsilon)^2}}$$

15

$$\varepsilon = 1 - \frac{W}{\rho A L}$$

SW: specific surface area of a powder sample
[cm²/g]

20 e: void ratio of a packed sample layer

ρ: density of the powder sample [g/cm³]

η: viscosity coefficient of fluid (air)
[g/cm.sec]

L: thickness of the sample layer [cm]

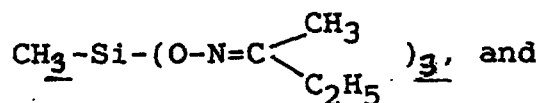
25 Q: amount of fluid having passed the sample
layer [cc]

ΔP: pressure different between both ends of the

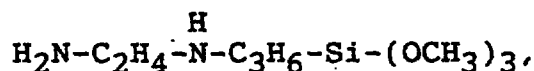
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the resultant siloxane was washed sufficiently with water and dissolved in a toluene-methyl ethyl ketone-butanol mixture solvent to prepare a silicone varnish with a solid matter content of 10 %.

- 5 To 100 parts of the silicone varnish were added 2.0 parts of deionized water, 2.0 parts of the following curing agent



- 10 3.0 partsof the following aminosilane coupling agent

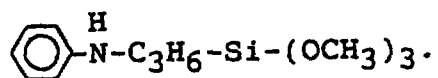


respectively based on the siloxane solid matter content, to prepare Carrier Coating liquid I.

- 15 The above-prepared Ferrite carrier core particles A - G were respectively coated with Coating liquid I thus-prepared so as to provide a resin coating rate of 1.0 wt. %, by using a coater ("Spira Coater", mfd. by Okada Seiko K.K.), thereby to obtain
- 20 Coated Carriers 1 - 7.

(Carrier Production Example 8)

- Coated Carrier 8 was prepared in the same manner as in Carrier Production Example 1 except for replacing the aminosilane coupling agent with the
- 25 following aminosilane coupling agent to prepare Coating liquid II and using Coating liquid II instead of Coating liquid I:



(Carrier Production Examples 11 - 15)

Coated Carriers 11 - 15 were prepared in the same manner as in Carrier Production Examples 1 - 7 except for replacing Ferrite carrier core particles A - G with Ferrite carrier core particles H - L.

Table 1 below shows characterization data of Coated Carriers 1 - 15 thus prepared.

Table 1

Carrier	Core	D ₅₀ (μ m)	+88 μ m (%)	+62 μ m (%)	-22 μ m (%)	-16 μ m (%)	S ₁ (cm ² /g)	S ₂ (cm ² /g)	S ₁ /S ₂	ρ_{ap} (g/cm ²)	Core elements	Coating	Current value (μ A)
1	A	35.8	0.8	8.0	7.4	0	540	364	1.48	2.2	Mg-Mn-Fe	I	120
2	B	26.0	0	1.0	14.2	0	780	502	1.55	2.0	Mg-Mn-Fe	I	140
3	C	61.3	7.6	30.3	1.6	0	270	213	1.27	2.5	Mg-Mn-Fe	I	90
4	D	36.5	0.8	8.4	7.5	0	590	355	1.66	2.3	Mg-Ni-Al-Fe	I	110
5	E	39.5	1.2	8.8	5.4	0	455	330	1.38	2.4	Ag-Mn-Fe	I	100
6	F	36.2	0.8	8.2	8.0	0.3	510	360	1.42	2.4	Ba-Zn-Fe	I	120
7	G	37.0	0.9	10.2	7.5	0.1	495	353	1.40	2.3	K-Ni-Fe	I	150
8	A	35.9	0.8	8.0	7.4	0	545	364	1.50	2.2	Mg-Mn-Fe	II	70
9	A	35.6	0.7	8.0	7.5	0	540	364	1.48	2.2	Mg-Mn-Fe	III	80
10	A	36.1	0.9	8.1	7.3	0	535	363	1.47	2.2	Mg-Mn-Fe	IV	100
11	H	37.5	1.0	8.5	7.0	0.3	490	345	1.42	2.2	Mg-Mn-Fe	I	110
12	I	35.5	0.8	7.9	7.3	0	545	364	1.50	2.3	Mg-Mn-Fe	I	130
13	J	35.8	0.8	8.2	7.1	0.3	543	364	1.49	2.4	Mg-Mn-Fe	I	150
14	K	36.3	0.9	8.5	6.8	0.5	515	354	1.45	2.3	Mg-Mn-Fe	I	150
15	L	38.5	1.3	9.2	6.5	0	495	339	1.46	2.2	Mg-Mn-Fe	I	220

 ρ_{ap} : apparent densityD₅₀: represents a 50 %-particle size of a coated carrier

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-80-

was prepared in a similar manner as in Example 1 except for using Carrier 3 instead of Carrier 1 and the above-mentioned toner concentration. The developer was evaluated in the same manner as in

5 Example 1. The results are also shown in Table 2.

Examples 4 - 6

Two component-type developers were prepared in a similar manner as in Example 1 except for using

10 Carriers 4, 5 and 8 instead of Carrier 1 in manners as shown in Table 2. The developers were evaluated in the same manner as in Example 1. The results are also shown in Table 2.

Comparative Examples 1 - 2

Two component-type developers were prepared

15 in a similar manner as in Example 1 except for using Carriers 6 and 7 instead of Carrier 1 in manners shown in Table 2. The developers were evaluated in the same manner as in Example 1. The results are also shown in Table 2.

20 Comparative Examples 4 - 9

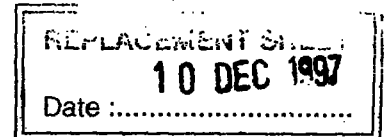
Two component-type developers were prepared in a similar manner as in Example 1 except for using Carriers 11 - 15 instead of Carrier 1 in manners shown in Table 2. The developers were evaluated in the same

25 manner as in Example 1. The results are also shown in Table 2.

Table 2

Ex. or Comp. Ex.	Carrier	Toner	C _{toner} (%)	Image density	Fog (%)	Durability (spent toner)	30°C/80% toner scattering	20°C/10% solid image uniformity
Ex. 1	1	a	7	1.6 - 1.7	~1.2	◎	◎	◎
" 2	2	a	9	1.7 - 1.8	~1.3	◎	◎	◎
" 3	3	a	5	1.5 - 1.6	~1.5	◎	△	○
" 4	4	a	7	1.6 - 1.7	~1.3	◎	◎	○
" 5	5	a	7	1.6 - 1.7	~1.3	◎	○	◎
Comp. Ex. 1	6	a	7	1.7 - 1.8	~2.0	△	△	○
" 2	7	a	7	1.7 - 1.9	~2.0	△	△	△
Ex. 6	8	a	7	1.6 - 1.7	~1.3	◎	◎	◎
Comp. Ex. 3	9	a	7	1.6 - 1.9	~2.0	△	△	○
Ex. 7	10	a	7	1.7 - 1.8	~1.3	◎	○	◎
Comp. Ex. 4	11	a	7	1.8 - 2.0	~2.0	△	x	○
" 5	12	a	7	1.5 - 1.7	~2.0	△	△	x
" 6	13	a	7	1.5 - 1.8	~2.3	x	△	x
" 7	14	a	7	1.5 - 1.7	~2.5	x	x	x
" 8	15	a	7	1.2 - 1.4	~2.0	△	△	x

The manner of performance evaluation and the evaluation standards are supplemented at the end of this specification.



(Carrier Production Examples 17 and 18)

Coated Carriers 17 and 18 were prepared in the same manner as in Carrier Production Example 1 except for changing the amount of water added at the time of producing Coating liquid to 0 part and 7 parts, respectively.

Example 8

A two component-type developer was prepared and evaluated in the same manner as in Example 1 except for the use of Carrier 17. As a result, a slight fog of 1.5 % was caused in continuous image formation under 20 °C/10 %RH, while that was a practically acceptable level. The inferior performance might be attributable to insufficient resin coating due to non-use of the water.

Example 9

A two component-type developer was prepared and evaluated in the same manner as in Example 1 except for the use of Carrier 18. As a result, a slight toner scattering was observed when the toner concentration was close to the upper limit of the control range under 30 °C/80 %RH, while that was a practically acceptable level. The result might be attributable to the use of too much water causing a excessive self-crosslinking of the resin to result in a somewhat lower adhesion with the carrier core particles.

Table 3

Carrier	Core	D ₅₀ (μ m)	+88 μ m (%)	+62 μ m (%)	-22 μ m (%)	-16 μ m (%)	S ₁ (cm ² /g)	S ₂ (cm ² /g)	S ₁ /S ₂	ρ_{ap} (g/cm ²)	Core elements	Coating	Current value (μ A)
16	M	35.8	0.8	8.0	7.4	0	540	364	1.48	2.2	Mg-Mn-Fe	I	120
17	N	38.3	1.0	8.3	6.5	0	510	340	1.50	2.3	Mg-Mn-Si-Fe	I	60
18	O	40.5	1.3	9.0	5.8	0	480	322	1.49	2.3	Mg-Li-Fe	I	42
19	P	43.2	1.4	10.0	4.2	0	450	302	1.49	2.2	Mg-Al-Fe	I	70
20	M	36.0	0.9	8.2	7.0	0	530	362	1.46	2.2	Mg-Mn-Fe	V	110

 ρ_{ap} : apparent densityD₅₀: represents a 50 %-particle size of a coated carrier

Table 5

Example	Carrier	Toner	C _{toner} (%)	Image- bearing member	Electric field	Image density	Fog (%)	Durability (spent toner)	30°C/80% toner scattering	20°C/10% solid image uniformity
17	16	f	7	I	Fig. 4	1.6-1.7	1.2	○	○	○
18	16	g	7	I	"	1.7-1.8	1.2	○	○	○
19	16	h	7	I	"	1.6-1.8	1.5	○	△	○
20	16	i	7	I	"	1.6-1.7	1.5	○	△	△
21	16	j	7	I	"	1.6-1.7	1.3	○	○	○
22	16	k	7	I	"	1.5-1.7	1.3	○	○	○
23	16	l	7	I	"	1.5-1.6	1.2	○	○	○
24	17	f	7	I	"	1.6-1.7	1.3	○	○	○
25	18	f	7	I	"	1.6-1.7	1.2	○	○	○
26	19	f	7	I	"	1.6-1.7	1.3	○	○	○
27	20	f	7	I	"	1.6-1.8	1.3	○	○	○
28	16	f	7	II	"	1.6-1.7	1.2	○	○	○
29	16	f	7	III	"	1.5-1.6	1.1	○	○	○
30	16	f	7	IV	"	1.5-1.6	1.1	○	○	△
31	16	f	7	I	Fig. 5	1.6-1.7	1.2	○	○	○
32	16	f	7	I	Fig. 2	1.6-1.7	1.3	○	○	○
33	16	f	7	I	Fig. 3	1.4-1.5	1.5	○	○	△

The manner of performance evaluation and the evaluation standards are supplemented at the end of this specification.

WHAT IS CLAIMED IS:

1. A carrier for electrophotography, comprising:
magnetic carrier core particles and a resin coating
layer coating the magnetic carrier core particles,
5 wherein

the carrier core particles comprise a
magnetic ferrite component represented by the
following formula (I):



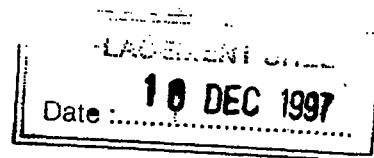
- 10 wherein A denotes a member selected from the group
consisting of MgO, AgO and mixtures thereof; B denotes
a member selected from the group consisting of
MnO, CaO, Al₂O₃, SiO₂ and mixtures thereof; and
x, y and z are numbers representing weight ratios and
15 satisfying the relation of: $0.2 \leq x \leq 0.95$, $0.005 \leq y$
 ≤ 0.3 , $0 < z \leq 0.795$, and $x+y+z \leq 1$.

2. The carrier according to Claim 1, wherein x,
y and z in the formula (I) further satisfying the
20 conditions of:

$$x+y < 1 \text{ and } z = 1-x-y.$$

3. The carrier according to Claim 1, wherein
said carrier core particles contains 0.5 - 30 wt. % of
25 MgO calculated as its oxide form.

4. The carrier according to Claim 2, wherein



said carrier core particles contains 0.5 - 30 wt. % of MgO calculated as its oxide form.

5 5. The carrier according to Claim 1, wherein the carrier has a 50 %-particle size of 15-60 μ m, and contains 1-20 wt.% of carrier particles of below 22 μ m, 0 wt.% of carrier particles of below 16 μ m, and 2-20 wt.% of carrier particles of at least 62 μ m.

10 6. The carrier according to Claim 1, wherein the component B in the formula (I) is selected from the group consisting of MnO, CaO, and mixtures thereof.

15 7. The carrier according to Claim 1, wherein the carrier has a 50 %-particle size of 15 - 60 μ m, and contain 1 - 20 wt. % of carrier particles of below 22 μ m, 0.01 - 3 wt. % of carrier particles of below 16 μ m, 2 - 20 wt. % of carrier particles of at least 62 μ m, and at most 3 wt. % of carrier particles of at
20 least 88 μ m.

25 8. The carrier according to Claim 2, wherein the carrier has a 50 %-particle size of 15 - 60 μ m, and contain 1 - 20 wt. % of carrier particles of below 22 μ m, 0.01 - 3 wt. % of carrier particles of below 16 μ m, 2 - 20 wt. % of carrier particles of at least 62 μ m, and at most 3 wt. % of carrier particles of at



least 88 μm .

9. The carrier according to Claim 1, wherein the carrier has a specific area ratio S_1/S_2 of 1.2 - 2.0, wherein S_1 represents a specific surface area measured by the air permeation method and S_2 denotes a specific surface area calculated by the following formula (II):
- $$S_2 = [6/(\rho \times D_{50})] \times 10^4 \quad (\text{II}),$$
- wherein ρ denotes a density and D_{50} denotes a 50 %- particle size, respectively, of the carrier.

10. The carrier according to Claim 9, wherein the carrier has an S_1/S_2 ratio of 1.3 - 1.8.

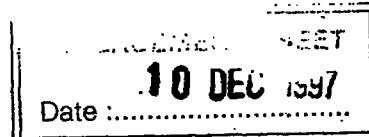
11. The carrier according to Claim 1, wherein the carrier has an apparent density of 1.2 - 3.2 g/cm^3 .

12. The carrier according to Claim 1, wherein the carrier has an apparent density of 1.5 - 2.8 g/cm^3 .

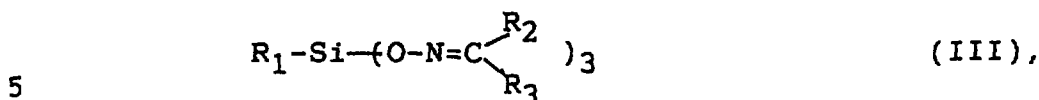
13. The carrier according to Claim 1, wherein the carrier has a current value of 20 - 300 μA .

14. The carrier according to Claim 1, wherein the carrier has a current value of 20 - 250 μA .

15. The carrier according to Claim 1, wherein the



resin coating layer comprises a reactive silicone resin containing a curing agent represented by the following formula (III):



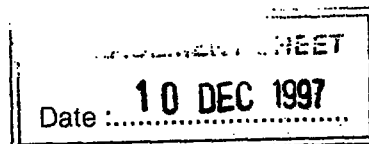
wherein R_2 denotes a substituent selected from the group consisting of CH_3 , C_2H_5 and  each capable of having a substituent; and R_2 and R_3 independently denote CH_3 and C_2H_5 each capable of having a
10 substituent.

16. The carrier according to Claim 2, wherein the resin coating layer comprises a reactive silicone resin containing a curing agent represented by the
15 following formula (III):

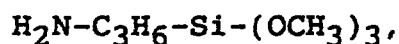
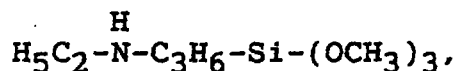
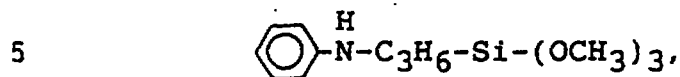


wherein R_2 denotes a substituent selected from the group consisting of CH_3 , C_2H_5 and  each capable
20 of having a substituent; and R_2 and R_3 independently denote CH_3 and C_2H_5 each capable of having a substituent.

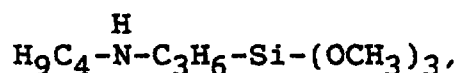
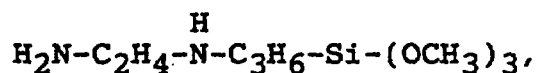
17. The carrier according to Claim 1, wherein the
25 resin coating layer comprises a reactive silicone resin containing an aminosilane coupling agent.



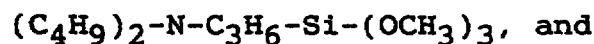
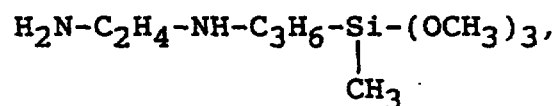
18. The carrier according to Claim 17, wherein the amino silane coupling agent is a member selected from the group consisting of:



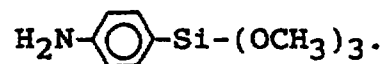
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15



20



19. The carrier according to Claim 17, wherein the reactive silicone resin contain 0.1 - 8 wt. parts of the aminosilane coupling agent per 100 wt. parts of siloxane solid matter.



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20. The carrier according to Claim 17, wherein the reactive silicone resin contains 0.3 - 5 wt. parts of the aminosilane coupling agent per 100 wt. parts of siloxane solid matter.

5

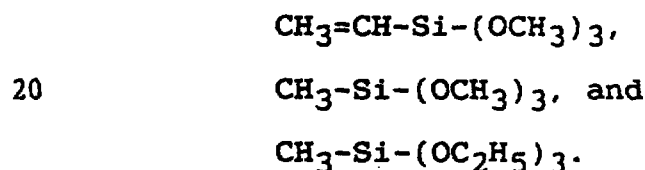
21. The carrier according to Claim 17, wherein the reactive silicone resin further contains a coupling agent represented by the following formula (IV):



wherein R denotes a substituent selected from the group consisting of vinyl, methacryl, epoxy, amino, mercapto and derivatives of these; X denotes a halogen or alkoxy group; and a is an integer of 1 - 3.

15

22. The carrier according to Claim 21, wherein the coupling agent is a member selected from the groups consisting of:



23. The carrier according to Claim 1, wherein the resin coating layer comprises a reactive silicone resin containing:

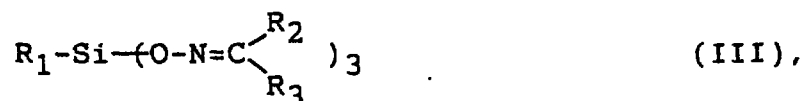
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a curing agent represented by the following formula (III):



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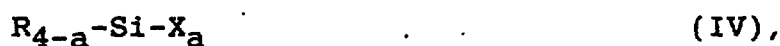
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wherein R_2 denotes a substituent selected from the group consisting of CH_3 , C_2H_5 and  each capable of having a substituent; and R_2 and R_3 independently denote CH_3 and C_2H_5 each capable of having a substituent;

an aminosilane coupling agent; and

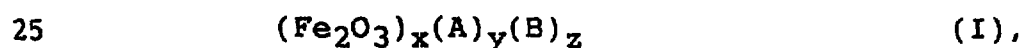
a coupling agent represented by the following formula (IV):



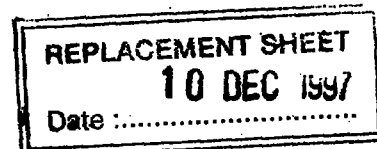
wherein R denotes a substituent selected from the group consisting of vinyl, methacryl, epoxy, amino, mercapto and derivatives of these; X denotes a halogen or alkoxy group; and a is an integer of 1 - 3.

24. A two component-type developer, comprising: a toner comprising toner particles, and a carrier comprising magnetic carrier core particles and a resin coating layer coating the magnetic carrier core particles, wherein

the carrier core particles comprise a magnetic ferrite component represented by the following formula (I):



wherein A denotes a member selected from the group consisting of MgO , AgO and mixtures thereof; B denotes



a member selected from the group consisting of Li_2O ,
 MnO , CaO , SrO , Al_2O_3 , SiO_2 and mixtures thereof; and
 x , y and z are numbers representing weight ratios and
satisfying the relation of: $0.2 \leq x \leq 0.95$, $0.005 \leq y$
5 ≤ 0.3 , $0 < z \leq 0.795$, and $x+y+z \leq 1$.

25. The developer according to Claim 24, wherein
 x , y and z in the formula (I) further
satisfying the condition of $x+y < 1$ and $z = 1-x-y$;
10 the toner comprises toner particles and an
external addition;
the toner has a weight-average particle size
of 1 - 9 μm ; and
the external additive surface treated
15 inorganic fine particles having a weight-average
particle size of 0.001 - 0.2 μm .

26. The developer according to Claim 2, wherein
 x , y and z in the formula (I) further satisfy the
20 conditions of:

$$x+y < 1 \text{ and } z = 1-x-y.$$

27. The developer according to Claim 24, wherein
said carrier core particles contains 0.5 - 30 wt. % of
25 MgO calculated as its oxide form.

28. The developer according to Claim 25, wherein



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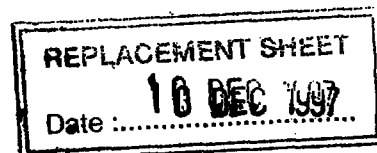
said carrier core particles contains 0.5 - 30 wt. % of MgO calculated as its oxide form.

29. The developer according to Claim 24, wherein
5 the component B in the formula (I) is selected from the group consisting of MnO, CaO, SiO₂, Al₂O₃ and mixtures thereof.

30. The developer according to Claim 24, wherein
10 the component B in the formula (I) is selected from the group consisting of MnO, CaO, and mixtures thereof.

31. The developer according to Claim 24, wherein
15 the carrier has a 50 %-particle size of 15 - 60 μ m, and contain 1 - 20 wt. % of carrier particles of below 22 μ m, 0.01 - 3 wt. % of carrier particles of below 16 μ m, 2 - 20 wt. % of carrier particles of at least 62 μ m, and at most 3 wt. % of carrier particles of at
20 least 88 μ m.

32. The developer according to Claim 25, wherein
the carrier has a 50 %-particle size of 15 - 60 μ m, and contain 1 - 20 wt. % of carrier particles of below
25 22 μ m, 0.01 - 3 wt. % of carrier particles of below 16 μ m, 2 - 20 wt. % of carrier particles of at least 62 μ m, and at most 3 wt. % of carrier particles of at



least 88 μm .

33. The developer according to Claim 24, wherein the carrier has a specific area ratio S_1/S_2 of 1.2 - 2.0, wherein S_1 represents a specific surface area measured by the air permeation method and S_2 denotes a specific surface area calculated by the following formula (II):

$$S_2 = [6/(\rho \times D_{50})] \times 10^4 \quad (\text{II}),$$

wherein ρ denotes a density and D_{50} denotes a 50 %-average particle size, respectively, of the carrier.

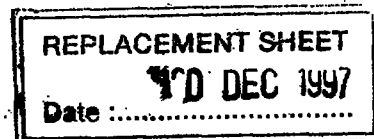
34. The developer according to Claim 33, wherein the carrier has an S_1/S_2 ratio of 1.3 - 1.8.

35. The developer according to Claim 24, wherein the carrier has an apparent density of 1.2 - 3.2 g/cm^3 .

36. The developer according to Claim 24, wherein the carrier has an apparent density of 1.5 - 2.8 g/cm^3 .

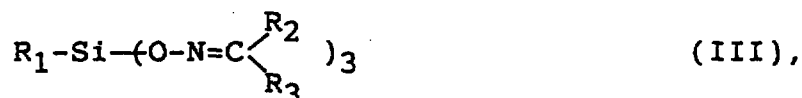
37. The developer according to Claim 24, wherein the carrier has a current value of 20 - 300 μA .

38. The developer according to Claim 24, wherein



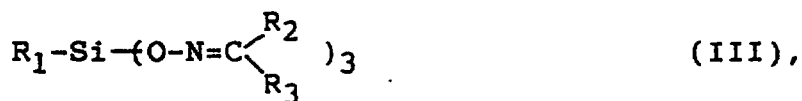
the carrier has a current value of 20 - 250 μ A.

39. The developer according to Claim 24, wherein the resin coating layer comprises a reactive silicone resin containing a curing agent represented by the following formula (III):



wherein R_2 denotes a substituent selected from the group consisting of CH_3 , C_2H_5 and  each capable of having a substituent; and R_2 and R_3 independently denote CH_3 and C_2H_5 each capable of having a substituent.

40. The developer according to Claim 25, wherein the resin coating layer comprises a reactive silicone resin containing a curing agent represented by the following formula (III):



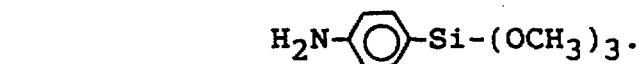
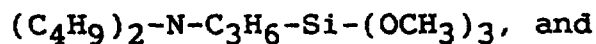
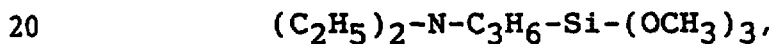
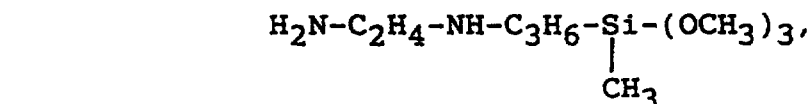
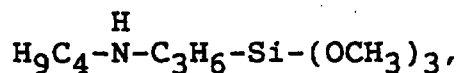
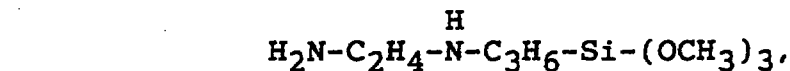
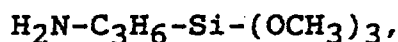
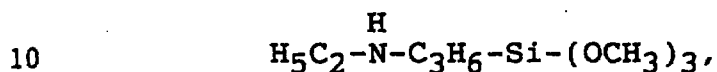
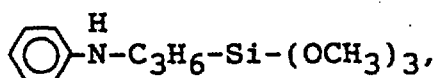
wherein R_2 denotes a substituent selected from the group consisting of CH_3 , C_2H_5 and  each capable of having a substituent; and R_2 and R_3 independently denote CH_3 and C_2H_5 each capable of having a substituent.

41. The developer according to Claim 24, wherein

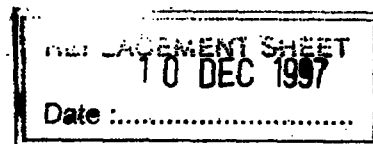


the resin coating layer comprises a reactive silicone resin containing an aminosilane coupling agent.

42. The developer according to Claim 41, wherein
5 the amino silane coupling agent is a member selected from the group consisting of:



43. The developer according to Claim 41, wherein the reactive silicone resin contains 0.1 - 8 wt. parts



of the aminosilane coupling agent per 100 wt. parts of siloxane solid matter.

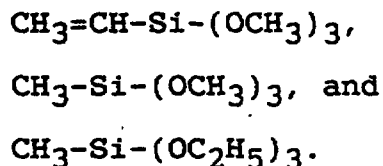
44. The developer according to Claim 41, wherein
5 the reactive silicone resin contain 0.3 - 5 wt. parts of the aminosilane coupling agent per 100 wt. parts of siloxane solid matter.

45. The developer according to Claim 41, wherein
10 the reactive silicone resin further contains a coupling agent represented by the following formula (IV):



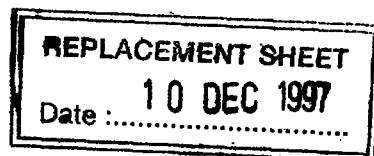
wherein R denotes a substituent selected from the
15 group consisting of vinyl, methacryl, epoxy, amino, mercapto and derivatives of these; X denotes a halogen or alkoxy group; and a is an integer of 1 - 3.

46. The developer according to Claim 45, wherein
20 the coupling agent is a member selected from the groups consisting of:



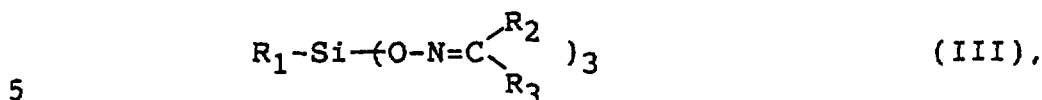
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47. The developer according to Claim 24, wherein the resin coating layer comprises a reactive silicone



resin containing:

a curing agent represented by the following formula (III):



wherein R_2 denotes a substituent selected from the group consisting of CH_3 , C_2H_5 and  each capable of having a substituent; and R_2 and R_3 independently denote CH_3 and C_2H_5 each capable of having a
10 substituent;

an aminosilane coupling agent; and

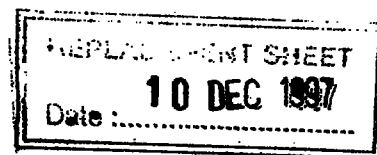
a coupling agent represented by the following formula (IV):

$$R_4-a-Si-X_a \quad (IV),$$

15 wherein R denotes a substituent selected from the group consisting of vinyl, methacryl, epoxy, amino, mercapto and derivatives of these; X denotes a halogen or alkoxy group; and a is an integer of 1 - 3.

20 48. The developer according to Claim 24, wherein the toner has a weight-average particle size of 1 - 9 μm .

25 49. The developer according to Claim 24, wherein the toner comprises toner particles, and an external additive comprising hydrophobic inorganic fine particles.



50. The developer according to Claim 49, wherein the hydrophobic inorganic fine particles comprise at least one member selected from the group consisting of alumina fine particles, titanium oxide fine particles and silica fine particles.

51. The developer according to Claim 49, wherein the hydrophobic inorganic fine particles have a hydrophobicity of 20 - 80 %.

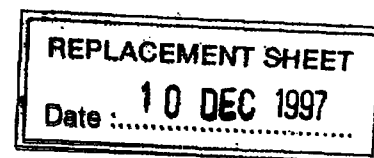
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52. The developer according to Claim 49, wherein the hydrophobic inorganic fine particles have a weight-average particle size of 0.001 - 0.2 μm .

53. The developer according to Claim 49, wherein the hydrophobic inorganic fine particles have an optical transmittance of at least 40 % at a wavelength of 400 nm.

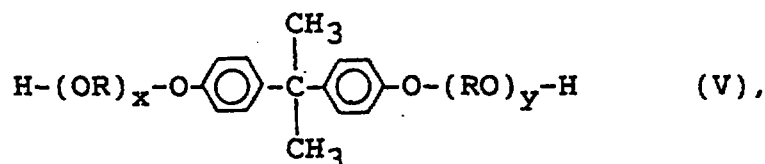
54. The developer according to Claim 24, wherein the toner particles comprise a binder resin and a colorant, and the binder resin comprises a polyester resin.

55. The developer according to Claim 54, wherein the polyester resin comprises a condensation copolymer of an etherified bisphenol and a polycarboxylic acid



having at least two functional groups.

56. The developer according to Claim 55, wherein the etherified bisphenol comprises a compound
5 represented by the following formula (V):



wherein R denotes an ethylene or propylene group, x
10 and y are independently a positive integer of at least 1 with the proviso that the average of x+y is in the range of 2 - 10.

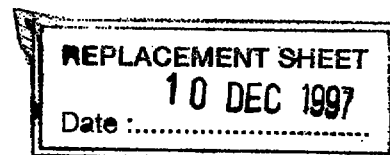
57. The developer according to Claim 54, wherein
15 the binder resin has an acid value of 1 - 20 mgKOH/g.

58. The developer according to Claim 55, wherein said polycarboxylic acid includes 0.1 - 20 mol. % of a polycarboxylic acid component having at least three
20 functional groups.

59. The developer according to Claim 54, wherein the toner particles have a glass transition temperature (T_g) of 45 - 47 °C.

25

60. The developer according to Claim 54, wherein the toner particles have a temperature providing an



apparent viscosity of 10^5 poises (Tm) in the range of 80 - 120 °C.

61. An image forming method, comprising:
- 5 circulatively conveying a two component-type developer comprising a toner and a carrier on a developer-carrying member, and
- developing, in a developing region, an electrostatic latent image held on an electrostatic
- 10 image-bearing member with the toner in the two component-type developer, wherein
- the toner comprises toner particles, and the carrier comprises magnetic carrier core particles and a resin coating layer coating the magnetic carrier
- 15 core particles, wherein
- the carrier core particles comprise a magnetic ferrite component represented by the following formula (I):
- $$(Fe_2O_3)_x(A)_y(B)_z \quad (I),$$
- 20 wherein A denotes a member selected from the group consisting of MgO, AgO and mixtures thereof; B denotes a member selected from the group consisting of Li₂O, MnO, CaO, SrO, Al₂O₃, SiO₂ and mixtures thereof; and x, y and z are numbers representing weight ratios and
- 25 satisfying the relation of: $0.2 \leq x \leq 0.95$, $0.005 \leq y \leq 0.3$, $0 < z \leq 0.795$, and $x+y+z \leq 1$.



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62. The method according to Claim 61, wherein the electrostatic latent image is developed with the toner in the two component-type developer under application of a developing bias comprising a succession of
5 voltages including a first voltage directing a toner from the image bearing member toward the developer-carrying member, a second voltage directing the toner from the developer carrying member toward the image-bearing member and a third voltage intermediate
10 between the first and second voltages, respectively, to the developer-carrying member.

63. The method according to Claim 62, wherein a period (T_1) for applying the first voltage and the
15 second voltage is set to be shorter than a period (T_2) for applying the third voltage.

64. The method according to Claim 61, wherein said electrostatic latent image-holding member.
20 comprises a photosensitive layer and a protective layer coating the photosensitive layer; the protective layer containing fluorine-containing resin particles.

65. The method according to Claim 61, wherein
25 said protective layer has a ten point average surface roughness (R_z) of 0.01 - 1.5 μm .



68. The method according to Claim 67 wherein the reactive group is a hydrolyzable reactive group.

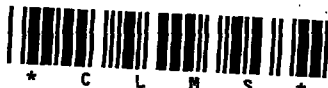
69. The method according to Claim 68 wherein the hydrolyzable reactive group is attached to a silicone atom of the silicone resin and the hydrolyzable reactive group is selected from the group consisting of an oxime group, an alkoxy group and a halogen.

70. The method according to Claim 67 wherein the developing bias comprises a succession of voltages including (i) at least one cycle of a first voltage directing a toner from the image-bearing member toward the developer-carrying member and a second voltage directing the toner from the developer-carrying member toward the image-bearing member, and (ii) a third voltage at a substantially constant level intermediate between those of the first and second voltages; wherein a period (T_1) for applying said at least one cycle of the first and second voltages is shorter than a period (T_2) for applying the third voltage.

71. The method according to Claim 67 wherein said electrostatic latent image-holding member comprises a photosensitive layer and a protective layer coating the photosensitive layer; the protective layer containing fluorine-containing resin particles.

72. The method according to Claim 67 wherein said protective layer has a ten point average surface roughness (R_z) of 0.01 - 1.5 μm .

73. The method according to Claim 67 wherein the developing bias comprises a superposition of a direct current component with the intermittent alternating current component.



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74. The method according to Claim 67 wherein the alternating current component comprises substantially rectangular waves.

75. The method according to Claim 67 wherein x , y and z in the formula (I) further satisfy the conditions of:

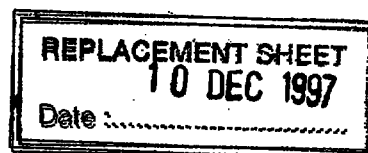
$$x+y < 1 \text{ and } z = 1-x-y.$$

76. The method according to Claim 67 wherein x , y and z in the formula (I) further satisfying the condition of $x+y < 1$ and $z = 1-x-y$; the toner comprises toner particles and an external additive; the toner has a weight-average particle size of 1 - 9 μm ; and the external additive comprises surface-treated inorganic fine particles having a weight-average particle size of 0.001 - 0.2 μm .

77. The method according to Claim 67 wherein said carrier core particles contains 0.5 - 30 wt. % of MgO calculated as its oxide form.

78. The method according to Claim 67 wherein the carrier has a 50 %-particle size of 15-60 μm , and contains 1-20 wt.% of carrier particles of below 22 μm , 0 wt.% of carrier particles of below 16 μm , and 2-20 wt.% of carrier particles of at least 62 μm .

79. The method according to Claim 78 wherein the carrier has a 50 %-particles size of 15-60 μm , and contains 1-20 wt.% of carrier particles of below 22 μm , 0 wt.% of carrier particles of below 16 μm , 2-20 wt.% of carrier particles of at least 62 μm and 0 wt.% of carrier particles of at least 88 μm .



80. The method according to Claim 67 wherein the carrier has a 50%-particle size of 15-60 μm and contains 1-20 wt.% of carrier particles of below 22 μm , 0-3 wt.% of carrier particles below 16 μm , 2-20 wt.% of carrier particles of at least 62 μm and at most 3 wt.% of carrier particles of at least 88 μm .

81. The method according to Claim 67 wherein the carrier has a specific area ratio S_1/S_2 of 1.2 - 2.0, wherein S_1 represents a specific surface area measured by the air permeation method and S_2 denotes a specific surface area calculated by the following formula (II):

$$S_2 = [6/(\rho \times D_{50})] \times 10^4 \quad (\text{II}).$$

wherein ρ denotes a density and D_{50} denotes a 50 %-average particle size, respectively, of the carrier.

82. The method according to Claim 81 wherein the carrier has an S_1/S_2 ratio of 1.3 - 1.8.

83. The method according to Claim 67 wherein the carrier has a current value of 20 - 300 μA .

84. The method according to Claim 67 wherein the resin coating layer comprises the reactive silicone resin containing a curing agent represented by the following formula (III):

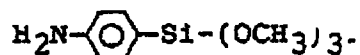
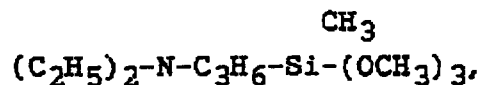
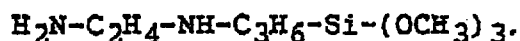
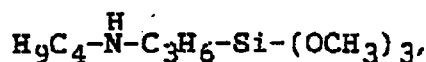
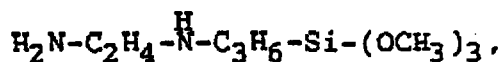
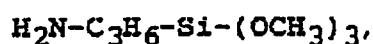
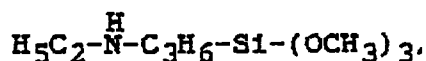
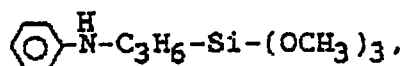


wherein R_1 denotes a substituent selected from the group consisting of CH_3 , C_2H_5 and C_6H_5 each capable of having a substituent; and R_2 and R_3 independently denote CH_3 and C_2H_5 each capable of having a substituent.



85. The method according to Claim 67 wherein the resin coating layer comprises the reactive silicone resin containing an aminosilane coupling agent.

86. The method according to Claim 85 wherein the amino silane coupling agent is a member selected from the group consisting of:



87. The method according to Claim 85 wherein the reactive silicone resin further contains a coupling agent represented by the following formula (IV):



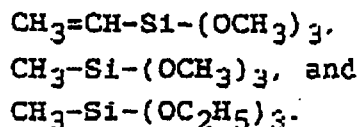
wherein R denotes a substituent selected from the group consisting of vinyl, methacryl, epoxy, amino, mercapto and derivatives of these; X denotes a halogen or alkoxy group; and a is an integer of 1 - 3.



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88. The method according to Claim 87 wherein the coupling agent is a member selected from the groups consisting of:



89. The method according to Claim 87 wherein the resin coating layer comprises a reactive silicone resin containing:

a curing agent represented by the following formula (III):



wherein R_1 denotes a substituent selected from the group consisting of CH_3 , C_2H_5 and  each capable of having a substituent; and R_2 and R_3 independently denote CH_3 and C_2H_5 each capable of having a substituent;

an aminosilane coupling agent; and

a coupling agent represented by the following formula (IV):



wherein R denotes a substituent selected from the group consisting of vinyl, methacryl, epoxy, amino, mercapto and derivatives of these; X denotes a halogen or alkoxy group; and a is an integer of 1 - 3.

90. The method according to Claim 67 wherein the toner has a weight-average particle size of 1 - 9 μm .

91. The method according to Claim 67 wherein the toner comprises toner particles, and an external additive comprising hydrophobic inorganic fine particles.



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92. The method according to Claim 91 wherein the hydrophobic inorganic fine particles comprise at least one member selected from the group consisting of alumina fine particles, titanium oxide fine particles and silica fine particles.

93. The method according to Claim 91 wherein the hydrophobic inorganic fine particles have a hydrophobicity of 20 - 80 %.

94. The method according to Claim 91 wherein the hydrophobic inorganic fine particles have a weight-average particle size of 0.001 - 0.2 μm .

95. The method according to Claim 91 wherein the hydrophobic inorganic fine particles have an optical transmittance of at least 40 % at a wavelength of 400 nm.