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(54) Developer and developing process using said developer.

(57) Disclosed is a two-component type developer comprising a toner having an electroconductivity lower than 3.5×10^{-10} S/cm, in which an amino group-containing silicone resin is used as the coating resin for a magnetic carrier. By using the amino group-containing silicone resin as the coating resin for the magnetic carrier, reduction of the image density caused by a lowly electroconductive toner is prevented, and even in a color developer for which a lowly electroconductive toner is used, a high-density image can be formed. According to a developing process using this developer, the development is possible even under a high bias voltage condition, and a high-quality image having a high density can be formed.

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DEVELOPER AND DEVELOPING PROCESS USING SAID DEVELOPER

Background of the Invention

(1) Field of the Invention

The present invention relates to a developer for use in the electronic reproduction and the like. More particularly, the present invention relates to a two-component type developer comprising a toner and a magnetic carrier, which can provide a high-density image even when a toner having a low electroconductivity is used, and a developing process using this developer.

(2) Description of the Related Art

In the field of commercial electronic reproduction, magnetic brush development using a two-component type magnetic developer is widely adopted for developing an electrostatic image. As the two-component type magnetic developer, there is widely used a mixture comprising a magnetic carrier composed of an iron powder or sintered ferrite particles and a toner composed of particles formed by dispersing additives such as a colorant and a charge-controlling agent in a binder resin.

An ordinary developing mechanism in which a developer as described above is used has a structure as shown in Fig. 1. More specifically, a box-shaped toner supply mechanism 4 is arranged on the developing mechanism 2 and a toner 6 is supplied from above. The toner 6 is fed into a developing device 10 disposed below through a supply opening 8 equipped with a feeder and is stirred together with a carrier in the developing device 10 by stirrers 12 to form a two-component type developer 14.

A developing sleeve (developer-supporting member) 16 equipped with many magnetic poles is arranged in the developing device 10. The developer 14 having the frictionally charged toner is supplied into the developing sleeve 16 and a magnetic brush 18 of the developer is formed on the surface of the sleeve by a magnetic force. The length of the magnetic brush 18 is adjusted by a brush-cutting mechanism 20, and a uniform layer of the developer is formed on the surface of the developing sleeve 16. This developer layer is delivered to the nip position to a surface photosensitive layer 24 of an electrophotographic photosensitive material drum (image carrier) 22. The photosensitive material drum 22 is arranged apart by a distance DD-S from the developing sleeve 16, and the developing sleeve 16 and photosensitive material 22 are rotatably supported and are driven so that the moving directions (indicated by arrows) of the sleeve 16 and the drum 22 are the same at the nip position (the rotation directions are reverse to each other).

A corona charger 26 connected to a variable high voltage power source 25 and an optical system 28 for the light exposure are arranged around the photosensitive material drum 22 upstream of the developing device 10 to form an electrostatic latent image having a predetermined surface voltage. A bias power source 33 equipped with a voltage-adjusting mechanism 30 is connected between the photosensitive drum 22 and the developing sleeve 12 so that an optional value voltage (bias voltage)which has the same polarity as that of the surface voltage and is lower than the surface voltage is applied onto the photosensitive layer 24. A transfer mechanism 34 for transferring a toner image to a copying machine is arranged around the photosensitive layer 24 downstream of the developing zone.

In the above-mentioned structure, the developer 14 forms the magnetic brush 18 on the developing sleeve 16 and at the nip position, this magnetic brush 18 reacts with the electrostatic latent image of the photosensitive layer 24 to form a visible image of the toner on the photosensitive layer 24.

At this image-forming step, the electric resistance (the inverse number of the electroconductivity) of titanium oxide used for a white toner or coloring toner or a coloring pigment is higher than that of a black pigment such as carbon and its charge quantity tends to increase, and it sometimes becomes impossible to maintain the image density (ID) of the toner image at a high level. As the means for solving this problem, there has been considered a method in which the amount of the resin coated on the surface of the magnetic carrier is reduced to reduce the resistance and reduce the charge quantity of the toner.

In case of an acrylic resin conventionally used for coating the magnetic carrier, in order to reduce the resistance, the amount coated of the resin should be controlled to less than 0.01%. However, if the amount coated of the resin is small, the surface of the carrier core is not sufficiently covered and protected, and there is a risk of contamination of the toner by oxidation of the carrier core or the like. Especially, when a developer comprising a white toner is used, the obtained image is yellowish and the whiteness is insufficient.

In case of a developer comprising a magnetic carrier having a low resistance and a toner having a high resistance, the change of the resistance value of the developer relative to the toner concentration (T/D) (the weight ratio of the toner to the two-component type developer) is large, and if only the T/D value is a little decreased, blanking is caused in the image (the phenomenon that a white portion to which the toner is not fixed is formed in the solid image area). It is considered that blanking will be prevented by increasing the particle size of the carrier. However, if the particle size of the carrier is excessively increased, the image quality is degraded and the consumption of the toner increases. If the particle size of the toner is too small, also because of the low resistance of the magnetic carrier, random transfer of the toner in the form of spots to the transfer surface other than the area of the electrostatic latent image and the carrier dragging, that is, the phenomenon that the carrier is transferred together with the toner to the photosensitive material, are caused.

An organic photosensitive material which has a good processability and is advantageous in the manufacturing cost and has a large freedom of the design of functions is recently used as the photosensitive material for the electrophotography. The organic photosensitive material includes a negatively chargeable type and a postively chargeable type. Since the negatively chargeable type often induces contamination of the copying environment, use of the positively chargeable photosensitive material (OPC) is now expected.

In this positively chargeable photosensitive material, however, the residual voltage.is apt to become larger than in the conventional Se type photosensitive material, and therefore, in the case where the positively chargeable photosensitive material is used, the bias voltage should be maintained at a level higher than 250 V. Elevation of the bias voltage increases the charge repulsion between the magnetic carrier and the developing sleeve. Accordingly, when an image is formed by using a positively chargeable organic photosensitive material and a white toner or color toner, prevention of carrier dragging and improvement of the image quality are required.

Furthermore, in the case where the above-mentioned DD-S width is narrowed for moderating the degradation of the quality by elevation of the bias voltage, a stress is imposed on the developer, and therefore, carrier dragging is readily caused.

Summary of the Invention

It is therefore a primary object of the present invention to provide a developer which can give a high-density image with a good reproducibility by stabilizing the charge quantity of the developer within an appropriate range even if a white toner or color toner having a low electroconductivity is used.

Another object fo the present invention is to provide a developer which can give a high-density image without such disadvantages as blanking, random spot-like transfer of the toner and carrier dragging even if a white toner or color toner having a low electroconductivity is used.

Still another object of the present invention is to provide a white developer capable of giving a clear and sharp image.

Still another object of the present invention is to provide a developer which is preferably applied to a positively chargeable organic photosensitive material.

More specifically, in accordance with one fundamental aspect of the present invention, there is provided a developer comprising a developer toner having an electroconductivity lower than 3.5×10^{-10} S/cm and a magnetic carrier coated with an amino group-containing silicone resin.

According to one preferred embodiment of the developer, the electroconductivity of the toner is in the range of from 2.0×10^{-10} to 3.0×10^{-10} S/cm and the current value of the magnetic carrier is in the range of from 0.1 to 70 μA.

According to another preferred embodiment of the developer, in the magnetic carrier coated with the amino group-containing silicone resin, the amount of the coating resin is 0.01 to 0.5% by weight based on the carried core.

According to still another preferred embodiment of the developer, the diameter D_{50} of the weight average particle size corresponding to 50% of the weight of entire carrier particles in the magnetic carrier is in the range of from 70 to 120 μm.

A white toner comprising titanium oxide can be used for the developer of the present invention.

In accordance with another fundamental aspect of the present invention, there is provided a developing process which comprises feeding a two-component type developer comprising a developer toner having an electroconductivity lower than 3.5 x 10^{-10} S/cm and a magnetic carrier coated with an amino-group-containing silicone resin between a developer carrier and an electrostatic image carrier, to which a bias voltage of at least 250 V is applied to effect development.

According to one preferred embodiment of the developing process, the distance between the electrostatic image carrier and the developer carrier is adjusted to less than 1.2 mm.

According to another preferred embodiment of the developing process, the current value of the magnetic carrier is adjusted to 0.1 to 70 μA.

According to still another preferred embodiment of the developing process, the diameter D_{50} of the weight average particle size corresponding to 50% of the weight of entire carrier particles in the magnetic carrier is adjusted to 70 to 120 μm.

According to still another preferred embodiment of the developing process, the diameter D_{50} of the weight average particle size corresponding to 50% of the weight of entire carrier particles in the magnetic carrier is adjusted to 70 to 90 μm and an Se type photosensitive material is used as the electrostatic image carrier.

According to still another preferred embodiment of the developing process, the diameter D_{50} of the weight average particle size corresponding to 50% of the weight of entire carrier particles in the magnetic carrier is adjusted to 80 to 120 μm and a positively chargeable organic photosensitive material is used as the electrostatic image carrier.

Brief Description of the Drawings

Fig. 1 is a diagram illustrating the developing mechanism.

Fig. 2 is a graph illustrating the relation between the amount coated of the resin and the charge quantity of the carrier.

Fig. 3 is a graph illustrating the relation between the bias voltage and the occurrence of carrier dragging.

Fig. 4 is a diagram illustrating the apparatus for measuring the current value.

Detailed Description of the Preferred Embodiments

The present invention is based on the finding that if a developer is formed by combining a toner having a low electroconductivity with a magnetic carrier coated with an amino group-containing silicone resin, an image having a good quality and a high density can be formed without occurrence of any trouble or disadvantage in the coated carrier.

The present invention is also based on the finding that if the particle size of the magnetic carrier coated with the above-mentioned coating resin is uniformly adjusted within a specific range, occurrence of carrier dragging and random spot-like transfer of the toner, which are readily caused on reduction of the resistance of the carrier, can be prevented.

In most of white toners and color toners, the electroconductivity is lower than 3.5 x 10^{-10}, especially lower than 3.0 x 10^{-10}. This reduction of the electroconductivity of the toner is due to the presence of colorants in the toner. Many colorants for toner satisfying the above requirement of the low electroconductivity are present and available as the organic pigment, and therefore, colorants can be freely selected over a broad range. However, in toners not satisfying the above requirement of the electroconductivity, the range of selection of colorants is narrow and a desirable color can hardly be obtained. According to the present invention, toner pigments can be freely selected and the range of the color of the developer can be broadened.

However, if the electroconductivity of the toner is lower then 3.5 x 10^{-10} S/cm, especially 2.0 x 10^{-10} to 3.0 x 10^{-10} S/cm, when this toner is used in combination with an ordinary carrier, the transferability is degraded by increase of the charge quantity per unit weight, and a high-density image can hardly be obtained.

In the present invention, in order to moderate this charge of the charge quantity which is due to the low electroconductivity, it is important that an amino group-containing silicone resin should be used as the coating resin for the magnetic carrier. The amino group-containing silicone resin reduces the resistance of the magnetic carrier, as compared with the resistance attained by the convention coating resin. If this magnetic carrier is stirred with the toner having a low electroconductivity, increase of the charge quantity in the toner is controlled, and the toner can be supplied to the photosensitive material (electrostatic image carrier) in the appropriately charged state.

As is apparent from the results shown in Example 1 and Comparative Example 1 given hereinafter, even if a developer comprising a carrier coated with an amino group-containing silicone resin is used for a long time, yellowing of the image is not caused but a high density can be maintained. It is preferred that the coating amount of the amino group-containing silicone resin be 0.05 to 5% by weight based on the carrier core.

Fig. 2 shows the appropriate charge quantity of the magnetic carrier found for the use of the toner having a low electroconductivity.

As shown in Fig. 2, in the conventional magnetic carrier coated with an acrylic resin, the amount coated of the resin can be 0.05% by weight at largest or smaller. In contrast, in the magnetic carrier coated with an amino group-containing silicone resin, even if the coating amount is increased to 0.1% by weight, no problem arises in connection with the charge quantity. Accordingly, in the case where an amino group-containing silicone resin is used as the coating resin for the magnetic carrier, the charge quantity of the magnetic carrier is reduced and a satisfactory protecting coating layer can be formed on the carrier core. This reduction of the charge quantity of the magnetic carrier by the use of the specific coating resin controls the increase of the charge quantity of the toner, and the amount coated of the coating resin can be increased.

The current value, described hereinafter, of the magnetic carrier has a close relation to the carrier material and the amount coated of the resin. It is preferred that the current value of the magnetic carrier be adjusted to 0.1 to 70 μA, especially 0.5 to 3 μA when an Se type photosensitive material is used or 30 to 40 μA when a positively chargeable organic photosensitive material is used. In case of a developer satisfying this requirement, reduction of the density, such as blanking, is not found in the formed image, and an excellent image having a high density can be obtained. In the instant specification and appended claims, by the current value is meant the current value observed when the carrier is connected to a direct current power source of 200 V in the state where a magnetic brush is formed on the developing speed and is moved. Incidentally, blanking means the phenomenon that in the solid image area of the electrostatic latent image, the toner is not transferred to a certain part because of the adhesion of the carrier to the drum or the like.

In the present invention, it is preferred that the particle size of the carrier be adjusted so that the diameter D_{50} of the weight average particle size corresponding to 50% of the weight of entire carrier particles is 70 to 120 μm, especially 70 to 90 μm when an Se type photosensitive material is used or 80 to 120 μm when a positively chargeable organic photosensitive material is used, and that the carrier having the particle size thus adjusted be coated with the above-mentioned coating resin.

If the particle size of the carrier is adjusted within the above-mentioned range, blanking, random spot-like transfer of the toner and carrier dragging are hardly-caused. If the particles size of the magnetic carrier is below the above-mentioned range, also because of the low resistance of the carrier, carrier particles having a relatively small particle size induce blanking, random spot-like transfer of the toner and carrier dragging. On the other hand, if the particle size of the carrier exceeds the above range, the consumption of the toner increases.

The diameter D_{50} of the weight average particle size corresponding to 50% of entire carrier particles is determined as follows. The weight of the carrier is counted in order from particles having a small particle size, and when the counted weight reaches 50% of the entire weight, the median particle size of the carrier is determined as the diameter D_{50}. Sieves having a predetermined mesh size are used for this counting.

Fig. 3 shows the relation between the bias voltage and the state of carrier dragging, observed with respect to the developer comprising the conventional carrier and the developer comprising the carrier of the present invention. In the carrier of the present invention, the particle size is adjusted in the above-mentioned manner and the content of particles having a size smaller than 250 mesh is adjusted below 8% by weight.

As shown in Fig. 3, in the conventional developer, carrier dragging becomes conspicuous with increase of the bias voltage. It is understood that the reason is that since the charge repulsion between the magnetic carrier and the developing sleeve gradually increases, the transfer of the magnetic carrier to the photosensitive material becomes easier. In contrast, in the developer of the present invention, by adjusting the particle size of the magnetic carrier in the above-mentioned manner, the occurrence of carrier dragging is drastically controlled even if the bias voltage is increased.

According to the developing process of the present invention, the developer can be used under a bias voltage of at least 250 V, especially at least 280 V. Elevation of the bias voltage results in diminishment of the influence of the residual voltage. Namely, if the residual voltage is as high as at least about 150 V, the photosensitive material provides an excellent image quality without occurrence of carrier dragging.

As the photosensitive material having such a high residual voltage, there can be mentioned a positively chargeable photosensitive material (OPC), and the OPC has conditions under which the developer of the present invention is preferably used. By increase of the bias voltage, the development voltage difference, that is, the difference between this voltage and the surface voltage, is reduced, and according to certain circumstances, the development has to be conducted under a low voltage. At this low voltage development, the image density is degraded. However, if the above-mentioned condition of a DD-S width smaller than 1.2 mm, especially smaller than 1.0 mm, is adopted, both of the gradient and image density can be maintained at high levels and occurrence of carrier dragging is prevented. Also for this reason, the developer of the present invention can be satisfactorily applied to a positively chargeable organic sensitive material.

Preferred embodiments of the developer of the present invention will now be described.

The developer of the present invention is a two-component type developer comprising a magnetic carrier and a toner. The magnetic carrier, the toner and the developer will now be described in order.

Magnetic Carrier

In the present invention, ferrite particles coated with an amino group-containing silicone resin are preferably used as the magnetic carrier, and it is preferred that the particle size distribution be adjusted in the above-mentioned manner.

The amino group-containing silicone resin is a silicone resin containing an amino group, and it is preferred that the content of the amino group be 0.1 to 10% by weight, especially 0.1 to 5% by weight. A silicone resin containing a hydrocarbon alone, such as an acrylic silicone resin, and a silicone resin containing a halogen atom or the like alone, are not included. The amount of the resin coated on ferrite particles is preferably 0.01 to 1.0% by weight, especially preferably 0.02 to 0.7% by weight. If the amount coated of the resin is below this range, corrosion of the surfaces of the ferrite particles cannot be sufficiently prevented, and if the amount coated of the resin exceeds the above-mentioned range, the charge quantity of the magnetic carrier increases and no good results can be obtained.

As specific examples of the amino group-containing silicone resin, there can be mentioned an alkylamine silicone resin and aromatic amine silicone resins, and an aromatic amine silicone resin such as a benzylamine silicone resin is especially preferably used.

A ferrite can be mentioned as a specific example of the magnetic carrier, and sintered ferrite particles composed of at least one member selected from the group consisting of zinc iron oxide ($ZnFe_2O_4$), yttrium iron oxide ($Y_3Fe_5O_{12}$), cadmium iron oxide ($CdFe_2O_4$), gadolinium iron oxide ($Gd_3Fe_5O_{12}$), lead iron oxide ($PbFe_{12}O_{19}$), nickel iron oxide ($NiFe_2O_4$), neodium iron oxide ($NdFeO_3$), barium iron oxide ($BaFe_{12}O_{19}$), magnesium iron oxide ($MgFe_2O_4$), manganese iron oxide ($MnFe_2O_4$) and lanthanum iron oxide ($LaFeO_3$ are used. Especially, a soft ferrite comprising at least one member, preferably at least two members, selected from the group consisting of Cu, Zn, Mg, Mn and Ni, for example, a copper/zinc/magnesium ferrite, is used.

In the present invention, from the viewpoint of the flowability, it is preferred that the resin-coated magnetic carrier particles should have a spherical shape, and it is important that the carrier particles should satisfy the above-mentioned requirement of the diameter D_{50} of the weight average particle size corresponding to 50% of the weight of entire particles. This adjustment of the particle size can be performed according to a known method, and this adjustment can be carried out at the step of sintering ferrite or after coating with the amino group-containing silicone resin. By adjusting the size of the carrier particles in the above-mentioned manner, troubles such as blanking mentioned above can be prevented and the toner transfer efficiency can be increased.

If the difference between the diameter D_{25} of the weight average particle size corresponding to 25% of the weight of entire carrier particles and the diameter D_{75} of the weight average particle size corresponding to 75% of the weight of entire carrier particles is adjusted to 0 to 20 μm simultaneously with the above-mentioned adjustment of the particles size of the carrier particles, the particles size distribution becomes sharper, and even if the DD-S width is further reduced from 1 mm, carrier dragging is not caused. Moreover, even in the state where the bias voltage is high, carrier dragging can be prevented. In the magnetic carrier having the above-mentioned particle size distribution, the image density can be increased. In the case where the photosensitive material and the developing sleeve are of the drum type, because of increase of the lower limit of the particle size by sharpening of the particle size distribution, the torque is reduced and the sliding contact force of the drum is reduced.

In order to prevent the occurrence of carrier dragging more sufficiently, it is preferred that the content of fine particles having a size smaller than 250 mesh be as low as possible, that is, lower than 8% by weight, especially lower than 5% by weight. In the developer satisfying this requirement, carrier dragging is sufficiently prevented even under a high bias voltage, and an effect of controlling fogging can be attained as an additional effect.

The magnetic carrier having a saturation magnetization of 50 to 70 emu/g, especially 55 to 65 emu/g, is used. This range of the saturation magnetization is lower than the saturatization magnetization range of the carrier for the conventional developer. As compared with the conventional carrier, this magnetic carrier promotes softening of the magnetic brush, which results in reduction of the drum stress. This saturation magnetization is preferred when the DD-S width is smaller than 1.2 mm, especially smaller than 1.0 mm. Incidentally, it is preferred that the flowability of the carrier used in the present invention be 15 to 35 sec/50 g, especially 20 to 30 sec/50 g.

The current value of the magnetic carrier has a close relation to the carrier material and the amount coated of the resin, and it is preferred that the current value of the magnetic carrier be in the range of from 0.1 to 70 μA. The current value can be measured by a measurement apparatus shown in Fig. 4. Referring to Fig. 4, a direct current power source (200 V) 62 is connected in series to a developing box 64, a resistor 66 of 10 kΩ and a resistor 68 of 1 MΩ, and a voltage meter 69 is arranged in the resistor 66 of 10 kΩ. A magnet drum 70 assumed as the developing sleeve and a photosensitive material drum 72 are arranged in the developing box 64, and a magnetic carrier layer 74 is disposed between the two drums. The distance between the magnet drum 70 and the photosensitive material drum 72 is adjusted to 4.5 mm. In this structure, the magnet drum and photosensitive material drum are rotated, and the current value is determined by dividing the measured value of the voltage meter 69 by the resistance value of the resistor 66.

Toner

The toner used in the present invention is formed by incorporating a colorant and a charge controlling agent, and optionally other known toner additives, into a binder resin, and has an electroconductivity lower than 3.5×10^{-10} S/cm, especially 2.0×10^{-10} to 3.0×10^{-10} S/cm. A binder resin for a toner, a colorant, a charge controlling agent and other toner additives are appropriately selected and combined, so that the above requirement is satisfied.

A styrene resin, an acrylic resin, a styrene/acrylic copolymer resin, a polyester resin, a silicone resin, a polyurethane resin, a polyamide and a modified resin are generally used as the binder resin.

A styrene/acrylic copolymer resin is one of preferred binder resins. It is preferred that the styrene monomer (A)/acrylic monomer (B) weight ratio be in the range of from 50/50 to 90/10, especially from 60/40 to 85/15. In general, a resin having an acid value of from 0 to 25 is preferably used. From the viewpoint of the fixing property, it is preferred that the resin should have a glass transition temperature (Tg) of 50 to 65°C.

Known colorants customarily used in this field can be used as the colorant to incorporated into the resin binder, so far as the above-mentioned requirement of the electroconductivity is satisfied.

The colorants are roughly divided into white, cyan, magenta and yellow pigments. It is preferred that the colorant be incorporated in an amount of 1 to 20 % by weight based on the binder resin. Specific examples of the colorant that can be used in the present invention are described below.

As the magenta type colorant, there can be mentioned C.I. Pigment Red 81, C.I. Pigment Red 122, C.I. Pigment Red 57, C.I. Solvent Red 49, C.I. Solvent Red 19, C.I. Solvent 52, C.I. Basic Red 10 and C.I. Disperse Red 15. As the cyan type colorant, there can be mentioned C.I. Pigment Blue 15, C.I. Pigment Blue 16, C.I. Solvent Blue 25, C.I. Solvent Blue 55, C.I. Solvent Blue 70, C.I. Direct Blue 86 and C.I. Direct Blue 25. As the yellow type colorant, there can be mentioned C.I. Pigment Yellow 17, C.I. Pigment Yellow 12, C.I. Pigment Yellow 1, C.I. Pigment Yellow 97, C.I. Pigment Yellow 138, C.I. Pigment Yellow 12, C.I. Pigment Yellow 73, C.I. Pigment Yellow 13, C.I. Solvent Yellow 29, C.I. Solvent Yellow 162 and C.I. Solvent Yellow 93. As the white pigment, there can be mentioned zinc flower, titanium oxide, antimony white and zinc sulfide, and titanium oxide is especially preferably used.

Known charge controlling agents, for example, oil-soluble dyes such as Nigrosine Base (CI 50415), Oil Black (CI 26150) and Spiron Black, metal salts of naphthenic acid, fatty acids, soaps and resin acid soaps, can be optionally used as the charge controlling agent.

Preferably, the particle size of toner particles is 8 to 14 μm, especially 10 to 12 μm, as the median size based on the volume, measured by a Coulter counter. The shape of the toner particles may be an indeterminate shape formed through melt kneading and pulverization, or a spherical shape formed by dispersion or suspension polymerization. The flowability of the toner can be improved by sprinkling the surface of the toner with a known surface-treating agent such as finely divided hydrophobic silica or resin powder.

Developer

In the developer of the present invention, it is preferred that the above-mentioned magnetic carrier and toner be mixed at a weight ratio of from 99/1 to 90/10, especially 98/2 to 95/5. It also is preferred that the initial charge quantity of the developer, as measured by the blow-off method, be 5 to 25 μc/g, especially 10 to 20 μc/g, and that the loose apparent specific gravity be 1.7 to 2.1 g/cm^3, especially 1.8 to 2.0 g/cm^3.

The developer of the present invention is used under ordinary development conditions customarily adopted in the art. In order to especially improve the image density, it is preferred that the developer of the present invention be used under such development conditions that the distance DD-S between the image carrier and the developer carrier is smaller than 1.2 mm and the development voltage difference is smaller than 500 V. The image carrier and the developer carrier in the developing device used may be of the plane type, or they may be of the drum type as shown in Fig. 1, and the type is optional so far as DD-S is within the above-mentioned range.

Under development conditions where the DD-S width is smaller than 1.2 mm, especially smaller than 1.0 mm, the developer of the present invention gives an image having an excellent gradient and an excellent image density even by low-voltage development, and if the above-mentioned requirements for the carrier are additionally satisfied, carrier dragging and other troubles are not caused. Furthermore, it is preferred that with diminishment of the DD-S width, the brush cut length be adjusted to 0.5 to 1.5 mm, especially 0.7 to 1.2 mm.

The developer of the present invention is used in the state where the development voltage difference is smaller than 500 V, especially smaller than 480 V. Accordingly, in the case where a surface voltage of 750 to 850 V is applied to the photosensitive material drum, a bias voltage of 250 to 350 V can be applied to the photosensitive material drum and the like. If the bias voltage is thus elevated, the photosensitive material drum can be used even if the residual voltage is higher than about 150 V, especially about 200 V.

In the present invention, the developer is preferably used for a positively chargeable photosensitive material (OPC). The positively chargeable photosensitive material comprises a charge-generating material and a charge-transporting material, which are mixed mainly in one layer, and therefore, an electron and a hole migrate in this one layer and one of them acts as a trap, with the result that the residual voltage tends to increase. This photosensitive material should have a bias voltage of at least 250 V or at least 280 V under certain circumstances. The developer of the present invention can form an excellent image even under such a high bias voltage, and carrier dragging is not caused.

A photosensitive material formed by combining a known charge-generating material with a known charge-transporting material can be used as the positively chargeable photosensitive material. An organic photosensitive material previously proposed in Japanese Patent Application No. 62-277158 is especially preferably used as the positively chargeable photosensitive material.

According to the present invention, since a toner having an electroconductivity lower than 3.5 x 10^{-10} S/cm, especially 2.0 x 10^{-10} to 3.0 x 10^{-10} S/cm is used and an amino group-containing silicone resin is used for coating a magnetic carrier, an image having a high density can be formed without any trouble in the covering of the magnetic carrier.

Moreover, in case of a white developer, contamination of the toner with the oxide of the carrier core can be prevented and a sharp white image having a high whiteness can be obtained.

Furthermore, by adjusting the particle size of the magnetic carrier, occurrence of the troubles such as blanking and carrier dragging at the development can be prevented, and by changing the developing conditions for the customarily adopted conditions, the density of the image can be further improved. Still further, the developer of the present invention is advantageously used for the development using an organic photosensitive material which is often used recently, especially a positively chargeable organic photosensitive material.

The present invention will now be described in detail with reference to the following examples that by no means limit the scope of the invention.

Examples 1 through 4 and Comparative Examples 1 through 3

The components of the developers and the development conditions were set as follows.

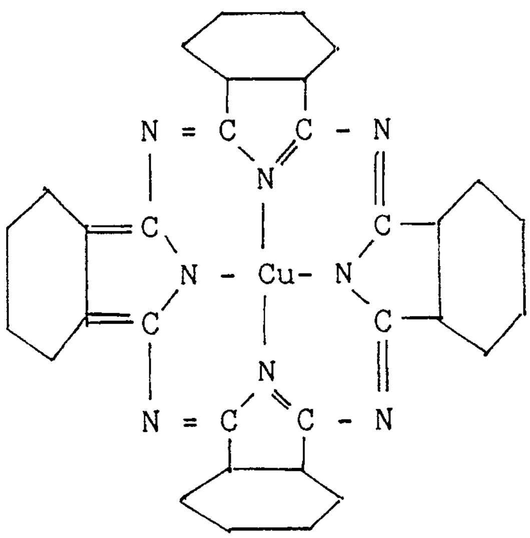
Components

Spherical ferrite carriers coated with an amino group-containing silicone resin or an acrylic polymer were used as the magnetic carrier. The physical properties of the carriers are shown in Table 1.

The amino group-containing silicone resin was N-β-(aminoethyl)-γ-aminopropyltrimethoxysilane, $H_2NC_2H_4NHC_3H_6Si(OCH_3)_3$, KBM 603 supplied by Shinetsu Silicone (Toray Silicone SH6020).

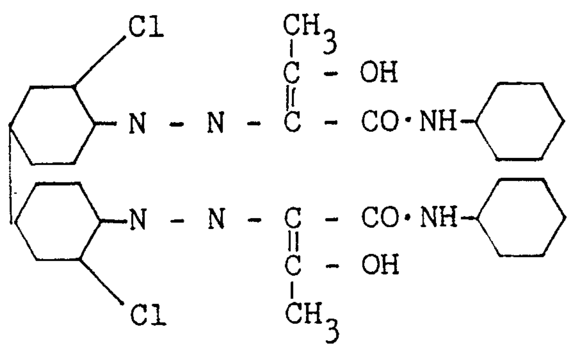
Toners having the known particle size, pigment component and electroconductivity were used. The physical properties of the toners are shown in Table 1.

The pigments used for the toners were as follows. Phthalocyanine Blue B (C.I. Pigment Blue 15)



$C_{32}H_{16}N_8Cu$

Benzidine Yellow G (C.I. Pigment Yellow 12)



3,3'-dichlorobenzidine = acetoacetanilide (2 moles)

$C_{32}H_{20}Cl_2N_6O_4$

Developers were formed by mixing the toner and carrier at a weight ratio of 4.5/95.5. The basic physical properties of the developers are shown in Table 1.

Developing Conditions

The DD-S width, the brush cut length, the development voltage difference, the bias voltage and the photosensitive material are shown in Table 1.

The results (carrier dragging and image density) obtained by carrying out the development under the above-mentioned developing conditions by using the above-mentioned developers are shown in Table 1.

Table 1

Components	Physical Properties	Example 1	Example 2	Example 3	Example 4	Comparative Example 1	Comparative Example 2	Comparative Example 3
magnetic carrier	coating resin	*1	*1	*1	*1	acrylic polymer	acrylic polymer	amino group-free silicone
	amount coated (%)	0.1	0.05	0.50	0.48	0.1	0.50	0.49
	current value (μA)	30.0	35.0	2.0	2.3	32	2.1	2.2
	apparent density(g/cm^3)	2.60	2.65	2.87	2.91	2.61	2.84	2.87
	saturation magnetization (emu/g)	65	65	65	63	65	65	65
	flowability (sec/50g)	27	27	24	22	26	24	23
	diameter D_{50} of weight average particle size corresponding to 50% of weight of entire carrier particles (μm)	99	99	82	78	83	65	80
	content of particles having size smaller than 250 mesh (% by weight)	3	2	8	7	10	12	8
toner	colorant	titanium oxide	titanium oxide	C.I. Pigment Blue 16	C.I. Pigment Yellow 12	titanium oxide	C.I. Pigment Blue 16	C.I. Pigment Yellow 12
	electroconductivity (S/cm)	2.9×10^{-10}	2.9×10^{-10}	2.5×10^{-10}	2.7×10^{-10}	2.9×10^{-10}	2.5×10^{-10}	2.7×10^{-10}
	particle size (μm)	13	13	12	11	13	12	11
developer	apparent density (g/cm^3)	1.92	1.98	2.09	2.15	1.94	2.12	2.12
	initial charge quantity (μ/g)	18	15	17	18	23	26	11
Developing Conditions	D_{D-S} width (mm)	0.8	0.8	1.1	1.2	0.8	1.2	1.1
	brush cut length (mm)	0.7	0.7	1.0	1.1	0.7	1.1	1.0
	development voltage difference (V)	460	460	590	600	460	600	590
	bias voltage (V)	290	290	230	240	290	240	230
Results	carrier dragging (g/500copies)	0.1	0.09	0.07	0.08	0.35	0.41	0.09
	blanking	-	-	not caused	not caused	-	caused	not caused
	image density	good	good	good	good	fair	fair	fair
	image quality (by visual observation)	high whiteness	high whiteness	sharp	sharp	yellowing	sharp	uneven
Photosensitive Material		*3 OPC	*2 OPC	Se type	Se type	*2 OPC	Se type	Se type

Note *1: amino group-containing silicone *2: positively chargeable OPC

Example 5

In the developer used in Example 1, the coating amount of the amino group-containing silicone resin was charged to examined the influence of the coating amount of the resin. The development conditions were the same as in Example 1. The obtained results are shown in Table 2.

If the amount coated of the coating resin was smaller than 0.01% by weight, the solid image area became uneven, and the durability of the developer was poor. On the other hand, if the amount coated of the coating resin was larger than 0.5% by weight, the image density became insufficient.

Table 2

Components	Physical Properties	Run No. 1	2	3	4	5	6	7	8
magnetic carrier	amount coated of coating resin	no coating	*1 0.005	0.01	0.05	0.1	0.5	0.7	1.0
	current value	48.0	39.0	38.0	35.0	30.0	10.0	5.0	1.5
	apparent density	2.60							
	saturation magnetization	65							
	flowability	27							
	diameter D_{50}	99							
	content (% be weight) of particles having size smaller than 250 mesh	3							
toner	colorant	titanium oxide							
	electroconductivity(S/cm)	2.9×10^{-10}							
	particle size (µm)	13							
developer	apparent density	1.95	1.98	1.96	1.98	1.92	1.90	1.89	1.86
	initial charge quantity	20	14	16	15	18	19	18	19 *2
Developing Condition	DD-S width	0.8							
	brush cut length	0.7							
	development voltage difference	460							
	bias voltage	290							
Results	carrier dragging	0.1	0.1	0.1	0.09	0.1	0.1	0.1	0.1
	blanking*3	-	-	-	-	-	-	-	-
	image density	low	good	good	good	good	good	low	low
	image quality(whiteness)	low	low*4	high	high	high	high	low*5	low*5
Photosensitive Material		positively chargeable OPC							

Note

*1: durability was poor and preparation was trouble

*2: initial charge quantity tended to increase

*3: blanking was not evaluated because white toner was used

*4: uneven solid image area

*5: insufficient image density

Example 6

The development was carried out under various current values to examine the influence of the current value.

In case of the Se type photosensitive material, the current value of the carrier was changed in the developer of Example 3 and the development was carried out under the same conditions as in Example 3. Incidentally, the current value of the carrier was charged by adjusting the apparent density while keeping the amount coated of the coating resin constant. The obtained results are shown in Table 3. If the current value was smaller than 0.5 µA, the image density became insufficient, and if the current value was larger than 3.0 µA, fogging was caused.

In case of the positively chargeable OPC photosensitive material, the current value was changed in the developer of Example 2 and the development was carried out under the same developing conditions as in Example 2. Incidentally, the current value of the carrier was changed by adjusting the apparent density while keeping the amount coated of the resin constant. The obtained results are shown in Table 3. If the current value was smaller than 30 µA, the image density was insufficient, and if the current value was larger than 40 µA, the solid image area became uneven.

Table 3

Components	Physical Properties	Run No. 9	10	11	12	13	14	15	16	17	18
magnetic carrier	amount coated of coating resin			0.50					0.05		
	current value	0.3	0.5	2.0	3.0	3.5	27	30	35	40	42
	apparent density	2.92	2.90	2.87	2.85	2.83	2.68	2.66	2.65	2.63	2.62
	saturation magnetization			65					65		
	flowability			24					27		
	diameter D_{50}			82					99		
	content of particles having size smaller than 250 mesh			8					2		
toner	colorant			C.I. Pigment Blue 16					titanium oxide		
	electroconductivity			2.5×10^{-10}					2.9×10^{-10}		
	particle size			12					13		
developer	apparent density	2.10	2.05	2.09	2.11	2.09	1.91	1.92	1.98	1.99	1.97
	initial charge quantity	19	19	17	15	14	19	18	15	14	14
Developing Conditions	DD-S width			1.1					0.8		
	brush cut length			1.0					0.7		
	development voltage difference			590					460		
	bias voltage			230					290		
Results	carrier dragging	0.1	0.1	0.07	0.1	0.1	0.1	0.1	0.09	0.1	0.1
	blanking	not caused	not caused	not caused	not caused	not caused		-	-		
	image density	low	good	good	good	good	low	good	good	good	good
	image quality	low	sharp	sharp	sharp	low	low	high	high	high	low
Photosensitive Material				Se type photosensitive material					positively chargeable OPC		

Example 7

Influences of the particle size (diameter D_{50}) of the carrier were examined.

In case of the Se type photosensitive material, the particle size of the carrier was changed in the developer of Example 3, and the development was carried out under the same conditions as in Example 3. The obtained results are shown in Table 4. If the diameter D_{50} was smaller than 70 µm, the image density was insufficient, and if the diameter D_{50} was larger than 90, fogging was caused.

In case of the OPC photosensitive material, the particle size of the carrier was changed in the developer of Example 1, and the development was carried out under the same conditions as in Example 1. The obtained results are shown in Table 4. If the diameter D_{50} was smaller than 80 µm, the image became uneven, and if the diameter D_{50} was larger than 120 µm, fogging was caused.

Table 4

Components	Physical Properties	Run No. 19	20	21	22	23	24	25	26	27	28
magnetic carrier	amount coated of coating resin	0.50	0.45	0.50	0.40	0.35	0.12	0.1	0.1	0.09	0.08
	current value			2.0					30		
	apparent density	2.83	2.85	2.87	2.90	2.92	2.55	2.57	2.60	2.62	2.65
	saturation magnetization			65					65		
	flowability	21	22	24	27	29	23	24	27	29	30
	diameter D_{50}	67	71	82	90	95	77	80	99	119	125
	content of particles having size smaller than 250 mesh	10	8	8	5	3	7	6	3	2	1
toner	colorant			C.I. Pigment Blue 16				titanium oxide			
	electroconductivity			2.5×10^{-10}				2.9×10^{-10}			
	particle size			12				13			
developer	apparent density	1.99	2.01	2.09	2.05	2.10	1.88	1.91	1.92	1.93	1.93
	initial charge quantity	21	18	17	16	17	18	19	18	18	17
Developing Conditions	DD-S width			1.1					0.8		
	brush cut length			1.0					0.7		
	development voltage difference			590					460		
	bias voltage			230					290		
Results	carrier dragging	0.35	0.10	0.07	0.10	0.07	0.4	0.1	0.1	0.1	0.1
	blanking	caused	not caused	not caused	not caused	not caused	-	-	-	-	-
	image density	low	good	good	good	good	low	good	good	good	good
	image quality	*1 low	sharp	sharp	sharp	*2 low	*3 low	high	high	high	*4 low
Photosensitive Material		Se type photosensitive material					positively chargeable OPC				

Note

*1: insufficient image density

*2: fogging was caused

*3: uneven solid image area

*4: fogging was caused

Example 8

Influences of the bias voltage and DD-S width were examined.

By using the developer of Example 1, the development was carried out under the same conditions as in Example 1 except that the bias voltage was changed as shown in Table 5. The obtained results are shown in Table 5. If the bias voltage was lower than 250 V, fogging was caused.

By using the developer of Example 1, the development was carried out under the same conditions as in Example 1 except that the DD-S width was changed as shown in Table 5. The obtained results are shown in Table 5. If the DD-S width was larger than 1.2 mm, the image density was insufficient.

Table 5

Components	Physical Properties	Run No. 29	30	31	32	33	34	35
magnetic carrier	amount coated of coating resin		0.1			0.1		
	current value		30			30		
	apparent density		2.60			2.60		
	saturation magnetization		65			65		
	flowability		27			27		
	diameter D_{50}		99			99		
	content of particles having size smaller than 250 mesh		3			3		
toner	colorant		titanium oxide			titanium oxide		
	electroconductivity		2.9×10^{-10}			2.9×10^{-10}		
	particle size		13			13		
developer	apparent density		1.92			1.92		
	initial charge quantity		18			18		
Developing Conditions	DD-S width			0.8	0.8	1.0	1.2	1.4
	brush cut length			0.7	0.7			
	development voltage difference	510	495	460	460			
	bias voltage	240	255	290	290			
Results	carrier dragging	0.05	0.05	0.1	0.1	0.1	0.1	0.1
	blanking	-	-	-	-	-	-	-
	image density	good	good	good	good	good	good	low
	image quality	*1 low	high	high	high	high	high	*2 low
Photosensitive Material			positively chargeable OPC			positively chargeable OPC		

Note *1: fogging was caused *2: insufficient image density

Claims

1. A developer comprising a developer toner having an electroconductivity lower than 3.5×10^{-10} S/cm and a magnetic carrier coated with an amino group-containing silicone resin.

2. A developer as set forth in claim 1, wherein the electroconductivity of the toner is in the range of from 2.0×10^{-10} to 3.0×10^{-10} S/cm and the current value of the magnetic carrier is in the range of from 0.1 to 70 µA.

3. A developer as set forth in claim 1 or 2, wherein in the magnetic carrier coated with the amino group-containing silicone resin, the amount of the coating resin is 0.01 to 0.5% by weight based on the carrier core.

4. A developer as set forth in any of claims 1 through 3, wherein the diameter D_{50} of the weight average particle size corresponding to 50% of the weight of entire carrier particles in the magnetic carrier is in the range of from 70 to 120 µm.

5. A developer as set forth in claim 4, wherein the content of particles having a size smaller than 250 mesh in the magnetic carrier is controlled below 8% by weight.

6. A developer as set forth in any of claims 1 through 5, wherein the toner is a white toner comprising titanium oxide.

7. A developing process which comprises feeding a two-component type developer comprising a developer toner having an electroconductivity lower than 3.5×10^{-10} S/cm and a magnetic carrier coated with an amino-group-containing silicone resin between a developer carrier and an electrostatic image carrier, to which a bias voltage of at least 250 V is applied to effect development.

8. A developing process according to claim 7, wherein the distance between the electrostatic image carrier and the developer carrier is adjusted to less than 1.2 mm.

9. A developing process according to claim 7 or 8, wherein the current value of the magnetic carrier is adjusted to 0.1 to 70 μA.

10. A developing process according to any of claims 7 through 9, wherein the diameter D_{50} of the weight average particle size corresponding to 50% of the weight of entire carrier particles in the magnetic carrier is adjusted to 70 to 120 μm.

11. A developing process according to claim 10, wherein the diameter D_{50} of the weight average particle size corresponding to 50% of the weight of entire carrier particles in the magnetic carrier is adjusted to 70 to 90 μm and an Se type photosensitive material is used as the electrostatic image carrier.

12. A developing process according to claim 10, wherein the diameter D_{50} of the weight average particle size corresponding to 50% of the weight of entire carrier particles in the magnetic carrier is adjusted to 80 to 120 μm and a positively chargeable organic photosensitive material is used as the electrostatic image carrier.

FIG. 1

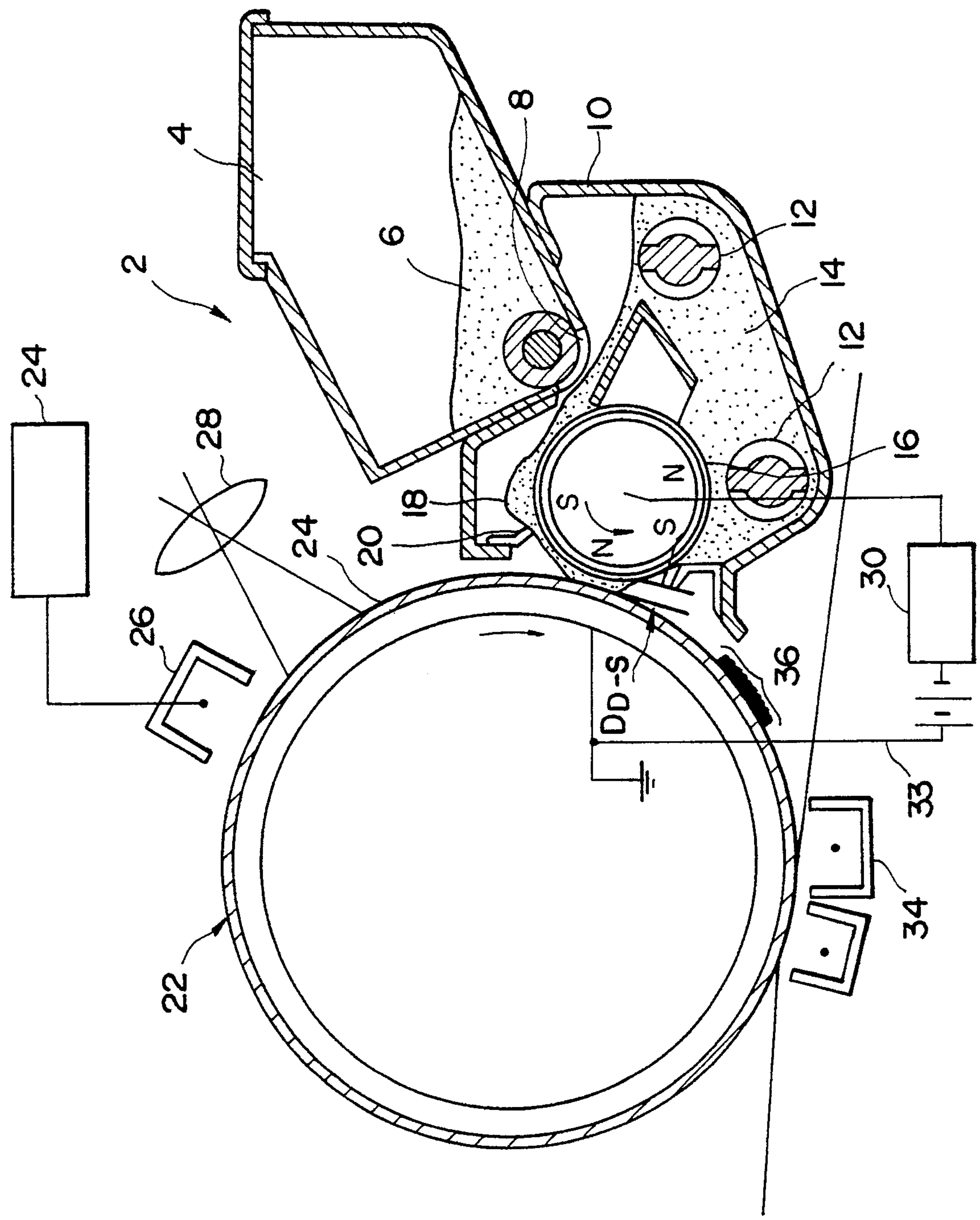


FIG. 2

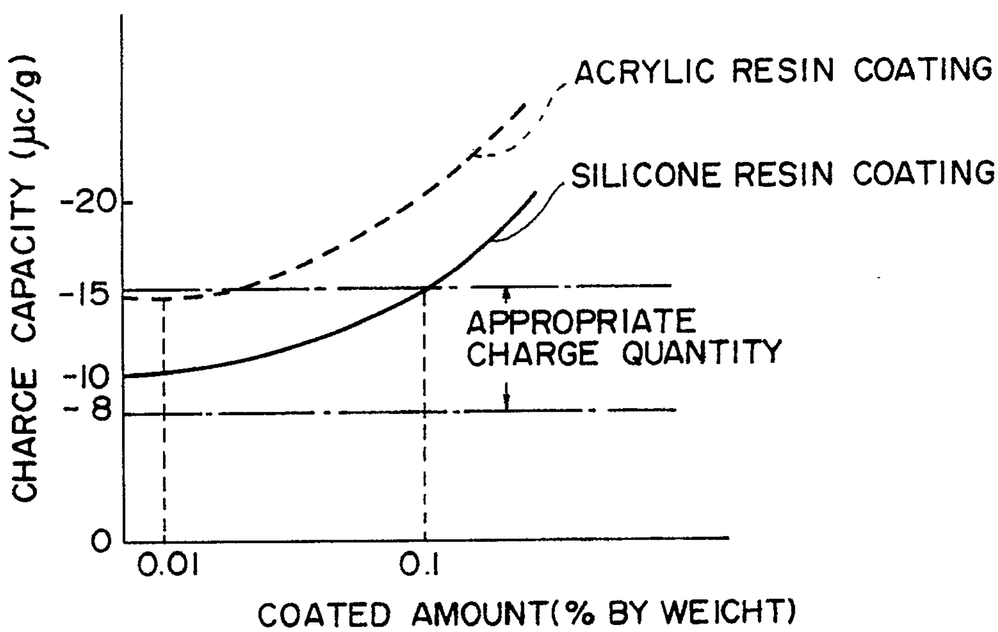
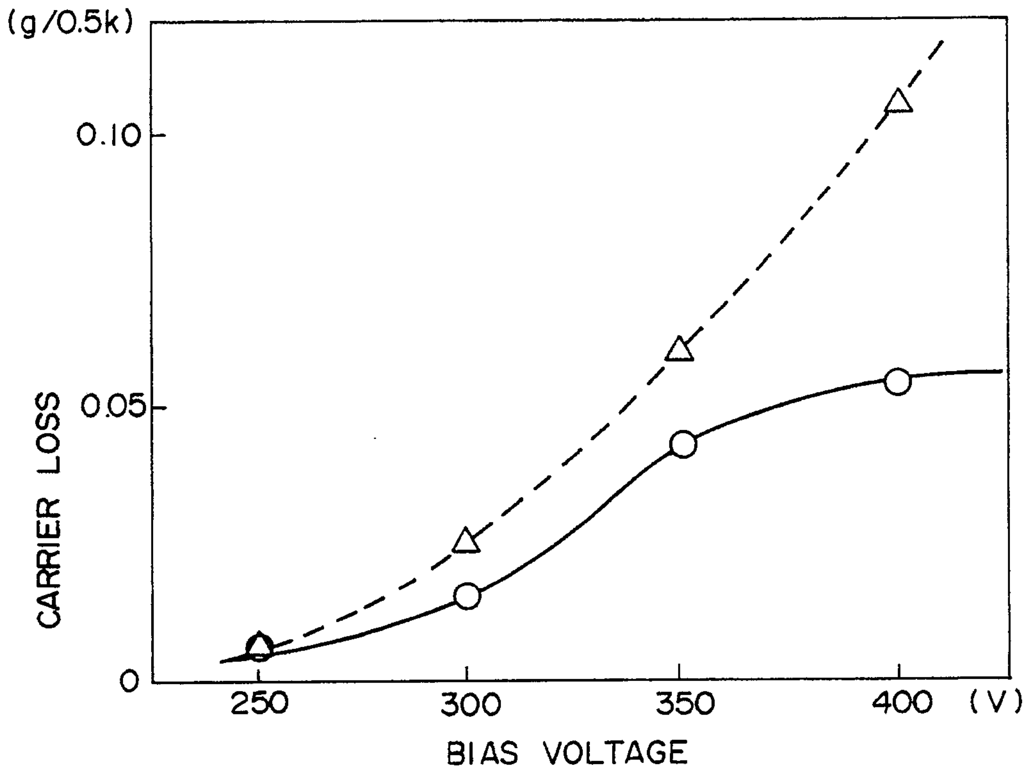

ACRYLIC RESIN COATING
SILICONE RESIN COATING
CHARGE CAPACITY (μc/g)
-20
-15
-10
- 8
0
APPROPRIATE
CHARGE QUANTITY
0.01
0.1
COATED AMOUNT(% BY WEICHT)

FIG. 3



PRESENT INVENTION : ○ TwY-5 (CONTENT OF FINE PARTICLES HAVING SIZE SMALLER THAN 250 MESH IS LOWER THAN 8% BY WEIGHT)

CONVENTIONAL TECHNIQUE : △ F2 (CONTENT OF FINE PARTICLES HAVING SIZE SMALLER THAN 250 MESH IS 27% BY WEIGHT)

FIG. 4