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(54) **Two-component type developer for magnetic brush development.**

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Description

The present invention relates to a two-component type developer for the magnetic brush development. More particularly, the present invention relates to a two-component type developer which can develop an electrostatic latent image under broad developing conditions according to the magnetic brush developing method, which can give an excellent printing resistance to a photosensitive plate and which can provide an image having a high quality. Especially, the present invention relates to a two-component type developer comprising a mixed carrier having a novel composition.

In the electrophotographic process using a two component type magnetic developer, a two-component composition formed by mixing an electroscopic toner with a magnetic carrier is supplied on a developing sleeve having a magnet in the interior thereof to form a magnetic brush of this composition, and an electro-photographic photosensitive plate is brought into sliding contact with this magnetic brush to form an electroscopic toner image on the photosensitive plate. The electroscopic toner is charged with the polarity reverse to the polarity of the electrostatic latent image on the photosensitive plate by friction with the magnetic carrier, and the electroscopic toner particles on the magnetic brush are caused to adhere to the electrostatic latent image by the Coulomb force, whereby the development of the electrostatic latent image is accomplished. On the other hand, the magnetic carrier is attracted by the magnet in the sleeve, and since the charge polarity of the magnetic carrier is the same as that of the electrostatic latent image, the magnetic carrier is left on the sleeve. In order to form a clear image having a high density, it is important that a sufficient difference of the relative speed should be provided between the photosensitive plate and the magnetic brush so that the photosensitive plate is sufficiently brought into sliding contact with the magnetic brush.

Ordinarily, an iron powder carrier is broadly used as the magnetic carrier. However, this iron powder carrier has various defects. More specifically, in case of a two-component type developer comprising an iron powder carrier, the rising of the developing sensitivity curve (the curve showing the relation of the image density to the difference of the voltage between the electrostatic latent image and the developing sleeve) is very sharp, and the gradation property is inferior and the half tone-reproducing property is poor. Moreover, this developer comprising an iron powder carrier sometimes forms a hard magnetic brush and there is a risk of damaging a photosensitive layer. Furthermore, in the reproduction of a solid black portion, brush marks, that is, many thin and short white lines extending in the sliding direction of the brush, are formed. Still further, the iron powder carrier is very sensitive to the moisture, and the developing characteristics are changed by influences of the moisture or rusting is readily caused in the iron powder carrier. Still in addition, a large torque is necessary for driving the magnetic brush.

Recently, use of ferrite, especially soft ferrite, as the magnetic carrier of a two-component type developer has been proposed. Since a ferrite carrier has a higher electric resistance than the iron powder carrier, at the developing step, carrier drawing, that is, a trouble of bleeding of the carrier to the photosensitive layer, is readily caused and a so-called edge effect is often produced in the formed image. Moreover, no satisfactory image can be obtained unless the space between the developing sleeve and the photosensitive layer is narrowed. Furthermore, in case of the developer comprising a ferrite carrier, cleaning with the magnetic brush is difficult.

FR—A—2346747 discloses a ferromagnetic toner comprising:

(a) at least one ferreomagnetic component,

(b) at least one dye and/or chemical treating agent and,

(c) a readily fusible, water-soluble or water-solubilizable resin which substantially encapsulates (a) and (b).

The resin is such that heat treatment, including treatment with steam, renders the resin adhesive. The ferromagnetic component may consist of hard and/or soft magnetic particles. The magnetically soft particles can be iron or another high-permeability, low-remanence material such as iron carbonyl, certain ferrites, such as $(Zn,Mn)Fe_2O_4$ or permalloys. The magnetically hard particles can be iron oxide, other ferrites such as $BaFe_{12}O_{19}$, chi-iron carbide, chromium dioxide or mixtures of Fe_3O_4 and nickel or cobalt. The toners can be employed to print, by magnetic printing processes, a variety of substrates such as textiles, film, paper, metal and wood. The toners are one-component toners.

It is a primary object of the present invention to provide a two-component type developer for the magnetic brush development, in which the above-mentioned various defects are eliminated.

Another object of the present invention is to provide a two-component type developer which can develop an electrostatic latent image according to the magnetic brush development method under broad developing conditions, which can give a higher printing resistance to a photosensitive layer than the conventional developers and which can provide an image having a high density and being excellent in the gradation property without such troubles as formation of brush marks and carrier drawing.

More specifically, in accordance with the present invention there is provided a two-component type developer suitable for the magnetic brush development of an electrostatic latent image comprising a mixture of magnetic carrier particles and toner particles chargeable by friction with the magnetic carrier particles, wherein the developer comprises particles of an iron powder as a first type of magnetic carrier particles and particles of a ferrite as a second type of magnetic carrier particles at a weight ratio of iron powder: ferrite of from 60:40 to 5:95.

Fig. 1 is a diagram illustrating the principle of the development with a two-component type developer.

Fig. 2 is an enlarged diagram illustrating the earing state of a magnetic brush.

Fig. 3 is a graph showing the developing sensitivities of developers obtained in Examples of the present invention and Comparative Examples.

The present invention is based on the novel finding that when an iron powder carrier and a ferrite carrier are used in combination as the magnetic carrier of a two-component type developer at a weight ratio of from 60/40 to 5/95, especially from 30/70 to 10/90, severe developing conditions become unnecessary and an electrostatic latent image can be developed stably under broad developing conditions, the printing resistance of a photosensitive layer can be improved as compared with the case where the conventional two-component type developer for the magnetic brush development is used, and a high quality image free of such defects as brush marks and carrier drawing can be obtained. For convenience, the combination of the two types of carrier particles is sometimes referred to herein as the "mixed carrier".

Referring to Fig. 1 illustrating the principle of the development using a two-component type developer according to the present invention, a magnet roll 1 comprising magnetic poles N and S is contained in a sleeve 2 formed of a non-magnetic material such as aluminum, and at least one of the magnet roll 1 and sleeve 2 is driven and rotated. A two-component type developer 3 is supplied on the peripheral surface of the sleeve 2 from a developer tank 4 to form a magnetic brush 5. The earing length of the magnetic brush 5 is adjusted by an ear-cutting mechanism 6, and the magnetic brush 5 is delivered to the sliding contact position on an electrophotographic photosensitive layer 7 on a drum substrate. An electrostatic latent image on the photosensitive layer 7 is developed by an electroscopic toner 8 to form a visible image.

Referring to Fig. 2 which is an enlarged diagram illustrating the earing state of the magnetic brush 5, in the mixed carrier of the present invention, it is believed that an iron powder carrier 9 is predominantly distributed in the portion close to the outer surface of the sleeve, while a ferrite carrier 10 is predominantly distributed in the portion close to the outer side of the magnetic brush 5. More specifically, if this mixed carrier is supplied onto the developing sleeve, the iron powder carrier 9 having a large coercive force is first attracted strongly to the surface of the sleeve, but the ferrite carrier 10 having a small coercive force is placed on the iron powder carrier 9, and in this state, the magnetic brush 5 is formed. Because of the characteristics of the preparation process, iron powder carrier particles 9 have ordinarily an indeterminate shape, while the ferrite carrier 10 has a substantially spherical particle shape formed by sintering.

In the mixed carrier of the present invention, since the magnetic brush having the above-mentioned micro-structure is formed, various advantages are attained. As pointed out hereinbefore, the magnetic carrier which forms a hard magnetic brush tends to damage the surface of the photosensitive layer and to form brush marks. However, with a carrier of the present invention, a soft tip of the ferrite carrier is formed on the top end portion of the ear of the iron powder carrier, and therefore, the tendency to damage the surface of the photosensitive layer and form brush marks in the toner image is drastically reduced.

When the ferrite carrier alone is used, since the coercive force is small, if the earing length of the magnetic brush is increased, the magnetic brush separates from the sleeve. Accordingly, the development is not satisfactorily accomplished unless the ear length is adjusted to such a short length as 0.5 to 2 mm. In contrast, according to the present invention, since the ferrite carrier is retained in the top end portion of the iron powder carrier having a large coercive force, even if the earing length of the magnetic brush is adjusted to a long length customarily adopted for the iron carrier, that is, 2 to 5 mm, an excellent developed image is formed without falling of the carrier, and therefore, disadvantages caused when the clearance between the sleeve and the photosensitive layer is drastically reduced, such as wearing of the photosensitive layer and the difficulty in designing the apparatus, can be eliminated. Furthermore, since the ferrite carrier is strongly retained in the top end portion of the iron powder carrier, troubles caused by use of the ferrite carrier such as toner drawing can be prevented from occurrence.

Moreover, in the mixed carrier of the present invention, even if the earing length of the magnetic brush is adjusted to such a short length as adopted in case of the ferrite carrier, a good image can be formed. Accordingly, an advantage that the range of applicable developing conditions is very broad can be attained according to the present invention.

In the magnetic brush development using a two-component type developer, if the electric resistance of the magnetic carrier is high, an image excellent in the gradation property is obtained. In the case where the mixed carrier of the present invention is used, since the ferrite carrier having a high electric resistance is present in the state where the ferrite carrier is connected in series to the iron powder carrier having a low electric resistance, even if the mixing ratio of the iron powder carrier in the mixed carrier is considerably increased, the electric resistance of the magnetic brush as a whole is maintained at a high level, and an image excellent in the gradation property can be obtained.

In the present invention, it is important that the iron powder carrier and ferrite carrier should be used at the above-mentioned weight ratio. If the amount of the ferrite carrier or iron powder carrier is too small and below the above-mentioned range, attainment of the above-mentioned advantages of the present invention becomes difficult.

Sintered ferrite particles, especially spherical sintered ferrite particles, are advantageously used as the ferrite carrier, and it is ordinarily preferred that the particle size of the sintered ferrite particles be 20 to 100 μm.

If the particle size of the sintered ferrite particles is smaller than 20 μm, good earing of the magnetic

brush can hardly be obtained, and if the particle size of the sintered ferrite particles is larger than 100 μm, the above-mentioned brush marks, that is, scratches, are readily formed in the formed toner image.

The sintered ferrite particles used in the present invention are known sintered ferrite particles. For example, there may be used sintered ferrite particles composed of at least one member selected from zinc iron oxide ($ZnFe_2O_4$), yttrium iron oxide ($Y_3Fe_5O_{12}$), cadmium iron oxide ($CdFe_2O_4$), gadolinium iron oxide ($Gd_3Fe_5O_{12}$), copper iron oxide ($CuFe_2O_4$), lead iron oxide ($PbFe_{12}O_{19}$), nickel iron oxide ($NiFe_2O_4$), neodymium 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 ($LaFeO_3$). Sintered ferrite particles composed of manganese iron oxide and zinc iron oxide are especially suitable for attaining the objects of the present invention.

Any of known iron powder carriers can be used as the iron powder carrier in the present invention. It is ordinarily preferred that the particle size of the iron powder carrier be 20 to 150 μm. An iron powder as the magnetic carrier is ordinarily prepared by subjecting soft steel scraps to the primary pulverization, oil quenching, mineral dressing and nitriding to form brittle primary particles, pulverizing the primary particles to form final particles, and subjecting the particles to the denitriding treatment and then to the surface-oxidizing treatment to increase the electric resistance of the surface. The so-prepared iron powder has an indeterminate shape. Of course, in the present invention, an iron powder carrier having a spherical or ellipsoidal shape can also be used.

The two-component type developer of the present invention can be prepared by mixing the above-mentioned mixed magnetic carrier with a known electroscopic coloring toner.

The developer can be formed by blending the magnetic carrier with the toner at a weight ratio of from 100/6 to 100/17, especially from 100/8 to 100/15. Any of coloring toners having an electroscopic property and a fixing property can be used in the present invention. A particulate composition having a particle size of 5 to 30 μm, which comprises a coloring pigment and a charge controlling agent, dispersed in a binder resin, is used. A thermoplastic resin or an uncured or pre-condensed thermosetting resin may be used as the binder resin. As preferred examples, there can be mentioned, in the order of importance, a vinyl aromatic resin, an acrylic resin, a polyvinyl acetal resin, a polyester resin, an epoxy resin, a phenolic resin, a petroleum resin and an olefin resin. As the pigment, there can be used at least one member selected from carbon black, cadmium yellow, molybdenum orange, Pyrazolone Red, Fast Violet B and Phthalocyanine Blue. As the charge controlling agent, there may be used oil-soluble dyes such as Nigrosine Base (CI 50415), Oil Black (CI 26150) and Spiron Black, and metal salts of naphthenic acid, metal soaps of fatty acids and soaps of resin acids according to need.

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 5

The following ferrite carrier (a), iron powder carrier (b) and toner (c) were mixed at various ratios shown in Table 1 and blended and stirred to form developers. The copying operation was carried out by using these developers in a copying machine (Mita PC-191 supplied by Mita Industrial Company Limited). Clear images excellent in the gradation property and free of brush mark, fogging and edge effect could be obtained in each case.

(a) Ferrite carrier:

Electric resistance of 1.8×10^9 Ω, maximum magnetization of 49.8 emu/g, residual magnetization of 0.25 emu/g, coercive force of 3.38 Oe, median particle size of 40 μm.

(b) Iron powder carrier:

Electric resistance of 4.0×10^6 Ω, maximum magnetization of 180.0 emu/g, residual magnetization of 15.0 emu/g, coercive force of 17.30 Oe, median particle size of 40 μm.

(c) Toner:

(the ingredients of the toner)

Himer SBM-73 (styrene type resin supplied by Sanyo Kasei Kogyo K.K.)	87 parts by weight
Viscol 550P (low-molecular-weight polypropylene supplied by Sanyo Kasei Kogyo K.K.)	5 parts by weight
Special Black 4 (carbon black supplied by Degusa Co.)	5.5 parts by weight
Bontron S-32 (dye supplied by Orient Kagaku K.K.)	1.5 parts by weight

A mixture comprising the above toners ingredients were melt-kneaded and dispersed by a hot three-roll mill, and the kneaded mixture was cooled and roughly pulverized to a size of about 2 mm by a

rough pulverizer (Rotoplex Cutting Mill supplied by Alpine Co.), and was finely pulverized to a size of about 10 to about 20 μm by an ultrasonic jet mill (supplied by Nippon Pneumatic Mfg. Co., Ltd.).

TABLE 1

Example No.	Ferrite carrier (g)	Iron powder carrier (g)	Toner (g)
1	900	100	100
2	800	200	100
3	700	300	100
4	500	500	100
5	400	600	100

Comparative Examples 1 through 4

The ferrite carrier, iron powder carrier and toner used in Examples 1 through 5 were sufficiently mixed at ratios shown in Table 2, and the copying operation was carried out under the same conditions as in Examples 1 through 5 in the copying machine Mita DC-191 by using the so-prepared developers. In the obtained copies, no fogging was observed, but such defects as edge effect, carrier drawing, brush mark and poor gradation were observed as indicated by marks "X" in Table 2.

TABLE 2

Comparative Example No.	Ferrite carrier (g)	Iron powder carrier (g)	Toner (g)	Edge effect	Carrier drawing	Grada-tion	Brush mark
1	1000	0	100	X	X	0	0
2	970	30	100	X	X	0	0
3	300	700	100	0	0	X	X
4	0	1000	100	0	0	X	X

The developing sensitivity curves of the developers obtained in Examples 1 through 5 and Comparative Examples 1 through 4 are shown in Fig. 3. In Fig. 3, the solid lines indicate the results obtained by using the toners of the present invention and dot lines show the results obtained by using the comparative toners. From the results shown in Fig. 3, it is seen that in the developers of the present invention, the rising is more gradual than in the developer composed solely of the iron powder carrier and toner (Comparative Example 4), and the toners of the present invention provide images excellent in the gradation property and have a good half tone-reproducing property.

Herein, particle sizes are average particle sizes unless otherwise specified.

Claims

1. A two-component type developer (3) suitable for the magnetic brush development of an electrostatic latent image comprising a mixture of magnetic carrier particles and toner particles (8) chargeable by friction with the magnetic carrier particles, characterised in that the developer (3) comprises particles (9) of an iron powder as a first type of magnetic carrier particles and particles (10) of a ferrite as a second type of magnetic carrier particles at a weight ratio of iron powder: ferrite of from 60:40 to 5:95.

2. A developer according to claim 1, wherein the weight ratio of the iron powder to the ferrite is from 30:70 to 10:90.

3. A developer according to claim 1 or 2, wherein the particulate ferrite (10) is composed of sintered ferrite particles having an average particle size of from 20 to 100 μm.

4. A developer according to any one of the preceding claims, wherein the particulate ferrite (10) is composed of sintered ferrite particles of at least one oxide selected from zinc iron oxide, yttrium iron oxide, cadmium iron oxide, gadolinium iron oxide, copper iron oxide, lead iron oxide, nickel iron oxide, neodymium iron oxide, barium iron oxide, magnesium iron oxide, manganese iron oxide and lanthanum iron oxide.

5. A developer according to any one of the preceding claims, wherein the iron powder (9) has an average particle size of from 20 to 150 μm.

6. A developer according to any one of the preceding claims, wherein the iron powder particles (9) have indeterminate shapes.

7. A developer according to any one of the preceding claims, wherein the carrier particles are mixed with the toner particles (8) at a weight ratio of carrier: toner (8) of from 100:6 to 100:17.

8. A developer according to any one of the preceding claims, wherein the toner particles (8) have an average particle size of 5 to 30 µm and are composed of a composition comprising a coloring pigment and a charge controlling agent, dispersed in a binder resin.

9. Use of a developer as claimed in any one of the preceding claims in the development by the magnetic brush method of an electrostatic latent image.

Patentansprüche

1. Entwickler vom Zweikomponententyp (3), der für die Magnetbürstenentwicklung eines elektrostatischen latenten Bildes geeignet ist, enthaltend ein Gemisch aus magnetischen Trägerteilchen und Tonerteilchen (8), die durch Reibung mit den magnetischen Trägerteilchen geladen werden können, dadurch gekennzeichnet, daß der Entwickler (3) Teilchen (9) eines Eisenpulvers als einen ersten Typ magnetischer Trägerteilchen und Teilchen (10) eines Ferrite als einen zweiten Typ magnetischer Trägerteilchen in einem Gewichtsverhältnis von Eisenpulver: Ferrit von 60:40 bis 5:95 enthält.

2. Entwickler nach Anspruch 1, worin das Gewichtsverhältnis des Eisenpulvers zu dem Ferrit von 30:70 bis 10:90 beträgt.

3. Entwickler nach Anspruch 1 oder 2, worin das teilchenförmige Ferrit (10) zusammengesetzt ist aus gesinterten Ferritteilchen mit einer durchschnittlichen Teilchengröße von 20 bis 100 µm.

4. Entwickler nach einem der voranstehenden Ansprüche, worin das teilchenförmige Ferrit (10) zusammengesetzt ist aus gesinterten Ferritteilchen von mindestens einem Oxid, welches ausgewählt ist unter Zinkeisenoxid, Yttriumeisenoxid, Cadmiumeisenoxid, Gadoliniumeisenoxid, Kupfereisenoxid, Bleieisenoxid, Nickeleisenoxid, Neodymeisenoxid, Bariumeisenoxid, Magnesiumeisenoxid, Manganeisenoxid, und Lanthaneisenoxid.

5. Entwickler nach einem der voranstehenden Ansprüche, worin das Eisenpulver (9) eine durchschnittliche Teilchengröße von 20 bis 150 µm aufweist.

6. Entwickler nach einem der voranstehenden Ansprüche, worin die Eisenpulver-Teilchen (9) unbestimmte Formen aufweisen.

7. Entwickler nach einem der voranstehenden Ansprüche, worin die Trägerteilchen mit den Tonerteilchen (8) in einem Gewichtsverhältnis von Träger: Toner (8) von 100:6 bis 100:17 vermischt sind.

8. Entwickler nach einem der voranstehenden Ansprüche, worin die Tonerteilchen (8) eine durchschnittliche Teilchengröße von 5 bis 30 µm aufweisen und aus einer Zusammensetzung bestehen, die ein farbgebendes Pigment und ein Beladungskontrollmittel, dispergiert in einem Binderharz, enthält.

9. Verwendung eines Entwicklers nach einem der voranstehenden Ansprüche bei der Entwicklung eines elektrostatischen latenten Bildes nach dem Magnetbürstenverfahren.

Revendications

1. Developpeur (3) du type à deux composants adapte au developpement par brosse magnétique d'une image latente électrostatique comprenant un mélange de particules de support magnétique et de particules de toner (8), pouvant être chargé par friction avec les particules de support magnétique, caractérisé en ce que le developpeur (3) comprend des particules (9) d'une poudre de fer comme premier type de particules de support magnétique et des particules (10) d'une ferrite comme second type de particules de support magnétique dans un rapport en poids poudre de fer ferrite de 60:40 à 5:95.

2. Developpeur selon la revendication 1, dans lequel le rapport en poids de la poudre de fer à la ferrite est de 30:70 à 10:90.

3. Developpeur selon la revendication 1 ou 2, dans lequel la ferrite particulaire (10) est composée de particules de ferrite fritées ayant une dimension moyenne des particules de 20 à 100 µm.

4. Développeur selon l'une quelconque des revendications précédentes, dans lequel la ferrite particulaire (10) est composée, de particules de ferrite frittées d'au moins un oxyde sélectionné parmi les oxyde de fer et de zinc, oxyde de fer et d'yttrium, oxyde de fer et de cadmium, oxyde de fer et de gadolinium, oxyde de fer et de cuivre, oxyde de fer et de plomb, oxyde de fer et de nickel, oxyde de fer et de neodgmium oxyde de fer et de baryum, oxyde de fer et de magnésium, oxyde de fer et de manganèse et oxyde de fer et de lanthanum.

5. Développeur selon l'une quelconque des revendications précédentes, dans lequel la poudre de fer (9) présente une dimension moyenne des particules de 20 à 150 µm.

6. Développeur selon l'une quelconque des revendications précédentes, dans lequel les particules de poudre de fer (9) présentent des formes indéterminées.

7. Développeur selon l'une quelconque des revendications précédentes, dans lequel les particules de support sont mélangées avec les particules de toner (8) dans un rapport en poids support: toner de 100:6 à 100:17.

8. Developpeur selon l'une quelconque des revendications précédentes, dans lequel les particules de toner (8) ont une dimension moyenne des particules de 5 à 30 µm et sont constituées par une composition contenant un pigment colorant et un agent contrôlant la charge dispersés dans une résine liante.

9. Utilisation d'un développeur selon l'une quelconque des revendications précédentes dans le developpement par le procédé à la brosse magnétique d'une image latente électrostatique.

Fig. 1

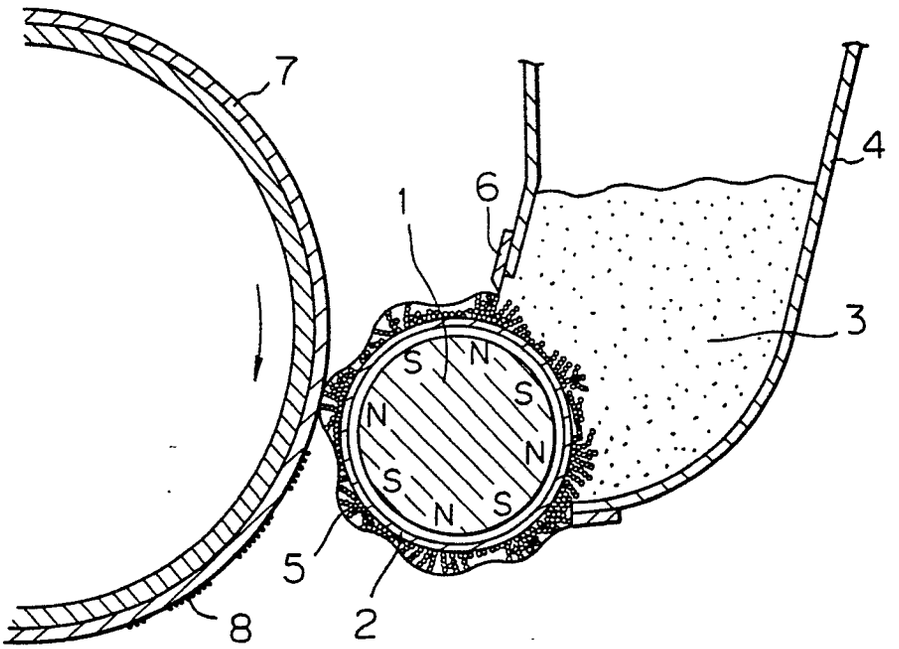


Fig. 2

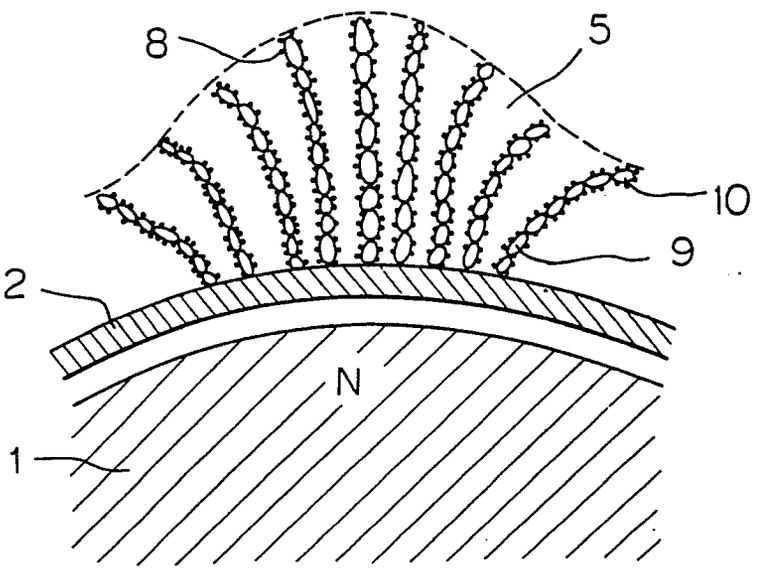
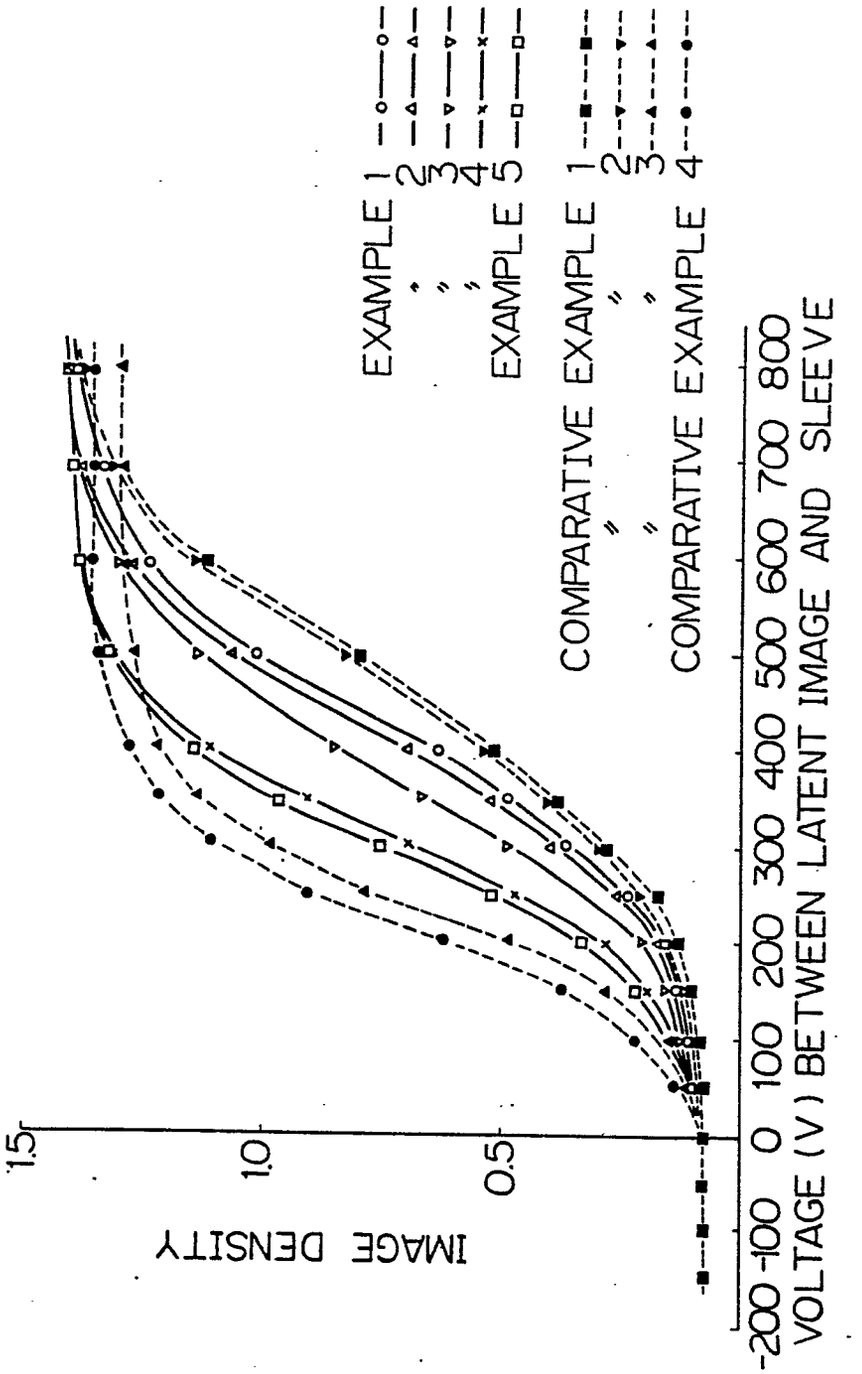


Fig. 3


EXAMPLE 1
2
3
4
EXAMPLE 5
COMPARATIVE EXAMPLE 1
2
3
COMPARATIVE EXAMPLE 4
IMAGE DENSITY
1.5
1.0
0.5
-200 -100 0 100 200 300 400 500 600 700 800
VOLTAGE (V) BETWEEN LATENT IMAGE AND SLEEVE