(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 423 341 A1**

(12) **EUROPEAN PATENT APPLICATION published in accordance with Art. 158(3) EPC**

(21) Application number: **89913088.4**

(51) Int. Cl.5: **G03G 9/08**

(22) Date of filing: **22.11.89**

(86) International application number:
PCT/JP89/01196

(87) International publication number:
WO 90/13065 (01.11.90 90/25)

(30) Priority: **14.04.89 JP 95700/89**

(43) Date of publication of application:
24.04.91 Bulletin 91/17

(84) Designated Contracting States:
CH DE FR GB LI

(71) Applicant: **MITA INDUSTRIAL CO., LTD.**
2-28, 1-chome, Tamatsukuri Chuo-ku
Osaka 540(JP)

(72) Inventor: **URANO, Akiyoshi**
6-5-104, Nakano-cho, Takarazuka-shi
Hyogo 665(JP)
Inventor: **SANO, Yumiko**
17-7, Kuwata-cho, Ibaraki-shi
Osaka 567(JP)
Inventor: **UMETANI, Yoshinobu 1284,**
Higaimoto, Oyodo-cho
Yoshino-gun
Nara 638(JP)
Inventor: **KADO, Seiji**
6-5-40-401, Mino, Mino-shi
Osaka 562(JP)

(74) Representative: **Sajda, Wolf E., Dipl.-Phys. et al**
MEISSNER, BOLTE & PARTNER
Widenmayerstrasse 48 Postfach 86 06 24
W-8000 München 86(DE)

(54) **PHOTOCONDUCTIVE TONER AND METHOD OF PRODUCING THE SAME.**

(57) A photoconductive toner is obtained by dispersing a fine granular inorganic photoconductive material having a specific surface area of 8 to 20 m^2/g in an amount of greater than 50 % by weight in a fixing resin. Therefore, photo-sensitivity is improved per a toner particle, the thin toner layer that is formed exhibits improved photo-sensitivity, and the toner exhibits good fluidity and charge characteristics making it possible to obtain vivid picture with excellent contrast.

EP 0 423 341 A1

PHOTOCONDUCTIVE TONER AND METHOD OF MANUFACTURING THE SAME

Field of the Invention

The present invention relates to photoconductive toner and more particularly to photoconductive toner which is made with the use of a fine photoconductive material and of which a variety of characteristics such as photosensitivity are remarkably improved.

Description of the Prior Art

As a method of forming an image without use of a photosensitive drum, there has been proposed an image forming method using photoconductive toner, with which an image forming apparatus may be made in a compact design. Accordingly, this method is recently attracting public attention.

The photoconductive toner is obtainable by granulating, in the form of particles of a micron order, a mixture in which a photoconductive material is being dispersed in a fixing resin having fixing properties and charge detecting properties. The toner thus obtained is itself photoconductive. We have already pro-posed an image forming method using photoconductive toner in Japanese Patent Application No. 295343/1987.

As set forth in the specification of the Application above-mentioned, the image forming method using photoconductive toner presents, in connection with the exposure of the charged toner layer to light, the following problems completely different from those encountered with normal chargeable toner. The photosensitive layer is composed of an independent layer of toner particles and an image is formed by the fact that the photoconductivity of the toner particles causes the electric charge and Coulomb force to be changed. This may easily provoke a decrease in image density, image fog and character halation. To obtain a clear image, a variety of characteristics required for the toner become more exacting as to photosensitivity, particle size characteristics, charge stability, flowability and the like. In fact, if even one of the toner characteristics above-mentioned is below a certain level, a good image may not be obtained.

As to zinc oxide, titanium oxide or the like serving as an inorganic photoconductive material conventionally used for photoconductive toner, there have been generally used particles of which specific surface areas are in a range from 2 to 7 m^2/g. To obtain such a photoconductivity as required for image forming, it is required to contain not less than 50 % by weight of the photoconductive material with respect to a fixing resin. This causes the inorganic photoconductive material to be exposed on the the surface of toner in which the photoconductive material is being dispersed. Accordingly, the toner flowability is decreased or the respective electric charges of toner particles are considerably different from one another. It is therefore difficult to form a thin toner layer having a uniform and even thickness and presenting a uniform and even surface potential. Even though the scattering of irradiation light in the toner particles is satisfactory, the photosensitivity (which represents the efficiency at which, from the level of the surface potential of the charged toner layer, the electric charge of the toner layer disappears by light irradiation) is lowered. Accordingly, it is still difficult to form a toner image excellent in contrast.

In view of the problems above-mentioned of the prior art, the present invention is proposed with the object of providing photoconductive toner capable of forming a toner image excellent in contrast free from character halation and image fog.

It is another object of the present invention to provide photoconductive toner excellent in flowability, the ability of forming a thin toner layer and friction-charging characteristics.

It is a further object of the present invention to provide photoconductive toner capable of forming an image presenting the vivid tone of color.

It is still another object of the present invention to provide photoconductive toner remarkably improved in photosensitivity, and also to provide a method for manufacturing such toner.

Disclosure of the Invention

The present invention provides photoconductive toner containing not less than 50 % by weight of an inorganic photoconductive material as dispersed in a fixing resin, the inorganic photoconductive material being fine particles of which specific surface areas are in a range from 8 to 20 m^2/g.

The present invention also provides photoconductive toner containing not less than 50 % by weight of an inorganic photoconductive material as dispersed in a fixing resin, the inorganic photoconductive material

being fine particles in which fatty acid and sensitizing dyestuff are being adsorbed to the surfaces thereof and of which specific surface areas are in a range from 8 to 20 m^2/g.

The present invention also provides a method of manufacturing photoconductive toner including the steps of immersing, in an organic solvent in which fatty acid is soluble, an inorganic photoconductive material of which specific surface area is in a range from 8 to 20 m^2/g, and adding fatty acid and sensitizer to the solvent so that the sensitizer is adsorbed on the surface of the inorganic photoconductive material.

The present invention is proposed based on the finding that, when toner is formed by dispersing, in a fixing resin, not less than 50 % by weight of a fine inorganic photoconductive material of which specific surface area is considerably increased as compared with that of a conventional photoconductive material, all the charging characteristics, flowability and photosensitivity of the photoconductive toner are improved, thus enabling to form a clear toner image free from character halation and image fog.

More specifically, the photoconductive toner, according to the present invention using a fine inorganic photoconductive material of which specific surface area is in a range from 8 to 20 m^2/g, presents a good dispersion even though not less than 50% of the inorganic photoconductive material is contained with respect to the fixing resin. This reduces the exposure of the inorganic photoconductive material on the toner particle surfaces, thereby to improve the toner in flowability, charge storage and the ability of forming a thin toner layer. Further, since the scattering of irradiation light in the toner becomes intense, the amount of light irradiated on the photoconductive material is substantially increased. Thus, a clear image excellent in contrast may be formed.

The photoconductive toner in accordance with the present invention may produce satisfactory results in any application as far as the toner is used in process in which a charged thin toner layer is formed and the thin toner layer is exposed to light to form an image.

Brief Description of the Drawings

Figure 1 is a view illustrating the relationship between the specific surface area of zinc oxide and the surface potential decay factor of a toner layer;
Figure 2 is a view illustrating the relationship between light exposure intensity and transfer sensitivity at the time when forming a thin toner layer by a magnetic brush is made simultaneously with scraping off the toner which has been exposed to light;
Figure 3 is an enlarged view of a simultaneous exposure and transfer portion;
Figure 4 is a schematic view of a device for measuring the transfer sensitivity of the toner in accordance with the present invention; and
Figure 5 is a view illustrating an example of an image forming apparatus to which the toner in accordance with the present invention is applied.

Preferred Embodiments of the Invention

The following description will discuss in more detail the present invention with reference to a specific example of an image forming process using photoconductive toner.

Fig. 3 is a view illustrating an image forming method using photoconductive toner, which adopts development by a binary magnetic brush comprising photoconductive toner and a magnetic carrier and in which a positive image is formed according to a voltage application/simultaneous exposure/simultaneous transfer method, which we have suggested in our previous patent application No. 295343/1987.

With reference to Fig. 3, disposed on a developing sleeve (conductive sleeve) 16 is a magnetic brush 15 comprising a mixture of a magnetic carrier 17 and photoconductive toner 13. The magnetic brush 15 comes in contact with a transparent electrode 2 of a transparent drum 3.

By its mixture with the magnetic carrier 17, the photoconductive toner 13 is charged to an electric charge of a predetermined polarity (for example, a minus polarity) and is attracted, by a Coulomb force, to the magnetic carrier 17 charged to an electric charge of the opposite polarity. A bias potential is applied to the transparent electrode surface 2 by a power supply 19 or the transparent electrode surface 2 is grounded such that the transparent electrode surface 2 presents the opposite polarity (for example, a plus polarity) to the polarity of the photoconductive toner 13. Thus, a thin layer 26 of the photoconductive toner 13 is formed on the transparent electrode surface 2. The toner layer 26 is subjected to slit exposure through the transparent drum 3 and the transparent electrode 2. In a dark part D, the photoconductive toner 13 remains held on the electrode surface 2 by a Coulomb force. In a light part L, the electric charge

disappears by the photoconductivity of the toner 13 or a charge having the opposite polarity (for example, a plus polarity) is introduced. Accordingly, the toner 13 is moved toward the magnetic brush 15 and a toner image 25 corresponding to the dark part D is formed.

As apparent from the image forming method above-mentioned, when a thin toner layer is to be formed on a toner application surface such as a transparent electrode surface or the like by the magnetic brush comprising a carrier and toner, it is required to sufficiently agitate the toner in the developing device and to form a magnetic brush in which the toner is being uniformly dispersed, in order to form the thin toner layer having a uniform and even thickness and presenting a uniform and even surface potential. According to the simultaneous exposure/simultaneous transfer method, the toner of which charge has been attenuated after exposure to light should be quickly scraped off by the magnetic brush. Accordingly, the mutual adhering force of toner particles after charge decay, should be in a suitable range. The surface condition and particle size of the toner exert a considerable influence upon such an adhering force.

According to the toner of the present invention containing the fine inorganic photoconductive material of which specific surface area is in a range from 8 to 20 m^2/g, as dispersed in the fixing resin, (i) it is possible to prevent the inorganic photoconductive material from being exposed to the toner surface, (ii) the respective toner particles contain the inorganic photoconductive material substantially at the same concentration since the photoconductive material may be finely and uniformly dispersed in the fixing resin, and (iii) the toner particles may be manufactured substantially in the same particle size. Accordingly, the toner is excellent in photosensitivity and flowability under a preferable range of particle size as desired. Further, the toner particles present less difference in characteristics. Thus, the photoconductive toner of the present invention may produce more favorable results in an image forming method in which the flowability of toner particles exerts a considerable influence upon an image, such as the method above-mentioned in which the thin toner layer is formed by the magnetic brush and the toner after exposed to light is scraped off (transferred) by the magnetic brush.

Inorganic Photoconductive Material

As the inorganic photoconductive material used in the present invention, there may be used any fine particles of zinc oxide, titanium oxide, cadmium sulfide, selenium, zinc sulfide or the like, of which specific surface areas are in a range from 8 to 20 m^2/g.

If there are used particles of the inorganic photoconductive material of which specific surface areas are smaller than 8 m^2/g, the resultant toner is unfavorable in view of photosensitivity and exposure of the inorganic material on the toner particle surfaces. On the other hand, if there are used particles of the inorganic photoconductive material of which specific surface areas are greater than 20 m^2/g, the particles cohere one another during production of the toner, making it difficult to disperse the particles uniformly and evenly in the toner.

As to the amount, the inorganic photoconductive material may be used preferably in a range from 50 to 500 parts by weight and more preferably from 100 to 350 parts by weight, for 100 parts by weight of the fixing resin of which examples are set forth below.

Fixing Resin

As the fixing resin in which the photoconductive material above-mentioned is dispersed, there may be used an electrically insulating resin known per se such as a styrene polymer, an acrylic polymer, a styrene-acrylic polymer, poly(vinyl chloride), polyester, polyamide, polyurethane, epoxy resin, diallyl phthalate resin, silicone resin, phenol resin, rosin modified phenol resin, rosin ester, polyvinyl butyral, polysulphone and the like. Further, a photoconductive resin such as polyvinyl carbazole or the like may also be used independently or in combination of the electrically insulating resin.

According to the present invention, when the fine inorganic photoconductive material presents no sensitivity in a visible area, a dyestuff sensitizer or a chemical sensitizer known per se may be additionally used.

Examples of the sensitizing agent include Rose Bengal, eosin, fluorescein, brilliant carmine, thioflavine, Acridine orange, Erythrosine, bromphenol blue and the like. The sensitizing agent may be used preferably in a range from 0.01 to 0.5 parts by weight and more preferably from 0.05 to 0.2 parts by weight for 100 parts by weight of the photoconductive material.

Alternately, a charge transferring material may be used as a fixing medium, and the photoconductive

material above-mentioned may be dispersed in this charge transferring material as a charge generating material. From the resultant dispersed system, photoconductive toner may be made.

As a charge transferring medium, there may be used a combination of the electrically insulating resin and the charg transferring material. Examples of the charge transferring material include a positive hole transferring material such as polyvinylcarbazole, phenanthrene, N-ethyl carbazole, 2,5-diphenyl-1,3,4-oxathiazole, 4,4'-bis-(diethylamino)-2,2'-dimethyl triphenylmethane, 2,5-bis-(4-diethylaminophenyl)-1,3,4-triazole, p-diethylaminobenzaldehyde-(diphenylhydrazone), and an electron transferring material such as 2-nitro-9-fluorene, 2-nitrobenzothiophene, anthraquinone and the like. The charge transferring material may be used, for 100 parts by weight of resin, preferably in a range from 10 to 200 parts by weight and more preferably from 30 to 120 parts by weight.

Toner Characteristic Imparting Agents

The photoconductive toner of the present invention may further contain, in addition to the indispensable components above-mentioned, toner characteristic imparting agents known per se according to a known prescription.

As such toner characteristic imparting agents, there may be used an offset preventive agent, a coloring agent and a charge control agent.

As the offset preventive agent, there may be used wax such as polyethylene wax, polypropylene wax, ethylene-propylene wax and the like, a monomeric olefin such as an olefin monomer having four or more carbon atoms, and the like. The offset preventive agent may be preferably used in an amount from 0.1 to 10 parts by weight for 100 parts by weight of the fixing resin.

As the coloring agent, there may be used, for example, one or more types of known agents such as carbon black, cadmium yellow, molybdenum orange, pyrazolone red, Fast Violet B, phthalocyanine blue and the like.

As the charge control agent, there may be used, for example, oil-soluble dyestuff such as nigrosine base (C.I. 50415), oil black (C.I. 26150), Spilon black and the like, naphthenic acid metal salt, fatty acid metal salt, soap resinate or the like.

Sensitizing Treatment of Inorganic Photoconductive Material and Toner Manufacturing Method

When the inorganic photoconductive material to be used for the photoconductive toner of the present invention presents no sensitivity in a visible area, the inorganic photoconductive material may be immersed in an organic solvent in which a sensitizer is being dispersed or with which a sensitizer is compatible, so that the sensitizer is adsorbed on the surface of the photoconductive material, thereby to improve the sensitivity.

Examples of the organic solvent include: alcohol such as methanol, ethanol, isopropanol, butanol, isobutanol, tert-butanol, hexanol, octanol or the like; ether such as dioxane, tetrahydrofuran, dimethyl ether, diethyl ether, ethyleneglycol monomethyl ether, ethyleneglycolmonoethylether or the like; ketone such as acetone, methyl ethyl ketone, cyclohexanone or the like; ester such as ethyl acetate, methyl acetate or the like; acetonitrile; formaldehyde; dimethyl formaldehyde; pyridine and the like. These examples of the organic solvent may be used alone or in combination of plural types.

To further improve the adsorption of the sensitizer onto the inorganic photoconductive material and the dispersion of the sensitized inorganic photoconductive material in the fixing resin, the inorganic photoconductive material may be immersed in the solvent in which fatty acid together with the sensitizing agent is being dissolved. In such a case, it is preferable to use, among the examples above-mentioned of the organic solvent, cyclic ether such as tetrahydrofuran or the like, or ketone such as acetone or the like, in view of the solubility of fatty acid and the removal of the solvent after treatment. When fatty acid is used, there are instances where the fatty acid contained in the toner decreases the friction-charging characteristics or flowability of the toner. It is therefore required to select specific fatty acid.

Examples of the fatty acid above-mentioned include caprylic acid, undecylic acid, lauric acid, tridecylic acid, myristic acid, stearic acid, behenic acid, lignoceric acid, cerotic acid, montanic acid, oleic acid, elaidic acid, linoleic acid, linolenic acid, erucic acid , ricinoleic acid, dihydroxystearic acid, cyclic fatty acid, dibasic acid, dimer acid which is a dimer of the unsaturated monomeric fatty acid above-mentioned, and the like. Among the examples above-mentioned, saturated fatty acid is preferable and above all stearic acid is more preferable. The mixing amount of the fatty acid depends on the photoconductive material to be used, but is

generally in a range from 0.1 to 10 parts by weight and preferably from 1 to 2 parts by weight for 100 parts by weight of the photoconductive material.

The immersing period of time depends on the photoconductive material and the sensitizing agent to be used, but is preferably in a range from 0.5 to 50 hours. The immersion may be efficiently carried out with the use of ultrasonic irradiation and a dispersing device such as a homoginizer.

The toner in accordance with the present invention may be made by a method comprising the steps of: dissolving a fixing resin in a solvent, such as toluene, in which the fixing resin may be dissolved; dispersing and dissolving, in the solvent, (i) a photoconductive material which has been sensitized in the manner above-mentioned and (ii) other additives to be added as necessary; either granulating the resultant mixture by a spray-drying method, or melting and kneading the fixing resin, the sensitized photoconductive material and other additives, and cooling and pulverizing the resultant molten/kneaded mixture; and classifying the resultant particles, thus producing photoconductive toner particles. The toner particles generally have the average particle size in a range from 3 to 20 μm. Preferably, the toner particles are manufactured such that their volume-basis median diameters are in a range from 5 to 10 μm and that the toner particles present such flowability that the standard deviation in the distribution of volume-basis particle sizes is not greater than 3.33 μm. Out of the manufacturing methods above-mentioned, the spray-drying method is preferable in that the produced toner particles are spherical.

According to the present invention, the toner of which particle sizes are in the range above-mentioned, is excellent in the ability of forming a thin toner layer and the decay of electric charge after light irradiation. Further, the toner charge amount per unit weight and the light decay speed per particle are balanced in the optimum manner. This assures, in the case using the magnetic brush, a smooth movement of the toner after charge decay, toward the magnetic brush. Thus, more favorable results may be produced.

According to the present invention, more favorable results may be produced with the toner made in a spherical shape of which roundness (D) as defined by the following formula is in a range from 0.9 to 1.0:

$$D = \frac{\sqrt{r_l \cdot r_s}}{r_l}$$

where r_l : the longer diameter of a toner particle,
r_s : the shorter diameter of a toner particle.

When the particles present the roundness in the range above-mentioned, the ability of forming a thin toner layer may be improved and the toner particles of which charges have been attenuated after exposure to light, may be readily separated from the thin toner layer.

To improve a variety of physical properties of the toner, the photoconductive toner of the present invention may contain silica, alumina or titanium oxide as a flowability improving agent, and silicone oil as a dispersion improving agent, each in an amount of 0.4 to 2.0 parts by weight for 100 parts by weight of the toner.

When a developer is to be produced by mixing the toner of the present invention with the magnetic carrier mentioned earlier, any magnetic carrier which has been conventionally used in the field of an electrophotography, may be used as the magnetic carrier. The carrier shape may be irregular or spherical.

The particle sizes (number average particle sizes) of the carrier is generally in a range from 40 to 110 μm and more preferably from 40 to 60 μm. In connection with the particle sizes, the specific surface area of the carrier is in a range from 50 to 500 cm^2/g and preferably from 300 to 400 cm^2/g.

As a preferred example of the magnetic carrier, there may be used chamfered iron powder in irregular shapes (hereinafter simply referred to irregularly spherical shape) which presents a distribution of particle sizes containing (i) not less than 90 % by weight of particles having particle sizes of not greater than 105 μm and (ii) not less than 50 % by weight of particles having particle sizes in a range from 37 to 74 μm, and which presents a relaxation-apparent specific weight from 2.65 to 3.20 g/cc.

As another preferred example of the magnetic carrier, there may be used particles called as a ferrite carrier particularly sintered ferrite particles more particularly spherical sintered ferrite particles, of which particle sizes are preferably in a range from 20 to 100 μm.

When the sizes of the sintered ferrite particles are less than 20 μm, it tends to be diffucult to assure a satisfactory earing operation of the magnetic brush. On the other hand, when the sizes of the sintered ferrite particles are greater than 100 μm, the brush marks mentioned earlier, i.e., scraped damages, tend to be put on a produced toner image.

The magnetic carrier particles may be thinly coated at the surfaces thereof with acrylic resin, silicone resin or the like.

Preferably, the sizes of the toner particles are within the distribution of particle size mentioned earlier. However, when the toner particles are to be used for forming a two-components type developer, the toner particles have particle sizes, as expressed in terms of specific surface area, in a range preferably from 5000 to 20000 cm^2/g and more preferably from 7500 to 10000 cm^2/g. The mixing ratio of the toner with the magnetic carrier, i.e., the toner concentration preferably satisfies the following equation:

$$C_t = K \cdot \frac{S_c}{S_t + S_c} \times 100$$

where S_c : Specific surface area (cm^2/g) of the magnetic carrier

K : Numeral of 1.0 to 2.0

That is, the thin toner layer is formed with a toner concentration considerably thinner than that for a normal two-components type developer (in which K in the equation above-mentioned is 0.8 to 1.14). When the toner layer is formed with this toner concentration, the toner sticking amount interacts with the optimized toner photosensitivity in the optimum manner, thereby to produce a toner image free from fog with the image density satisfied.

The following description will discuss the present invention with reference to Test Examples.

(Test Example 1)

Toners were produced with the use of zinc oxide particles having specific surface areas (m^2/g) of 2.1, 2.5, 4.5, 5.5, 8.3, 13.0, 18.5 and 23.0, according to the following prescription.

Sensitizing Treatment

100 Parts by weight of zinc oxide was immersed in 200 parts by weight of methanol. Only 0.2 part by weight of Erythrosine B (sensitizer) was added to one part of the zinc oxide thus sensitized, while 2 parts by weight of stearic acid together with Erythrosine B was added to the other part of the zinc oxide. The zinc oxides thus sensitized were filtered off and dried to produce sensitized zinc oxide particles having different specific surface areas.

Production of Toner

30 Parts by weight of the sensitized zinc oxide particles and 10 parts by weight of a fixing resin (styrene-acrylic resin) were added to and dissolved and dispersed in 300 parts by weight of toluene. The resultant resin solutions were dispersed and mixed, and dried, by a spray-drying method, to prepare toners having the average particle size of 10 μm.

The toners as obtained with the use of the zinc oxides sensitized only by the sensitizer were classified as A, B, C, D, E, F, G and H in order of specific surface area from the smallest one to the greatest one. The toners as obtained with the joint use of the stearic acid were classified as (1), (2), (3), (4), (5), (6), (7) and (8), in the same order as above-mentioned.

5 Parts by weight of each of the photoconductive toners thus obtained was mixed with 95 parts by weight of a ferrite carrier so that the toner was frictionally charged. With the use of a magnetic brush developing device for an electrophotographic copying apparatus, each photoconductive toner was let stick uniformly and evenly on an aluminium base plate.

Monochromatic light (550 nm) taken out from a monochromatic meter was irradiated, for 0.5 second, on each photoconductive toner layer thus formed. The initial surface potential and the surface potential after the passage of 1.5 second from light irradiation, were measured. The decay factor of each surface potential (maximum surface potential decay factor) was measured with a computer connected to a digital oscilloscope. The results are shown in Tables 1, 2 and Fig. 1.

Table 1

Toner	ZnO Specific Surface Area (m^2/g)	Maximum Surface Potential Attenuation Factor (%)	Image
A	2.1	33.2	Bad
B	3.5	35.0	Bad
C	4.5	37.3	Bad
D	5.5	38.8	Bad
E	8.3	46.2	Passable
F	13.0	53.2	Good
G	18.5	50.9	Good
H	23.0	20.1	Bad

Table 2

Toner	ZnO Specific Surface Area (m^2/g)	Maximum Surface Potential Attenuation Factor (%)	Image
(1)	2.1	3.0	Bad
(2)	3.5	4.1	Bad
(3)	4.5	27.0	Bad
(4)	5.5	30.2	Bad
(5)	8.3	49.8	Good
(6)	13.0	54.7	Good
(7)	18.5	43.5	Passable
(8)	23.0	30.1	Bad

The term of "Image" in Tables 1 and 2 refers to a copied image as obtained by exposing each photoconductive toner layer to light to form a toner image, overlapping transfer paper on the toner layer and carrying out corona discharge of the positive polarity from the back side of the paper to transfer the toner image to the paper. Such an image is evaluated on image fog and image density.

As apparent from Tables 1, 2 and Fig. 1, it is understood that the photoconductive toners using zinc oxide particles of which specific surface areas are in a range from 8 to 20 m^2/g according to the present invention, are improved in photosensitivity to efficiently attenuate the surface potentials of the toner layers, thus producing a high-density image with less fog. It is also understood that the treatment with fatty acid is effective for the particles of which specific surface areas are in a range from 8 to 20 m^2/g.

(Test Example 2)

With the use of a treating solvent of tetrahydrofuran instead of methanol, toner was produced with the use of the zinc oxide having a specific surface area of 13 m^2/g of Test Example 1, which had been sensitized with stearic acid.

In this toner, the maximum surface potential decay factor was 66%. The copied image obtained was good.

From the foregoing, it is understood that, when carrying out a sensitizing treatment using fatty acid such as stearic acid or the like, ether such as tetrahydrofuran or the like is preferable.

(Test Example 3)

Toners having the particle characteristics shown in Table 3 were produced with the use of zinc oxides having specific surface areas of 4.5, 8.3 and 13.0 m^2/g by a spray-drying method according to a prescription similar to that of Test Example 1. Each of the toners was mixed with a ferrite carrier having a particle size of 70 μm (number average particle size) and a specific surface area of 350 cm^2/g such that the toner concentration was 5%. As to each toner, the transfer sensitivity was measured with a device shown in Fig. 4 and a 100-times continuous image forming was made with an apparatus shown in Fig. 5.

Table 3

Toner	ZnO Specific Surface Area (m^2/g)	Volumetric Average Dia. (μm)	Standard Deviation of Particle Size Distribution (μm)	Toner Roundness	Treatment with Stearic Acid
a	13.0	8	3.31	0.98	Not done
b	8.3	12	3.45	0.97	"
c	8.3	9	3.37	0.96	"
d	13.0	10	3.32	0.94	"
e	4.5	15	3.42	0.87	Done
f	4.5	10	3.30	0.98	Not done
g	8.3	9	3.32	0.96	Done
h	13.0	6	3.30	0.99	Not done

The following description will discuss a method of measuring the transfer sensitivity with reference to Fig. 4, which shows a developing device 44 having an agitating roller 41 for agitating a magnetic carrier and toner, a developing sleeve 42 connected to a bias power supply 45 and a cutting plate 43 for adjusting the ear-length of the magnetic brush.

The developing device 44 was charged with a developer with the toner concentration made constant, thereby to form a magnetic brush. While the magnetic brush slided on and rubbed against the surface of a NESA glass 51 connected to the bias power supply, the contact surface of the magnetic brush was exposed, substantially at the same time, to light emitted from an exposure device 65 having a halogen lamp 61 as a light source, a slit 62 for regulating the light amount and the irradiation width and a Selfoc lens 64 provided on the surface thereof with an interference filter 63. In Fig. 4, indicated as 46 is the toner, and indicated as 47 is a portion wherein light does not irradiated.

At the light-irradiated portion and non-irradiated portion of the NESA glass surface, the weights of the respective portions to which the toner was sticking, were measured. With the irradiated portion set to M_L

and non-irradiated portion set to M_D, the transfer sensitivity was measured according to the following formula:

$$\text{Transfer Sensitivity} = \frac{M_D - M_L}{M_D} \times 100$$

Fig. 2 shows the values of light intensity and transfer sensitivity of the toners a , c , f . It is understood from Fig. 2 that, as compared with conventional toner having a specific surface area as small as 4.5 m^2/g, each of the toners a and c having a specific surface area greater than 8 m^2/g was considerably improved in transfer sensitivity.

The following description will discuss the image forming apparatus shown in Fig. 5.

A transparent drum 3 provided on the outer surface thereof with a transparent electrode 2 is drivingly rotatingly incorporated in a machine frame 1. A transparent plate 5 for supporting a document 4 is disposed on the top of the machine frame 1. An exposure mirror 6 is secured to the transparent drum 3 substantially at the center thereof. The exposure mirror 6 and the transparent plate 5 are optically connected to each other through, for example, a first movable mirror 7, a second movable mirror 8, an in-mirror lens 9 and a stationary mirror 10. To illumine the document 4 on the transparent plate 5, an exposure lamp 11 is disposed.

Along the periphery of the transparent drum 3, a developing device generally designated by a reference numeral 12 is disposed in an optical path extending from the exposure mirror 6. The developing device 12 has an agitating roller 14 for mixing photoconductive toner 13 and a magnetic carrier 17 (See Fig. 3) which are supplied to the device 12, and a developing sleeve 16 for forming a magnetic brush 15 of the toner-carrier mixture on the surface of the sleeve 16. The surface of the developing sleeve 16 is conductive. A magnet 18 for forming the magnetic brush is rotatably disposed in the developing sleeve 16. In this example, the transparent electrode 2 is disposed in order to apply a bias voltage between the transparent electrode surface 2 and the developing sleeve 16, and the developing sleeve 16 is connected to a bias power supply 19.

Downstream of the developing device 12, a toner image transfer mechanism 20 is disposed along the rotation direction of the transparent drum 3. More specifically, a copy paper feed mechanism 22 for feeding copy paper 21 is disposed such that the copy paper 21 comes in contact with the surface of the transparent drum 3 at the position of the transfer mechanism 20. In this example, the transfer mechanism 20 is a corona charger for discharging an electric charge having the opposite polarity to that of the toner charge, from the back side of the copy paper 21 with the copy paper 21 overlapping the drum 3 having a toner image 25, thereby to transfer the toner image 25 from the drum 3 to the copy paper 21. In the copy paper 21 delivery direction, a fixing mechanism 23 such as heating rollers or the like is disposed for thermally fixing the toner image transferred on the copy paper 21.

Downstream of the transfer mechanism 20, a cleaning mechanism 24 is disposed along the rotation direction of the transparent drum 3. The cleaning mechanism 24 is adapted to clean, after transfer of the toner image, the drum surface to remove the excess toner remaining thereon. With the use of each of the toners, a 100-times continuous copying was carried out with the image forming apparatus having the arrangement above-mentioned. With the toner a , there were formed uniform images free from fog and excellent in contrast, of which solid portions presented a high density. The resolving powers were located in a range from 3.6 to 4.0 lines/mm. With the toner b , there were formed images substantially free from fog with the density of the solid portions being sufficient. The resolving powers were located in a range from 3.2 to 3.6 lines/mm. With the toner c , the results were similar to those obtained with the toner b . With the toner d , there were formed images free from fog with the density of the solid portions being sufficient. The resolving powers were located in a range from 3.2 to 4.0 lines/mm. With the toner e , fog was produced and the best resolving power was 2.8 lines/mm, so that the formed images lacked clearness. With the toner f , fog was produced and the resolving powers were 3.0 lines/mm at best. With the toner g , the formed images were free from fog and the density of the solid portions was satisfactory. The resolving powers were located in a range from 3.2 to 3.6 lines/mm. With the toner h , fog was produced and the density of the solid portions was insufficient, so that the produced images were generally uneven and poor in quality.

As to the color tones of the formed images, the colors came out well in magenta to produce the clear and vivid tones of color. Thus, the toner of the present invention presents the advantage that the clear tone of color may be obtained even without a coloring agent.

Industrial Applicability of the Invention

The toner of the present invention is considerably improved not only in photosensitivity per toner particle and the photosensitivity of the thin toner layer when formed (surface potential decay factor), but also in flowability and charge characteristics, thereby to assure a smooth separation of the attenuated toner from the thin toner layer after light exposure. With the toner of the present invention, there may be formed a clear image excellent in contrast free from image fog without the image density decreased.

In particular, the toner of the present invention may produce more favorable results in a method in which the toner is mixed with a magnetic carrier to form a magnetic brush and a thin toner layer is formed and a toner image is transferred. Further, with the toner of the present invention, there may be formed an image having the vivid tone of color without use of a coloring agent.

Claims

1. Photoconductive toner comprising a fixing resin, and an inorganic photoconductive material dispersed, in an amount of not less than 50 % by weight, in the fixing resin,
said inorganic photoconductive material being fine particles of which specific surface areas are in a range from 8 to 20 m^2/g.

2. Photoconductive toner according to Claim 1, wherein the inorganic photoconductive material is dispersed in the fixing resin in an amount of 50 to 500 parts by weight for 100 parts by weight of said fixing resin.

3. photoconductive toner according to Claim 1 or 2, wherein the inorganic photoconductive material is zinc oxide.

4. Photoconductive toner comprising a fixing resin, and an inorganic photoconductive material dispersed, in an amount of not less than 50 % by weight, in the fixing resin,
said inorganic photoconductive material being fine particles having a specific surface area of 8 to 20 m^2/g, and fatty acid and sensitizing dyestuff being absorbed on the surface of said fine particles.

5. Photoconductive toner according to Claim 4, wherein the inorgainc photoconductive material is zinc oxide.

6. A method of manufacturing photoconductive toner comprising a step of immersing, in an organic solvent in which fatty acid is soluble, an inorganic photoconductive material of which specific surface area is in a range from 8 to 20 m^2/g, and a step of adding fatty acid and a sensitizing agent to said solvent so that said sensitizing agent is absorbed on the surface of said inorganic photoconductive material.

7. A method of manufacturing photoconductive toner according to Claim 6, wherein the inorganic phctoconductive material is zinc oxide.

Fig. 1

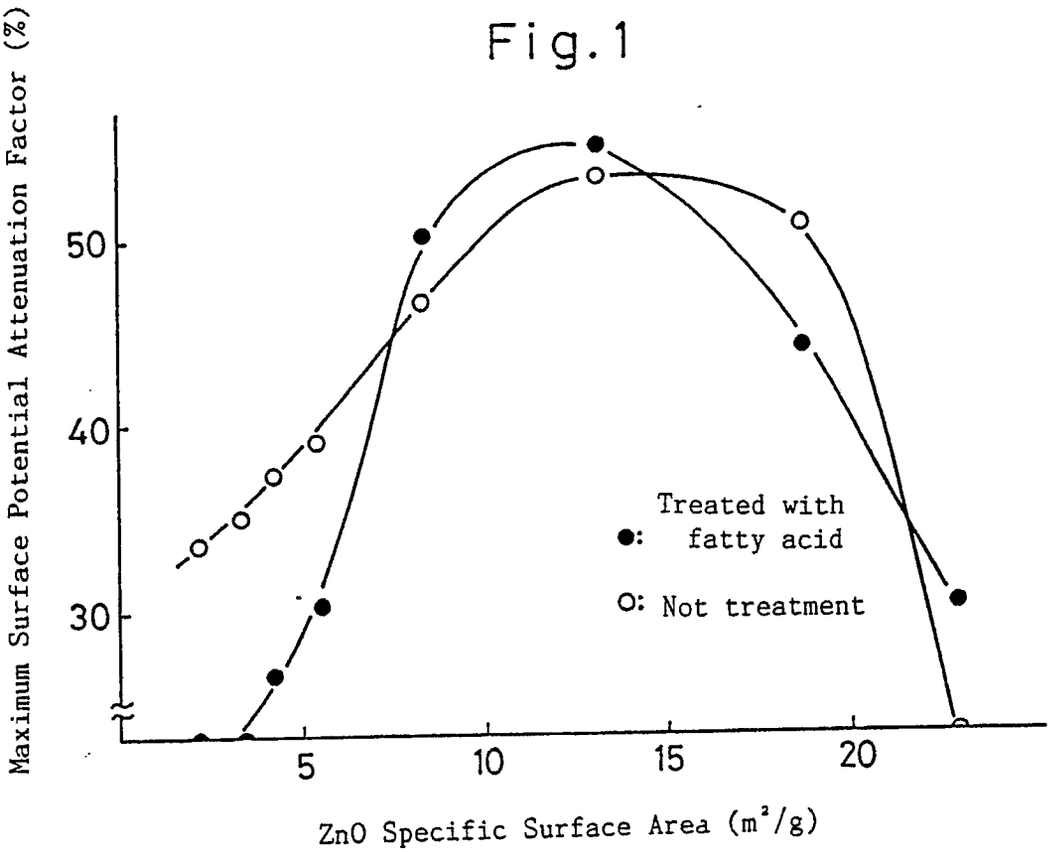

Maximum Surface Potential Attenuation Factor (%)
50
40
30
5
10
15
20
ZnO Specific Surface Area (m²/g)
Treated with
●: fatty acid
○: Not treatment

Fig. 2

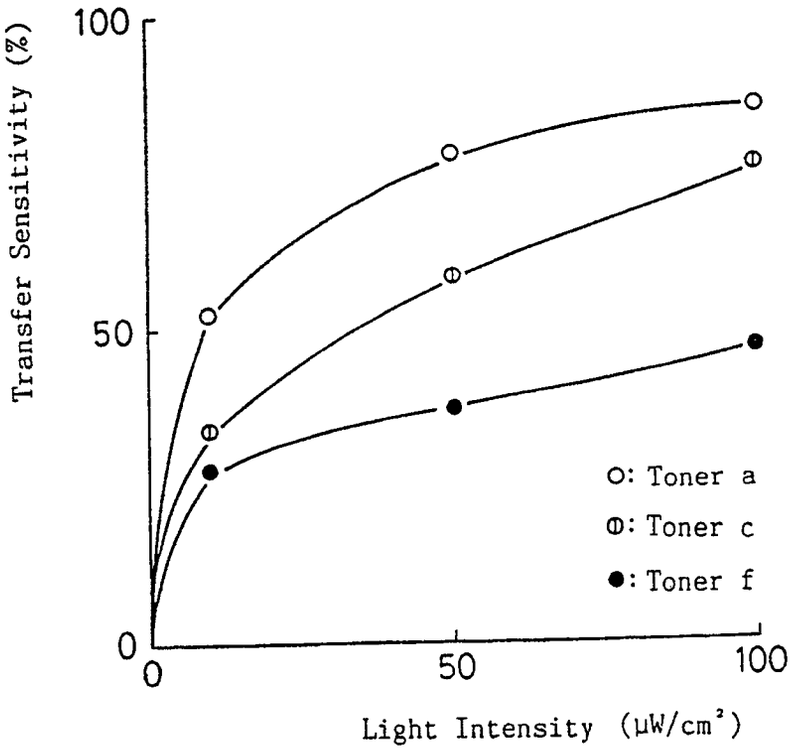

Transfer Sensitivity (%)
100
50
0
0
50
100
Light Intensity (μW/cm²)
○: Toner a
Φ: Toner c
●: Toner f

Fig. 3

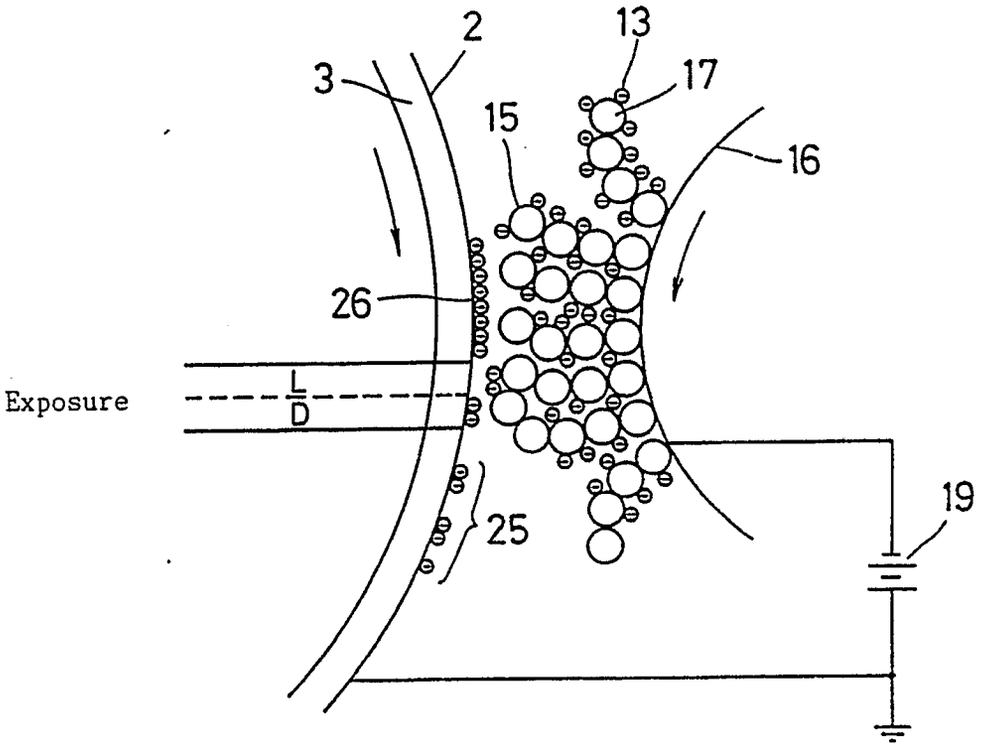

2
13
3
17
15
16
26
Exposure
L
D
19
25

Fig. 4

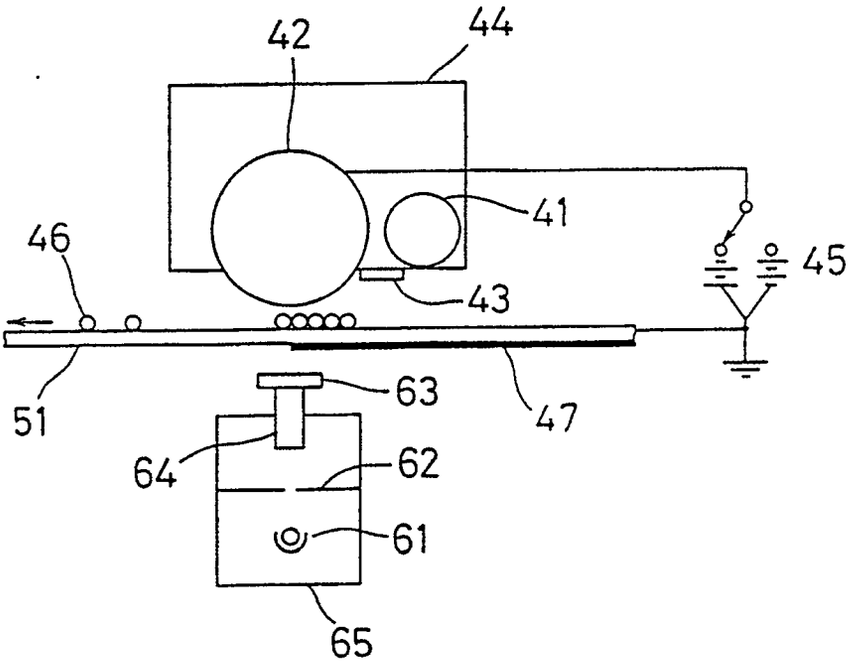
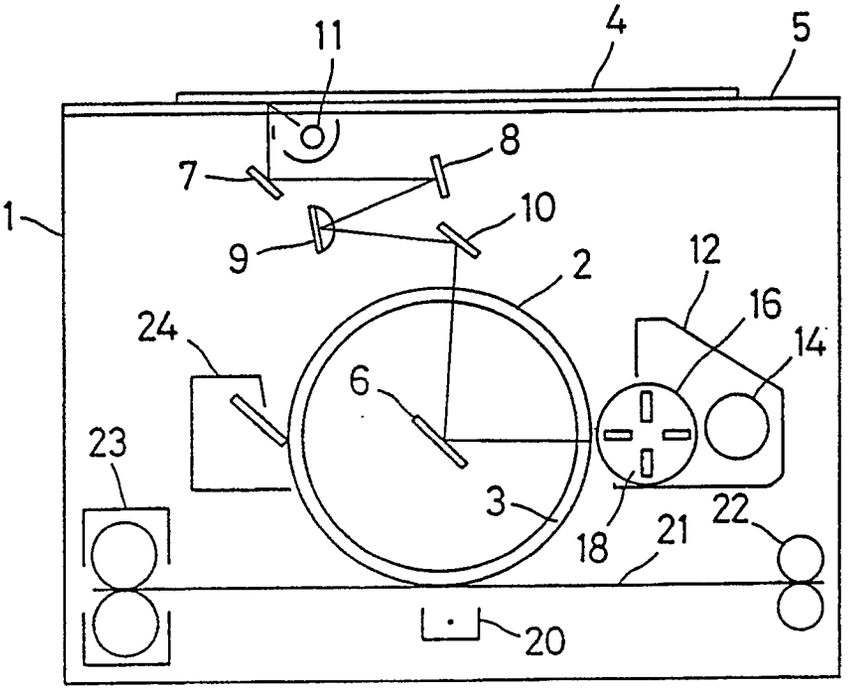

42
44
41
46
45
43
51
63
47
64
62
61
65

Fig.5



INTERNATIONAL SEARCH REPORT

International Application No PCT/JP89/01196

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [6]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int. Cl[5] G03G9/08

II. FIELDS SEARCHED

Minimum Documentation Searched [7]

Classification System	Classification Symbols
IPC	G03G9/08 - 9/135

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [8]

Jitsuyo Shinan Koho 1926 - 1989
Kokai Jitsuyo Shinan Koho 1971 - 1989

III. DOCUMENTS CONSIDERED TO BE RELEVANT [9]

Category *	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No. [13]
Y	JP, A, 60-133459 (Toshiba Corp.), 16 July 1985 (16. 07. 85), (Family: none)	1 - 3
Y	JP, A, 60-153054 (Sony Corporation), 12 August 1985 (12. 08. 85), (Family: none)	1 - 3
A	JP, A, 49-107246 (Fuji Photo Film Co., Ltd.), 11 October 1974 (11. 10. 74), (Family: none)	1 - 7

* Special categories of cited documents: [10]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
January 23, 1990 (23. 01. 90)	February 5, 1990 (05. 02. 90)
International Searching Authority	**Signature of Authorized Officer**
Japanese Patent Office	