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

(11) EP 0 703 502 A1

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
27.03.1996 Bulletin 1996/13

(51) Int Cl.^{6}: **G03G 9/087**, G03G 9/08

(21) Application number: **95305134.9**

(22) Date of filing: **21.07.1995**

(84) Designated Contracting States:
DE GB

(30) Priority: **22.07.1994 JP 170878/94**
14.09.1994 JP 219755/94

(71) Applicants:
- **KABUSHIKI KAISHA TOSHIBA**
  Kawasaki-shi, Kanagawa-ken 210, Tokyo (JP)
- **Kabushiki Kaisha TEC**
  Tagata-gun, Shizuoka-ken (JP)

(72) Inventors:
- **Tsunemi, Koichi, c/o Intellectual Property Div.**
  Minato-ku, Tokyo (JP)
- **Shinjo, Yasushi, c/o Intellectual Property Div.**
  Minato-ku, Tokyo (JP)
- **Saito, Mitsunaga, c/o Intellectual Property Div.**
  Minato-ku, Tokyo (JP)
- **Osugi, Yukihiro, c/o Intellectual Property Div.**
  1-1, Kanda-Nishikicho, Chiyoda-ku, Tokyo (JP)

(74) Representative: **Freed, Arthur Woolf**
MARKS & CLERK,
57-60 Lincoln's Inn Fields
London WC2A 3LS (GB)

(54) Positively-charging mono-component toner and developing method using same

(57) A positively-charging mono-component non-magnetic toner contains at least a binder resin and a coloring agent, wherein the binder resin is a polyester resin having an acid value of 5 mgKOH/g or below, and the toner has the maximum positive charge of 30 μC/g or below. And, a positively-charging mono-component toner contains at least a binder resin and a coloring agent, wherein the toner has a surface energy γs of 30 to 40 mN/m. A developing method using a positively-charging mono-component toner uses a toner having a surface energy γs of 30 to 40 mN/m as the positively-charging mono-component toner, and the toner for developing an electrostatic latent image has a total charge of 2 μC/g or above, or a total charge charged to a opposite polarity when developing an electrostatic latent image is 20% or below of the absolute value of a total charge charged to a normal polarity.

Printed by Jouve (FR), 18, rue Saint-Denis, 75001 PARIS

Description

This invention relates to a positively-charging mono-component toner and a developing method using this positively-charging mono-component toner, and more particularly to a positively-charging non-magnetic mono-component toner suitable for developing a high-quality image and a method for developing an electrostatic latent image.

A method for forming an image by developing or making visible an electrostatic latent image formed and held on the surface of an electrostatic latent image retaining member, e.g., a photosensitive drum, with a so-called developing powder (toner) is practically used extensively in various fields. For this type of developing method, a mono-component non-magnetic toner is attracting attention because image quality is hardly degraded due to the changes in the toner composition in a continuous image formation or development.

Fig. 1 is a sectional view showing the essential structure of a developing apparatus used for the above developing method. In the drawing, 1 stands for an electrostatic latent image retaining member, 2 for a developing device provided with an elastic developing roller 3 and others and using a contact type mono-component toner, 4 for a transfer device (transfer means), 5 for uniformizing means for uniformly dispersing the toner remaining after the transfer, 6 for a charging device for charging the electrostatic latent image retaining member 1 to a required positive polarity, and 7 for exposure means (e.g., laser beam) for forming an electrostatic latent image by exposing.

In the configuration of the developing apparatus, the electrostatic latent image retaining member 1 is a positively-charging type photosensitive drum provided with, e.g., an organic photosensitive member, an amorphous selenium photosensitive member or an amorphous silicon photosensitive member. The developing device 2 is provided with the elastic developing roller 3 and using the contact type mono-component toner. The developing roller 3 (toner carrier) has a conductive elastomer layer made of fluorine-containing elastomer or polyurethane-based elastomer, a conductive rubber, or a flexible conductive tube formed on the surface of an elastic body for an example. And, the developing device 2 is provided with a toner feeding member (developing powder feeding roller) 8, a toner stirring element 10 for stirring a toner 9, and a toner layer thickness regulating member 11 for regulating the toner layer thickness. The toner feeding member 8 comprises a foamed material such as fluorine-containing rubber or polyurethane rubber. The toner layer thickness regulating member 11 is formed in the shape of a blade using, for example, silicone rubber, fluorine-containing rubber, or polyurethane rubber. The toner layer thickness regulating member 11 elastically presses the developing roller 3, which is rotated with the application of a d.c. bias, a.c. bias, or a.c.-d.c. convolutional bias of 20-1000 V, by means of, e.g., a spring 11a, to form substantially a uniform toner layer thickness on the surface of the developing roller 3, and makes the toner layer to contact or not to contact with a latent image on the electrostatic latent image retaining member 1, thereby developing. In this developing process, the particles of toner 2 are positively charged in advance as they come in contact with the toner feeding roller 8, the developing roller 3, and the toner layer thickness regulating member 11.

The transfer device 4 is a negative polarity type conductive roller or conductive brush, which transfers the image developed from the surface of the electrostatic latent image retaining member 1 to a recording medium (transfer supporter/recording paper) carried by, e.g., a transfer belt 12. When the transfer device 4 is transferring the image, the recording medium is adsorbed to and supported by the transfer belt 12 by means of an unillustrated adsorption means such as a conductive brush or a conductive roller. The conductive transfer roller or transfer brush which is used as the transfer device 4 has advantages that the amount of ozone production can be decreased to one tenth or below, a transfer property is not largely varied due to a change in temperature, and the absolute value of a transfer voltage can be determined low as compared with a negative polarity corona charging device. It is to be understood that the corona charging device can be used for transfer.

The cleaning unit 5 for removing a toner 9' remaining after the transfer collects the toner by separating from the surface of the electrostatic latent image retaining member 1 by the sliding and rubbing actions of an elastic blade. For example, a method (cleanerless) which uniformly disperses the toner 9' remaining after the transfer on the surface of the electrostatic latent image retaining member 1 while applying a voltage through a stationary conductive brush or a rotary conductive brush can be used. For charging by means of the charging device 6, the application of a positive voltage of about 5 kV to the corona wire of the charging device 6 causes a corona discharge, and the surface of the electrostatic latent image retaining member 1 is charged to about 400 to 800 V. In the next exposure process, the charged surface of the electrostatic latent image retaining member 1 is exposed to a required level, and the toner 9' on the surface of the developing roller 3 is transferred onto the latent image surface of the electrostatic latent image retaining member 1 by the electric field, thereby making required development.

The toner for the mono-component non-magnetic developing method is generally prepared from a binder resin, a coloring agent, a charge controlling agent, and wax. The binder resin for the mono-component non-magnetic toner is usually a styrene-acrylate copolymer or a polyester resin.

It is known that when the styrene-acrylate copolymer is used as the binder resin, the toner is charged to a positive or negative polarity, and when the polyester resin is used as the binder resin, the toner has negative charge. But, the styrene-acrylate copolymer generally has a high melting point and is not suitable for fusing at a low temperature. When the toner based on a low melting point and a small molecular weight resin, it adheres to a charging member of the developing system, disabling to obtain a high quality image.

Using the polyester resin as the binder resin has advantages in quite easy negative charging, and fusing transparency and gloss owing to quick melting. Thus, it is practically used for a negatively-chargeable colored toner. But, when the polyester resin which is negatively chargeable is used for the binder, the charge easily becomes to saturate when an apparent charging time is long as in a two-component developing method used in a mixing system with a carrier (magnetic powder), and the resin is well charged negatively. Thus, it was hardly used for a positively-charged toner.

More specifically, the mono-component non-magnetic developing method has a less chance of being charged, different from a method using the two-component developing method. The mono-component non-magnetic toner is thought to be charged when contact-rubbed in the carrying process by a toner carrier and a developing roller in the developing device or when the particles of toner come to contact and rub one another. Since the toner is not charged to saturate, use of a common polyester resin does not exert negative charging characteristics so highly. But, a polyester resin having a high acid value which is negatively charged very easily could not be used as the binder for a positively-charging toner.

The above polyester resin includes an unreacted carboxylic acid residue because it is a well-known product by condensation polymerization of polybasic acid and polyhydric alcohol. Negative chargeability is enhanced as the acid value is increased, which indicates the unreacted carboxylic acid residue content, but for the polyester resin, the saturated charged polarity shows negative even if the acid value is low. Therefore, when mixed with a carrier such as magnetic powder, the two-component toner system having a long apparent charging time does not work as a positively-charging toner because the toner is easily charged to saturate.

In view of the above, a functional group such as amino group is tried to be incorporated into molecules to produce a binder resin for the positively-charging toner. But, when a required electrostatic latent image is developed with a mono-component non-magnetic toner which is prepared by using as the polyester resin having incorporated (modified) the functional group which tends to be positively charged, the following disadvantages are seen. A modifying residual component (functional group incorporated component) of the polyester resin adversely affects image quality, and background density tends to increase in hot and humid surroundings. In other words, the positively-charging mono-component non-magnetic toner, which is prepared using the polyester resin having incorporated (modified) the functional group having a tendency of being charged positively, can not provide high quality image prints which has sharp (clear) line and low background density. Thus, polyester cannot be used for positively charged toner system practically.

In view of the above disadvantages, this invention has been completed and aims to provide a positively-chargeable mono-component non-magnetic toner system which contains a polyester resin as the binder resin, can be charged uniformly, and can provide a high-quality image print with high image density and remarkable glossiness without any fog on the electrostatic latent image retaining member, adhesion to a charging member, or filming; and to provide a method for developing an electrostatic latent image.

A first positively-charging mono-component non-magnetic toner according to this invention contains at least a binder resin and a coloring agent, the binder resin is a polyester having an acid value less than 5 mg KOH/g, and the toner has maximum charge of 30 µC/g or below.

And, the first positively-charging mono-component non-magnetic toner according to this invention is further characterized by containing 0.2 to 10% by weight of waxes having an acid value of 20 mg KOH/g or below.

A second positively-charging mono-component non-magnetic toner according to this invention contains at least a binder resin, a polyester resin and a coloring agent, and the toner has a surface energy γs in a range from 30 to 40 mN/m.

A first method for developing an electrostatic latent image according to this invention is a developing method using a positively-charging mono-component toner containing a polyester resin as the binder resin, wherein the positively-charging mono-component toner has a surface energy γs in a range from 30 to 40 mN/m, and a total charge at developing the electrostatic latent image is 2 µC/g or more.

A second method for developing an electrostatic latent image according to this invention is a developing method using a positively-charging mono-component toner containing a polyester resin as a binder, wherein the positively-charging mono-component toner has a surface energy γs in a range from 30 to 40 mN/m, and the charge of opposite polarity when developing the electrostatic latent image is 20% or below of the absolute value of total charge of normal polarity on the developing roller.

The first and second positively-charging mono-component non-magnetic toners and the first and second methods for developing an electrostatic latent image according to the invention is described.

The first positively-charging mono-component non-magnetic toner according to the invention has been completed based on the following knowledge. Specifically, it has been completed with attention paid to the features of the positively-charging mono-component non-magnetic toner; (A) when an electrostatic latent image retaining member (photosensitive member) is charged, ozone is produced in a very small amount because the retaining member is positively charged in a developer such as a printer employing a reversal development, (B) high image print quality is obtained because of suitable charge, (C) the surface material for the toner carrying member (developing roller) can be selected from fluorine-containing elastomer, a combination of fluorine-containing elastomer and another elastomer, and polyurethane elastomer (resistivity was adjusted to $10^{+9}\Omega\cdot$cm or below), and (D) admixture of paper powder into the toner does not effect on an image.

The inventors have made a devoted study on the properties of a polyester resin to use it as the binder resin for the positively-charging mono-component non-magnetic toner and found that it serves as a positively-charging toner to provide an image print which is sharp and of high image density with remarkable glossiness and permeability with low background density by giving a uniform and stable charge easily when the polyester resin having an acid value of 5 (mg KOH/g) or below is selected as the binder, and the toner prepared has a maximum charge of 30 μC/g or below, preferably 3 to 30 μC/g.

Furthermore, it has been considered that a toner containing the polyester resin as the binder is not suitable for the positively-chargeable toner because it is negatively charged easily. But, when polyester is used for a mono-component non-magnetic toner having a short charging time, the toner itself is positively chargeable because the toner is not fully charged.

A study has been further made to find that when the polyester resin having an acid value of over 5 (mg KOH/g) which contributes to charge is used for the mono-component non-magnetic toner, negative chargeability becomes prominent; even when adjusted with a positive charge controlling agent, it still shows negative chargeable, and carboxylic acid residue related to acid value is well hydrophilic resulting in degradation of image quality. Therefore, the polyester resin is limited to have an acid value of 5 or below.

For the positively-charging mono-component non-magnetic toner using the polyester resin having an acid value of 5 (mg KOH/g) or below as the binder resin, selection is made so that the toner has a maximum charge of 30 μC/g or below.

The charge of the toner is measured as follows.

Ferrite carrier having a stable surface condition (e.g., trade name: F-10C, made by Powder Tech Co., Ltd.) is mixed with a toner at a weight ratio of 97 to 3 to prepare a mixture 50 g in total. The prepared toner carrier system is placed in a 100ml of polyethylene bottle, and stirred with a ball mill adjusted to rotate at 70 rpm for 10, 30, 60, and 120 minutes respectively. Each stirred system is measured for the charge per unit mass by a blowoff method, and the highest positive charge among the measured value is determined to be the maximum charge.

The inventors have noticed that as for a toner having a large amount of charge, the mono-component non-magnetic toner is chargeable either positive or negative because it is not charged up to tis saturated value, and applied polyester resin, which is negatively chargeable easily, into a positively-charging toner to suppress the saturated charge and ununiform charging. When the maximum charge exceeds 30 μC/g, distribution of toner is broadened, and the positively-charging mono-component non-magnetic toner which is required to be charged in a short time has its function of forming a uniform and stable image deteriorated. Thus, the charge is preferably in a range of 3 to 30 μC/g.

Besides, this invention has found that wax to be added and blended to improve offset resistance at fusing is selected to have an acid value of 20 (mg KOH/g) or below and its content is preferably determined to fall in a range of 0.2 to 10% by weight.

When the acid value exceeds 20 (mg KOH/g), the toner becomes more hygroscopic, adversely affecting the formation of an image in hot and humid surroundings. When the wax content is under 0.2% by weight, there is no effect on releasability or offset resistance, and when it exceeds 10% by weight, the toner particles aggregate one another, deteriorating fluidity.

Examples of the wax are oxidated or non-oxidated polyalkylene, styrene derivatives, polyalkylene which is grafted by unsaturated alkyl acid derivatives, and other natural waxes. It can be used in one-specimen or in a combination of two or more members.

In the same way as the first positively-charging mono-component toner, the second positively-charging mono-component toner of this invention has been found to be effective when its surface energy γs is 40 mN/m or below by devotedly studying on its connection with the surface property of the polyester to use for the binder of the positively-charging mono-component non-magnetic toner with attention.

In addition, the polymer resin is substantially not suitable for the positively-charging mono-component non-magnetic toner. When it is used for the toner, it is hard to charge negatively when its surface energy γs is under 30 mN/m. When the surface energy γs exceeds 40 mN/m by incorporating amino groups, background density of print increases.

The inventors have found that the positively-charging mono-component non-magnetic toner having a surface energy γs in the range from 30 to 40 mN/m can be decreased the background density even in hot and humid surrounding and can be obtained a high quality image print. The surface energy is preferably in a range from 31 to 34 mN/m.

To prepare a positively-charging mono-component non-magnetic toner having a surface energy γs from 30 to 40 mN/m, any polyester resin can be applied for the toner in this invention such as generally linear which has a number-average molecular weight-to-weight-average molecular weight ratio of around 1, branched ones, or a partially crosslinked, and is insoluble in a solvent.

The surface energy γs of the above toner is measured as follows by using a sample which is prepared by molten toner and forming into a plate having a thickness of 0.5 mm and surface roughness of 0.3 s or below.

$$\gamma s=\gamma L(1+\cos\theta)$$

where, γL is the surface tension of a liquid to be applied, and θ is a contact angle.

Besides, an extended Fowkes' equation is as follows.

$$\gamma L(1+\cos\theta)=2(\gamma L^{a}\gamma s^{a})^{1/2}+2(\gamma L^{b}\gamma^{b}s)^{1/2}+2(\gamma L^{c}\gamma s^{c})^{1/2}$$

where, γL^a, γL^b, and γL^c respectively designate a non-polar component, a polar component, and a hydrogen bonding component in the surface tension of the liquid, and expressed as follows.

$$\gamma L=\gamma L^{a}+\gamma L^{b}+\gamma L^{c}$$

Where, γs^a, γs^b, and γs^c are their components in solid surface energy.

Therefore, when a liquid having γL^a only, such as benzene, toluene, and any hydro-carbon liquid, is applied for a measuring contact angle θ, γs^a can be measured easily because these liquids are $\gamma L=\gamma L^a$, $\gamma L^b=\gamma L^c=0$. Next, γs^b can be determined from a contact angle θ with a liquid having γL^a and γL^b, and γs^c can be determined from a contact angle θ with a liquid having γL^a, γL^b, and γL^c.

The solid surface energy γs is the sum of them and expressed as follows.

$$\gamma s=\gamma s^{a}+\gamma s^{b}+\gamma s^{c}$$

For the measurement of the surface energy, details are given in Bulletion of Adhesion Society of Japan, Vol. 18, No. 3 (1972), pp. 131-141 (in Japanese).

The above polyester resin generally has carboxylic acid groups, hydroxyl groups and other residual groups in its molecules, and they have acid value or hydroxyl value. The number of these residual groups is related to a charge polarity. A high acid value leads to a negative-charge, and a high hydroxyl value to a positive-charged. For the second positively-charging mono-component non-magnetic toner of this invention, the acid value of the polyester resin is decreased as much as possible, preferably to 5 or below, in the same way as for the first positively-charging mono-component non-magnetic toner.

The components of the toner interact with the residual groups of the polyester resin, and also serve to change the critical surface tension of the positively-charging mono-component non-magnetic toner to be prepared, so that it is preferable to select a charge controlling agent which can control the interaction. An external additives such as silica powder has less effect on their surface properties.

The first and second positively-charging mono-component non-magnetic toners of this invention are prepared by kneading, pulverizing and classifying the selected coloring agent, binder resin, charge controlling agent, and wax. Specifically, the above components are molted and kneaded, then pulverized and classified into fine powder, a fluidizing agent such as silica powder is then added.

In another preparation method, a polyester resin is dissolved in a good solvent at a suitable concentration. This resin solution is dripped to suspend or emulsify in a poor solvent which does not mix with the above solvent. To stably suspend or emulsify, a surface-active agent may be added. Then, the required coloring agent, charge controlling agent, and wax are dissolved or dispersed into the suspension or emulsion to adhere to the drops or coacervation of polyester resin solution, then drying is made to obtain a toner. When suspended or emulsified in the above process, drying may be made to isolate fine particles as solids, and the suspension or emulsion may be prepared separately; the coloring agent, charge controlling agent, and wax may be dissolved or dispersed therein to adhere to the drops of the polyester solution; then drying may be made to obtain the toner.

The first and second positively-charging mono-component non-magnetic toners of this invention can be measured for their particle size distribution and average particle diameter by Coulter Counter®, Model TA-II (Nikkaki). As a volume average particle diameter (D_{50}) is made smaller, resolution is more improved, being advantageous for high quality. But, when the volume average particle diameter is excessively small, the surface area of the toner is increased, tending to be larger than the value of critical surface tension which is determined by measuring the surface energy and the contact angle. The inventors have found that the difference of surface energy is significant as the toner particle diameter is smaller. Thus, the positively-charging mono-component non-magnetic toner is desired to have a particle diameter is the range from 3 to 14 µm, preferably 6 to 11 µm.

In preparing the positively-charging mono-component non-magnetic toner, carbon black is generally used as a coloring agent which is generally used to prepare a black toner, but a black dye or a dye having another color may be used together, or only a black dye may be used.

For a color toner, it is significant which pigment or dye is selected. Namely, a coloring agent as well as a surface treating process must be selected carefully because an image to be developed is required to have colors close to ideal, and the surface energy and charging characteristics may also be affected.

For a yellow toner, benzidine-, azo-, and benzimidezorone-based pigments can be selected, and the surface can be treated with rosinate. Yellow with color index (C. I.) PY (pigment yellow) No. 17 or around is preferred, and a yellow-family dye may be added to the above pigments. Coloring with a yellow dye can be made if necessary.

For a magenta toner, quinacridone-, azo-, naphthol-, perylene-, and carmine-based pigments can be selected. Red with color index (C. I.) PR (pigment red) No. 122 or around is preferred, and a magenta-family dye may be added to the above pigments. Coloring with a magenta dye only can also be made.

For a cyan toner, phthalocyanine-, and copper phthalocyanine blue-copper phthalocyanine green mixture-based pigments are used. It is preferable to use PB15-3 or 15-4 for blue, and PG-7 or around for green. And, a blue, green, or cyan dye may be added to the above pigments. Coloring can also be made with a mixture of blue and green dyes, or only a cyan dye.

For full colors, the above yellow, magenta and cyan toners are required (black is additionally used because the above three colors scarcely develop colors ideally). If a full-color image is not required, red, blue and green colors may be combined to prepare red- and green-based toners.

In this invention, a colorless or light-colored charge controlling agent which does not affect on the color tone of the toner may be added to stabilize the charging ability of the toner.

As a fluidity modifier, Al_2O_3, TiO_2, GeO_2, ZrO_2, Sc_2O_3 and other metallic oxide power, and/or SiO_2 powder may be used without treating or after treating the surface. Particularly, SiO_2 powder which is treated by aminosilane and given a positive charge is preferably added in 0.1 to 2% by weight. And, addition of a mixture of SiO_2 powder with different hydrophobing rates in about 0.1 to 2% by weight considerably contributes to the improvement of moisture resistance, chargeability and fluidity.

As described above, the first method for developing an electrostatic latent image according to the invention is a developing method using a positively-charging mono-component toner containing a polyester as the binder, wherein the positively-charging mono-component toner has a surface energy γs in a range of 30 to 40 mN/m, and a total charge when developing the electrostatic latent image is 2 $\mu C/g$ or more.

The second method for developing an electrostatic latent image according to this invention is a developing method using a positively-charging mono-component toner containing a polyester as the binder, wherein the positively-charging mono-component toner has a surface energy γs in a range from 30 to 40 mN/m, and a total charge charged to opposite polarity when developing the electrostatic latent image is 20% or below of the absolute value of a total charge charged to a normal polarity on a developing roller.

The surface energy in the first and second developing methods is the same as described in connection with the second positively-charging mono-component toner of the invention.

The total charge when developing an electrostatic latent image and the total charge (total amount of charge, in coulomb (C) not per unit weight) of the toner charged to opposite polarity are measured as follows.

The total charge of the positively-charging mono-component non-magnetic toner is measured by sucking a toner for one turn of the developing roller which configures the developing mechanism, and referring to a residual charge and the sucked toner amount. In this case, the toner is charged in an non-magnetic developing device as shown in Fig. 1, and the toner for one turn of the developing roller is sucked, so that no bias is applied to the developing roller or the feeding roller. The obtained value is closely related to the quality of an image developed. If a sufficient charge cannot be kept, a high quality image print cannot be obtained. A practical value for using the positively-charging toner in the non-magnetic developing method is 2 $\mu C/g$ or more.

As described above, the total charge of the toner on the developing roller can be measured by the suction method, but the content of the oppositely charged toner cannot be seen. To determine the content of the oppositely charged toner, it is necessary to measure the charge of each particle of toner. For this purpose, E-SPART Analyzer® (Hosokawa Micron) is suitable, which is a system suitable to measure the charge distribution.

The inventors have experimentally found that a very high quality image can be obtained with the positively-charging toner, wherein the total electric of this toner charged to the opposite polarity is 20% or below of the charge with the normal polarity. The E-SPART Analyzer® can measure the charge distribution of the toner charged to the normal polarity and that of the toner charged to the opposite polarity. And, division of the absolute value of the charge with the opposite polarity by the absolute value of the electric charge of the toner charged to the normal polarity can determine a ratio of the charge with the opposite polarity.

In the positively-charging mono-component non-magnetic developing method, the quality of an image developed significantly depends on the amount of the toner charged to the opposite polarity; when this amount exceeds 20%, background density is sharply increased, and the latter half of a solid image is apparently blurred. Therefore, the total charge of the oppositely-charged toner is required to be 20% or below of the total charge of the positively-charging mono-component non-magnetic toner.

The charge distribution depends on the measuring condition, and particularly the amount of the toner with the opposite polarity is increased in hot and humid surroundings (temperature or humidity is 30 or 75% RH or more). But, the positively-charging mono-component non-magnetic toner of this invention can keep high quality without exceeding the above ratio in any surroundings.

The definition of the surface energy of the positively-charging mono-component non-magnetic toner, the total charge at developing, and the selection of the total charge of the charged toner in the developing method of this invention have been described above.

In connection with the definition of the surface energy, the critical surface tension of the toner will be described.

The critical surface tension of the positively-charging mono-component non-magnetic toner is measured as follows. First, the toner containing a binder resin, a coloring agent, a charge controlling agent and wax is melted, and formed into a plate having a surface roughness of 0.3 s or below. To the positively-charging mono-component non-magnetic toner, silica is added in about 0.2 to 5% by weight as an external additive, and other external additives are also added sometimes. But, they do not effect on the critical surface tension or the surface energy. The above toner has on its surface all of a polar component, a non-polar component, and a hydrogen bonding component, so that the surface tension is measured with a solvent having these components. Examples of such a solvent include water, glycerol, polyethylene glycol (molecular weight: 200, liquid at room temperature, hereinafter referred to as PEG 200). As far as the non-polar component and the hydrogen bonding component are contained, the solvent can be used in the same way as the aforementioned solvent even if the three components are not contained, so that it is used to obtain one Zisman plot.

Examples of the solvent having the non-polar component and the hydrogen bonding component include ethylene glycol, diethylene glycol, and dipropylene glycol. When a contact angle θ in such solvents is measured by means of a contact angle meter, Model CA-DTA, of Kyowa Kaimen Kagaku Co., Ltd., and the surface tension of each solvent and $\cos\theta$ are plotted (Zisman plot) to obtain a straight line; and the value on the horizontal axis when extrapolated to $\cos\theta=1$ becomes the critical surface tension of the toner. In the case of a liquid such as water and glycerol with a high surface tension, it is probable to deviate from the straight line due to the hydrogen bonding. Then, the plot may be removed.

The positively-charging mono-component non-magnetic toner of this invention consists of 1 to 5% by weight of a coloring agent, 1 to 8% by weight of a charge controlling agent, about 1% by weight each of wax and an external additive as required, and the remainder binder resin in the same way as an ordinary toner. At this time, the surface energy of the toner significantly depends on the surface energy of the binder resin. And, the surface energy of the polyester as the binder used for the negatively-charging toner is about 20 mN/m.

The surface energy (γL^b, γL^c described above) is considered to change depending on the number of functional groups and types of the polyester resin, and it is also changed by the interaction between the functional group and the charge controlling agent in the toner. Therefore, to set the surface energy of the toner at 30 to 40 mN/m, the polyester resin having a relatively low acid value and a small number of functional groups is used, and it is necessary to select a type and amount of the charge controlling agent as required.

The surface energy sometimes has a value close to the critical surface tension, but when the hydrogen bonding is produced, the surface energy is high even if the critical surface tension is small. The second positively-charging mono-component non-magnetic toner of this invention has been realized based on the finding that the surface energy is strongly correlated with image quality.

As described above, the first toner of this invention is a positively-charging mono-component non-magnetic toner using a polyester as the binder, wherein the polyester with an acid value of 5 or below is selected as the binder, and the maximum charge of the toner is selected to be 30 μC/g or below, securing stable positively charging characteristics. Therefore, the features of the positively-charging mono-component non-magnetic toner, or stable charging characteristics with less amount of ozone produced by corona discharge, can be used for the developing device. And, this toner can easily provide a high quality image having gloss without adhering to the developing roller or causing filming, and free from a beckground density.

In preparing the positively-charging mono-component non-magnetic toner using a polyester as the binder, the polyester is selected as the binder in a view of the interaction with other toner components, so that the surface energy falls in a given range when used as the toner. Thus, the second toner of the invention can easily provide a high quality image with low background density.

The first and second developing methods of this invention uses the second positively-charging mono-component non-magnetic toner of this invention to develop an image from an electrostatic latent image (developing treatment) and controls the relation of the total charge or the total charge charged to a opposite polarity, with the total charge charged to a normal polarity at a fixed level, to enhance and improve the features of the positively-charging mono-component non-magnetic toner, thereby enabling the formation of a high quality image.

Fig. 1 is a sectional view showing the essential structure of a developing apparatus.

Examples of the invention will be described in detail.

Example 1

Expressing in weight ratio (mass ratio), to 94 parts of a polyester resin having an acid value of 3 mgKOH/g, 2 parts of low-molecular polypropylene as a wax component, 1 part of tetraalkylammonium salt as a charge controlling agent, and 3 parts of copper phthalocyanine blue were added and mixed. The prepared mixture was melted and kneaded finely pulverized by means of an airborne pulverizer and classified by an air classifier to prepare powder having a volume average particle diameter of 7.6 μm. To the powder, 0.5 part in mass ratio of hydrophobic silica powder which was treated by aminosilane was added and dry-mixed to produce a cyan toner.

This toner was measured for the maximum charge. It was 15 μC/g.

To measure the maximum charge, a ferrite carrier having a stable surface (e.g., trade name: F-10C, made by Powder Tech Co., Ltd.) was mixed with the toner at a mass ratio of 97 to 3 to prepare a mixture 50g in total. The prepared toner-carrier system was placed in a 100ml-polyethylene bottle, and stirred with a ball mill adjusted to rotate at 70rpm for 10, 30, 60, and 120 minutes respectively. Each stirred system was measured for the charge per unit mass by a blowoff method, and the highest positive charge among the measured value was determined to be the maximum charge.

An image was outputted (development) by a developing apparatus with the prepared cyan toner in it.

As the developing apparatus, one whose essential part is shown in cross section in Fig. 1 was used. In the drawing, 1 stands for an electrostatic latent image retaining member, 2 for a developing device provided with an elastic developing roller 3 and using a contact type mono-component non-magnetic toner, 4 for a transfer device, 5 for uniformizing means for uniformly dispersing a toner remaining after the transfer, 6 for a charging device for charging the electrostatic latent image retaining member 1 to a required positive polarity, and 7 for exposure means for forming an electrostatic latent image by exposing. As the electrostatic latent image retaining member 1, an organic photosensitive drum having a diameter of 30 mm was used, and as the developing roller 3, a conductive polyurethane roller having a diameter of 18 mm was used. With respect to the organic photosensitive drum 1, the conductive polyurethane roller 3 was set and adjusted to have a nip width of 1.5 mm, the organic photosensitive drum 1 was charged to a positive polarity, an image was developed with the toner having the same polarity by a reversal developing method, and the developed image was evaluated.

It was found that the image had a sharp line and gloss with a low background density at a uniform high image density (ID is 1.35 by a Macbeth® densitometer). Besides, even after outputting 10,000 of test charts prints with a image area ratio of 5%, the image was sharp with no difference from the initial outputting, and the image outputted in surroundings at a temperature of 30°C and relative humidity of 85% was not deteriorated.

Furthermore, another cyan toner, which was prepared in the same way as the above cyan toner except that 2 parts of the low-molecular polypropylene as a wax component was not used, had the maximum charge of 13 μC/g. And, the development of a solid image resulted in the same results as above.

Example 2

Expressing in weight ratio (mass ratio), to 92 parts of a polyester resin having an acid value of 1 mgKOH/g, 2 parts of low-molecular weight and partially oxidized polyethylene having an acid value of 10 mgKOH/g, 3 parts of tetraalkylammonium salt, and 3 parts of C.I. pigment yellow 17 (yellow pigment) were added and mixed. The prepared mixture was treated by the same way as in Example 1 to prepare powder having a volume average particle diameter of 7.6 μm. To the powder, 0.5 part in mass ratio of hydrophobic silica powder which was treated aminosilane was added and dry-mixed to produce a yellow toner.

This yellow toner had the maximum charge of 15 μC/g.

This yellow toner was used in the same way as in Example 1 to output an image (development). The developed image had a sharp line and gloss with low background density at a uniform high image density (ID is 1.25 by a Macbeth® densitometer). Besides, even after outputting 10,000 of test charts prints with a image area ratio of 5%, the image was sharp with no difference from the initial outputting, and the image outputted in surroundings at a temperature of 30°C and relative humidity of 85% was not deteriorated.

Furthermore, another yellow toner, which was prepared in the same way as the above yellow toner except that 2 parts of the low-molecular weight and partially oxidized polyethylene (acid value of 10 mgKOH/g) as a wax component was not used, had the maximum charge of 26 μC/g. And, the development of a solid image resulted in the same results as above.

Example 3

Expressing in weight ratio (mass ratio), to 94 parts of a polyester resin having an acid value of 5 mgKOH/g, 2 parts of low-molecular oxidation polyethylene having an acid value of 10 mgKOH/g, 1 part of tetraalkylammonium salt, and 3 parts of C.I. pigment red 122 (magenta pigment) were added and mixed. The prepared mixture was treated by the same way as in Example 1 to prepare a magenta toner having a volume average particle diameter of 7.6 μm.

This magenta toner had the maximum charge of 11 μC/g.

This magenta toner was used in the same way as in Example 1 to output an image (development). The developed image had a sharp line and gloss with a low background density at a uniform high image density (ID is 1.25 by a Macbeth® densitometer). Besides, even after outputting 10,000 of test charts prints with a image area ratio of 5%, the image was sharp with no difference from the initial outputting, and the image outputted in surroundings at a temperature of 30°C and humidity of 85% was not deteriorated.

Furthermore, another magenta toner, which was prepared in the same way as the above magenta toner except that

2 parts of the low-molecular oxidation polyethylene as a wax component was not used, had the maximum charge of 11 µC/g. And, the development of a solid image resulted in the same results as above.

Example 4

Expressing in weight ratio (mass ratio), to 92.25 parts of a polyester resin having an acid value of 1 mgKOH/g, 1 part of styrene grafted polyethylene (no acid value), 3 parts of a styrene-acrylate acid-methacrylate copolymer (substituted alkylammonium sulfonate in part), and 3.75 parts of C.I. pigment red 122 (magenta pigment) were added and mixed. The prepared mixture was treated by the same way as in Example 1 to prepare a magenta toner having a volume average particle diameter of 7.6 µm.

This magenta toner had the maximum charge of 10 µC/g, and it had a surface energy of 33 mN/m when measured.

This magenta toner was used in the same way as in Example 1 to output an image (development). The developed image had a sharp line and gloss with a low background density at a uniform high image density (ID is 1.40 by a Macbeth® densitometer). Besides, even after outputting 10,000 of test charts prints with a image area ratio of 5%, the image was sharp with no difference from the initial outputting, and the image outputted in surroundings at a temperature of 30°C and humidity of 85% was not deteriorated.

Comparative Example 1

A cyan toner was prepared by following the procedure of Example 1 except that a styrene-acrylate copolymer was used instead of the polyester resin having the acid value of 3 mgKOH/g.

This cyan toner had the maximum chargr of 46 µC/g.

This cyan toner was used in the same way as in Example 1 to output an image (development). The developed image had a sharp line without gloss, but its block image had slight inconsistencies in density. Besides, after outputting 10,000 of test charts prints with a image area ratio of 5%, the image was heavily deteriorated, and the toner was adhered to the developing roller.

Comparative Example 2

A cyan toner was prepared by following the procedure of Example 1 except that a polyester resin having an acid value of 20 mgKOH/g was used instead of the polyester resin having the acid value of 3 mgKOH/g.

This cyan toner had the maximum charge of 2 µC/g.

This cyan toner was used in the same way as in Example 1 to output an image (development). The developed image had a sharp line, but its block image had an ununiform low image density (ID is 0.7 by a Macbeth® densitometer) and heavy fog. And, fog on the image outputted was increased in surroundings at a temperature of 30°C and humidity of 85%.

Comparative Example 3

A yellow toner was prepared by following the procedure of Example 2 except that low-molecular weight and partially oxidized polyethylene having an acid value of 30 mgKOH/g was used instead of the low-molecular oxidation polyethylene (wax) having the acid value of 10 mgKOH/g.

This yellow toner had the maximum charge of 18 µC/g.

This yellow toner was used in the same way as in Example 1 to output an image (development).

The developed image had a sharp line and gloss with a low background density at a uniform high image density (ID is 1.30 by a Macbeth® densitometer). Besides, even after outputting 10,000 of test charts prints with a image area ratio of 5%, the image was sharp with no difference from the initial outputting, but the image outputted in surroundings at a temperature of 30°C and humidity of 85% was heavily deteriorated and fog was increased.

Comparative Example 4

Expressing in weight ratio (mass ratio), to 85 parts of styrene-acrylate resin (no acid value), 2 parts of low-molecular polypropylene (no acid value), 10 parts of tetraalkylammonium salt, and 3 parts of copper phthalocyanine blue were added and mixed. Then, following the procedure of Example 1, powder having a volume average particle diameter of 7.6 µm was obtained. To this powder, 0.5 part in mass ratio of hydrophobic silica powder which was treated by aminosilane was added and dry-mixed to produce a cyan toner.

This cyan toner had the maximum charge of 61 µC/g.

This cyan toner was used in the same way as in Example 1 to output an image (development). The developed image had less fog and a sharp line without gloss. Its block image had apparent inconsistencies in density, and the image had low image density (ID is 0.8 by a Macbeth® densitometer) as a whole. Besides, after outputting 10,000 of test charts prints with a image area ratio of 5%, the image was heavily deteriorated, and the toner was adhered to the developing roller.

Example 5

Expressing in mass ratio, 100 parts of a branched polyester resin having an acid value of 1.0 mgKOH/g and a surface energy of 31.6 mN/m, 3 parts of carbon black, 3 parts of a copolymer prepared by copolymerizing a styrene-butylacrylate copolymer with sulfonate of trialkyl aminoethyl methacrylate as a charge controlling agent, and 1 part of polypropylene-based wax were melted and kneaded. The kneaded product was cooled and pulverized to produce a positively-charging mono-component non-magnetic toner having a volume average particle diameter (D_{50}) of 7.0 μm. The above branched polyester resin was not subject to amine modification and had an amine number of 0.

The above positively-charging mono-component non-magnetic toner was melted on a glass plate into the shape of a plate, and cooled to solidify. Its contact angles were measured with respect to water, glycerol, ethylene glycol, diethylene glycol, PEG 200 and dipropylene glycol, and its surface energy γs was measured to be 33 mN/m.

This positively-charging mono-component non-magnetic toner was subjected to ordinary positively-charging mono-component non-magnetic development. The image developed had high quality with its block image having high density without fog, and was hardly affected by a use surrounding such as humidity (10°C, 40% to 32°C, 80%).

The ordinary development was made using a laser printer, modified Model 1305, from Tokyo Electric Co., Ltd. And, the charging polarity was determined to be positive, the transfer polarity be negative, the shedding polarity be positive, the photosensitive member to +600 V, the developing roller bias to +400 V, and the toner feeding roller bias to +500 V. Then, six A4 sheets were outputted per minute.

The developing apparatus shown in Fig. 1 will be described in further detail. The electrostatic latent image retaining member 1 is a positively-charging type organic photosensitive drum provided with a single layered photosensitive member having a thickness of about 25 μm which is prepared by dispersing photoconductive powder into, e.g., a binder having an electron transport material. The positively-charging type organic photosensitive drum 1 may be replaced with, e.g., an amorphous selenium photosensitive member or an amorphous silicon photosensitive member.

The developing device 2 is provided with an elastic developing roller 3 and uses a contact type mono-component non-magnetic toner. The developing roller (toner carrier) 3 has a conductive elastomer layer made of fluorine-containing elastomer or polyurethane elastomer, a conductive rubber, or a flexible conductive tube formed on the surface of an elastic body for example. Furthermore, positively-chargeable hydrophobic silica powder may be adhered to such surfaces. The hydrophobic silica powder can be adhered easily by disposing an auxiliary roller to oppose the developing roller, rotating both rollers keeping their outer peripheries in contact to each other with the hydrophobic silica powder therebetween, and supplementarily heating the roller surfaces.

Besides, the developing device 2 has the toner feeding member (toner feeding roller) 8, the toner stirring element 10 for stirring the toner 9, and the toner layer thickness regulating member 11 for regulating the toner layer on the surface of the toner carrier 3. The toner feeding member (toner feeding roller) 8 comprises a negatively-charging material such as fluorine-containing rubber or polyurethane rubber, or with a negative polar charge controlling agent or metal mixed into the layer thereof.

The toner layer thickness regulating member 11 is formed in the shape of a blade using a negatively-charging material such as fluorine-containing rubber or polyurethane rubber, or with metal mixed therein, or a metal plate. Silicone rubber may also be used though not having negatively chargeable.

The toner layer thickness regulating member 11 presses the surface of the toner carrier 3, which is rotated with the application of a d.c. bias, a.c. bias, or a.c.-d.c. convolutional bias of 20-400 V from a power source to form substantially a toner layer having a substantially uniform thickness on the toner carrier 3, and makes the toner layer to contact or not to contact with a latent image on the electrostatic latent image retaining member 1, thereby effecting reversal development. In this developing process, the toner is previously charged positively by the contact between the developing roller 3 and the toner layer thickness regulating member 11.

The transfer device 4 is, for example, a negative polarity type conductive roller or conductive brush, which transfers the image developed on the surface of the electrostatic latent image retaining member 1 to a recording medium (transfer supporter/recording paper) carried by, e.g., a transfer belt. When the transfer device 4 is transferring the image developed on photoconductor, the recording medium is adsorbed to and supported by the transfer belt by means of an unillustrated conductive roller or conductive brush. The conductive roller or brush which is used as the transfer device 4 has advantages that amount of ozone production can be decreased to one tenth or below, a transfer property is not largely varied due to a change in temperature, and the absolute value of a transfer voltage can be determined low as compared with use of a negative polarity corona charging device. It is to be understood that the corona charging device can also be used for charging.

The remaining toner uniformizing member 5 for uniformly dispersing the toner 9' remaining after the transfer is such as a stationary conductive brush or a rotary conductive brush. The application of a voltage having a d.c. or a.c. voltage superimposed with an a.c. voltage uniformly disperses the remaining toner 9', thereby positively charging it together with the electrostatic latent image retaining member 1 by means of the charging device 6.

The voltage to be applied to the remaining toner uniformizing member 5 is preferably a d.c. voltage of -100 to -800 V, a negative a.c. voltage of 500 to 2000 V_{PP} with a frequency of 300 Hz to 10 kHz, or a voltage superimposed with them. And, the remaining toner uniformizing member 5 may be disposed in plural number. When the absolute value of the voltage applied to the remaining toner uniformizing member 5 is below the above range, uniformization is insufficient because Coulomb force upon the remaining toner is weakened. When the absolute value of the voltage applied to the remaining toner uniformizing member 5 exceeds the above range, however, electric field strength becomes excessively high, and the electrostatic latent image retaining member 1 (photosensitive member) may be broken. Although this is not a cleanerless structure, a conventionally known elastic blade may be used as the cleaner.

On charging by the charging device 6, the application of a positive voltage of about 5 KV to the corona wire of the charging device 6 produces a corona discharge, charging the surface of the electrostatic latent image retaining member 1 to about 400 to 800 V. The remaining toner 9' which has passed without being exposed to light in the next step of exposure is adhered to an area corresponding to the background of the latent image, and is transferred to the surface of the developing roller 3 by the action of an electric field and collected by the developing device 2 in the step of development. At the same time, the toner 9 on the surface of the developing roller 3 is transferred to the latent image of the electrostatic latent image retaining member 1, thereby effecting required development.

In the above developing procedure, the charge of toner on the developing roller 3 was measured to be +3.2 μC/g by a suction method.

Example 6

Expressing in mass ratio, 100 parts of a branch polyester resin having an acid value of 2.0 mgKOH/g and a surface energy of 33.0 mN/m, 3 parts of carbon black, 3 parts of a copolymer prepared by copolymerizing a styrene-butylacrylate copolymer with sulfonate of trialkyl aminoethyl methacrylate as a charge controlling agent, and 1 part of polypropylene-based wax were melted and kneaded. The kneaded product was cooled and pulverized to produce a positively-charging mono-component non-magnetic toner having a volume average particle diameter (D_{50}) of 7.0 μm. The above branch polyester resin was not subject to amine modification and had an amine number of 0.

The above positively-charging mono-component non-magnetic toner was melted on a glass plate into the shape of a plate, and cooled to solidify. Its contact angles were measured with respect to water, glycerol, ethylene glycol, diethylene glycol, PEG 200 and dipropylene glycol, and its surface energy was measured to be 31.5 mN/m.

This positively-charging mono-component non-magnetic toner was subjected to a positively-charging contact type mono-component non-magnetic development in the same way as Example 5. The image developed had high quality with its block image having high density without fog, and was hardly affected by a use surrounding such as humidity (10 , 40% to 32 , 80%).

In the above developing procedure, the charge on the developing roller 3 was measured to be +4.2 μC/g by a suction method. And, when the charge distribution was measured, the total charge with opposite polarity was 13% of the total charge with normal polarity.

Example 7

Expressing in mass ratio, 100 parts of a branch polyester resin having an acid value of 1.0 mgKOH/g and a surface energy of 31.5 mN/m, 3 parts of a yellow pigment (benzimidezorone-based pigment), 3 parts of a charge controlling agent (a copolymer prepared by copolymerizing a styrene-butylacrylate copolymer with sulfonate of trialkyl aminoethyl methacrylate), and 1 part of polypropylene-based wax were melted and kneaded. The kneaded product was cooled and pulverized to produce a positively-charging mono-component non-magnetic toner having a volume average particle diameter (D_{50}) of 6.5 μm. The above branched polyester resin was not subject to amine modification and had an amine number of 0.

The above positively-charging mono-component non-magnetic toner was melted on a glass plate into the shape of a plate, and cooled to solidify. Its contact angles were measured with respect to water, glycerol, ethylene glycol, diethylene glycol, PEG 200 and dipropylene glycol, and its surface energy was measured to be 30.4 mN/m.

This positively-charging mono-component non-magnetic toner was subjected to a positively-charging contact type mono-component non-magnetic development in the same way as Example 5. The image developed had high quality with its block image having high image density without fog, and was hardly affected by a use surrounding such as humidity (10°C, 40% to 32°C, 80%).

In the above developing procedure, the charge of toner on the developing roller 3 was measured to be +4.0 μC/g by a suction method. And, when the charge distribution was measured, the total charge with opposite polarity was 11% of the total charge with normal polarity.

Example 8

Expressing in mass ratio, 100 parts of a branch polyester resin having an acid value of 1.0 mgKOH/g and a surface energy of 32.5 mN/m, 3 parts of a magenta pigment (qunacridone-based pigment), 1 part of a charge controlling agent (tetraalkylammonium perchlorate), and 1 part of polypropylene-based wax were melted and kneaded. The kneaded product was cooled and pulverized to produce a positively-charging mono-component non-magnetic toner having a volume average particle diameter (D_{50}) of 7.5 μm. The above branched polyester resin was not subject to amine modification and had an amine number of 0. Four alkyl chains of tetraalkylammonium perchlorate as the charge controlling agent have saturated or partly double-bonded 1 to 18 carbon atoms, aralkyl group, naphthyl group, allyl group, or substituent group.

The above positively-charging mono-component non-magnetic toner was melted on a glass plate into the shape of a plate, and cooled to solidify. Its contact angles were measured with respect to water, glycerol, ethylene glycol, diethylene glycol, PEG 200 and dipropylene glycol, and its surface energy was measured to be 31.0 mN/m.

This positively-charging mono-component non-magnetic toner was subjected to a positively-charging contact type mono-component non-magnetic development in the same way as Example 5. The image developed had high quality with its block image having high image density without fog, and was hardly affected by a use surrounding such as humidity (10°C, 40% to 32°C, 80%).

In the above developing procedure, the charge of toner on the developing roller 3 was measured to be +4.2 μC/g by a suction method. And, when the charge distribution was measured, the total charge with opposite polarity was 14% of the total charge with normal polarity.

Example 9

Expressing in mass ratio, 100 parts of a branched polyester resin having an acid value of 1.0 mgKOH/g and a surface energy of 31.5 mN/m, 3 parts of a cyan pigment (mixture of copper phthalocyanine blue and copper phthalocyanine green), 1 part of a charge controlling agent (tetraalkylammonium perchlorate), and 1 part of polypropylene-based wax were melted and kneaded. The kneaded product was cooled and pulverized to produce a positively-charging mono-component non-magnetic toner having a volume average particle diameter (D_{50}) of 6.2 μm. The above branch polyester resin was not subject to amine modification and had an amine number of 0. Four alkyl chains of tetraalkylammonium perchlorate as the charge controlling agent have saturated or partly double-bonded 1 to 18 carbon atoms, aralkyl group, naphthyl group, allyl group, or substituent group.

The above positively-charging mono-component non-magnetic toner was melted on a glass plate into the shape of a plate, and cooled to solidify. Its contact angles were measured with respect to water, glycerol, ethylene glycol, diethylene glycol, PEG 200 and dipropylene glycol, and its surface energy was measured to be 34.6 mN/m.

This positively-charging mono-component non-magnetic toner was subjected to positively-charging contact type mono-component non-magnetic development in the same way as Example 5. The image developed had high quality with its block image having high image density without fog, and was hardly affected by a use surrounding such as humidity (10°C, 40% to 32°C, 80%).

In the above developing procedure, the charge on the developing roller 3 was measured to be +3.2 μC/g by a suction method. And, when the change distribusion was measured, the total charge with opposite polarity was 12% of the total charge with normal polarity.

Example 10

Using the branch polyester resin having an acid value of 1.0 mgKOH/g used as the binder resin component in Example 5, nine positively-charging mono-component non-magnetic toners were produced so as to have an surface energy γs in a range of 30.0 to 40.0 mN/m as shown in Table 1.

These positively-charging mono-component non-magnetic toners were subjected to positively-charging contact type mono-component non-magnetic development in the same way as Example 5. The images developed had high quality with the block image having high density without fog.

In the above developing procedures, the magnitudes of charging on the developing roller 3 were measured by a suction method. The measured results as well as those of the distributed magnitudes of charging at that time (ratio of the total charge with opposite polarity to the total charge with normal polarity) are shown in Table 1.

It is seen from Table 1 that the total charge and the charged polarity tend to be satisfactory when the toners have the surface energy of 31 to 34 mN/m.

Table 1

Sample No.	Toner surface energy (γs (mN/m)	Total charge (μC/g)	TCOP/TCNP (%)
1	38.9	2.7	16.2
2	33.1	3.0	11.0
3	31.6	4.0	8.5
4	39.0	2.7	17.3
5	32.5	3.8	16.2
6	36.0	3.1	15.8
7	34.0	4.0	9.5
8	36.2	3.8	10.3
9	35.0	3.6	8.5

*TCOP/TCNP: Total charge with opposite polarity/total charge with normal polarity

Comparative Example 5

Expressing in mass ratio, 100 parts of a branched polyester resin having an acid value of 1.0 mgKOH/g and a surface energy of 39.6 mN/m, 3 parts of a cyan pigment (mixture of copper phthalocyanine blue and copper phthalocyanine green), 1 part of a charge controlling agent (tetraalkylammonium perchlorate), and 1 part of polypropylene-based wax were melted and kneaded. The kneaded product was cooled and pulverized to produce a positively-charging mono-component non-magnetic toner having a volume average particle diameter (D_{50}) of 6.2 μm. The above branched polyester resin was not subject to amine modification and had an amine number of 0. Four alkyl chains of tetraalkylammonium perchlorate as the charge controlling agent have saturated or partly double-bonded 1 to 18 carbon atoms, aralkyl group, naphthyl group, allyl group, or substituent group.

The above positively-charging mono-component non-magnetic toner was melted on a glass plate into the shape of a plate, and cooled to solidify. Its contact angles were measured with respect to water, glycerol, ethylene glycol, diethylene glycol, PEG 200 and dipropylene glycol, and its surface energy was measured to be 43.8 mN/m.

This positively-charging mono-component non-magnetic toner was subjected to positively-charging contact type mono-component non-magnetic development in the same way as Example 5. The image developed had high background density and its block image with inconsistencies in density.

In the above developing procedure, the charge of toner on the developing roller 3 was measured to be +1.2 μC/g by a suction method. And, when the charge distribution was measured, the total charge with opposite polarity was 25% of the total charge with normal polarity.

Comparative Example 6

Expressing in mass ratio, 100 parts of a linear polyester resin having an acid value of 6.3 mgKOH/g and a surface energy of 42.5 mN/m, 3 parts of a magenta pigment qunacridone-based pigment), 3 parts of a charge controlling agent (tetraalkylammonium perchlorate), and 1 part of polypropylene-based wax were melted and kneaded. The kneaded product was cooled and pulverized to produce a positively-charging mono-component non-magnetic toner having a volume average particle diameter (D_{50}) of 6.2 μm. Four alkyl chains of tetraalkylammonium perchlorate as the charge controlling agent have saturated or partly double-bonded 1 to 18 carbon atoms, aralkyl group, naphthyl group, allyl group, or substituent group.

The above positively-charging mono-component non-magnetic toner was melted on a glass plate into the shape of a plate, and cooled to solidify. Its contact angles were measured with respect to water, glycerol, ethylene glycol, diethylene glycol, PEG 200 and dipropylene glycol, and its surface energy was measured to be 44.1 mN/m.

This positively-charging mono-component non-magnetic toner was subjected to positively-charging contact type mono-component non-magnetic development in the same way as Example 5. The image developed had heavy fog and its block image with inconsistencies in density.

In the above developing procedure, the charge of toner on the developing roller 3 was measured to be +0.8 μC/g by a suction method. And, when the charge distribution was measured, the total charge with opposite polarity was 27% of the total charge with normal polarity.

Examples of the inventions have been described above, but it is to be understood that the invention is not limited to the Examples and may be modified variously without departing from the spirit and scope of the invention. For example, combinations other than the above exemplified combinations can be suitably selected such as the ratio of binder resin components, the type and component ratio of wax, the type and component ratio of a charge controlling agent, and toner preparing means, according to the use and the functions of the developing apparatus to be used.

As obvious from the above description and Examples, the positively-charging mono-component non-magnetic toner of the invention is a positively-charging mono-component non-magnetic toner which is expected to produce less ozone and to have stable chargeability by using a polyester as the binder, and can stably provide a high quality image excelling in sharpness, high density, gloss and permeability when a first toner has the acid value of the polyester resin and the maximum charge limited to a given value, and when a second toner has its surface energy limited to a given range. Namely, the positively-charging mono-component non-magnetic toner of the invention, when used for a mono-component developing method, is easily and securely charged uniformly, and forms an image having high density and gloss without background density on the surface of an electrostatic latent image retaining member. And, this positively-charging mono-component non-magnetic toner hardly coagulates, does not adhere to the developing roller or the toner thickness regulating member, and does not cause filming, thereby contributing to the formation of a high quality image with satisfactory reproduction coupled with the uniformity of the charging.

The developing method of the invention, when developing an image from an electrostatic latent image by using a toner whose surface energy is limited to a given range, controls the total charge or the relation between the total charge charged to a opposite polarity and the total charge charged to a normal polarity, thereby further enhancing and improving the features of the positively-charging mono-component non-magnetic toner, to enable the formation of a high quality image prints.

Claims

1. A positively-charging mono-component non-magnetic toner comprising at least a binder resin and a coloring agent, characterized in that said binder resin is a polyester resin having an acid value has the maximum positive charge of 30 μC/g or below.

2. A positively-charging mono-component non-magnetic toner according to claim 1, wherein said toner contains 0.2 to 10% by weight of wax having an acid value of 20 mgKOH/g or below.

3. A positively-charging mono-component non-magnetic toner according to claim 1, wherein said toner has a maximum positive charge of 3 to 30 μC/g.

4. A positively-charging mono-component non-magnetic toner according to claim 1, said toner has a surface energy γs of 30 to 40 mN/m.

5. A positively-charging mono-component toner comprising at least a binder resin and a coloring agent, characterized in that said toner has a surface energy γs of 30 to 40 mN/m.

6. A positively-charging mono-component toner according to claim 5, wherein said toner is a non-magnetic toner.

7. A positively-charging mono-component toner according to claim 5, wherein said toner has a surface energy γs of 31 to 34 mN/m.

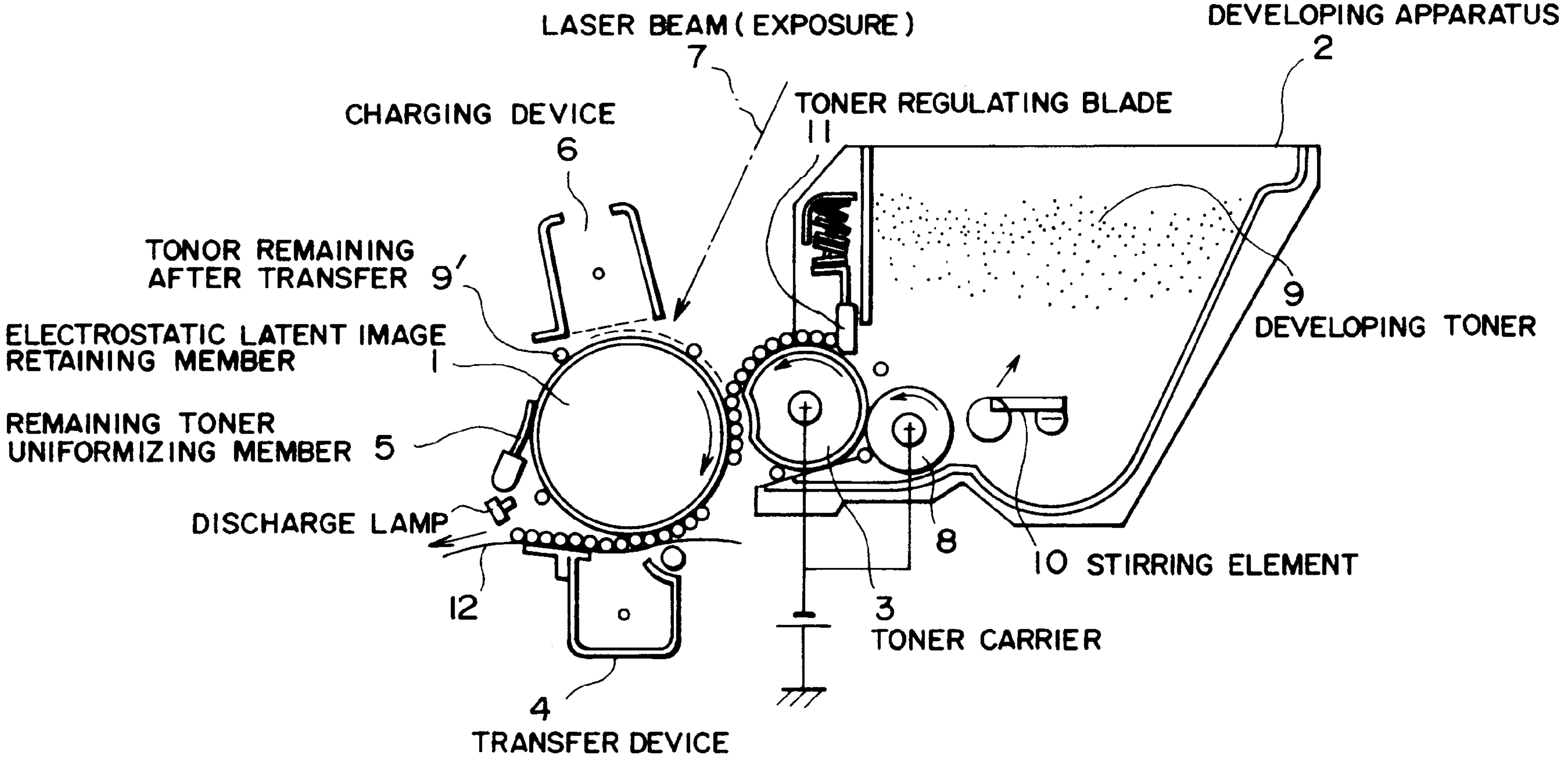
8. A positively-charging mono-component toner according to claim 5, wherein said toner has a volume average particle diameter (D_{50}) of 3 to 14 μm.

9. A developing method using a positively-charging mono-component toner containing a polyester resin as the binder resin component, characterized in that said positively-charging mono-component toner has a surface energy γs of

30 to 40 mN/m, and said toner for developing an electrostatic latent image has a total charge of 2 μC/g or above.

10. A developing method using a positively-charging mono-component toner containing a polyester resin as the binder resin component, characterized in that said positively-charging mono-component toner has a surface energy γs of 30 to 40 mN/m, and a total charge charged to a opposite polarity when developing an electrostatic latent image is 20% or below of the absolute value of a total charge charged to a normal polarity.

FIG. 1


LASER BEAM (EXPOSURE)
7
DEVELOPING APPARATUS
2
CHARGING DEVICE
6
TONER REGULATING BLADE
11
TONOR REMAINING AFTER TRANSFER 9'
9
DEVELOPING TONER
ELECTROSTATIC LATENT IMAGE RETAINING MEMBER
1
REMAINING TONER UNIFORMIZING MEMBER 5
DISCHARGE LAMP
8
10 STIRRING ELEMENT
12
3
TONER CARRIER
4
TRANSFER DEVICE

European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 95 30 5134

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X A	EP-A-0 463 822 (FUJITSU) * page 20; examples B-3 * * page 21; example COM.EX.4 *	5-8 9,10	G03G9/087 G03G9/08
X	EP-A-0 462 785 (MITSUBISHI) * page 6 - page 7; examples 3,4 * * page 21 - page 25; tables 5,6 *	1,3	
X	GB-A-2 237 399 (ARAKAWA) * page 19; example 5; table 2 * * page 21; example 10; table 3 *	1	
X	GB-A-2 207 438 (NIPPON) * page 16; examples 1-4; table 1 * * page 19; examples 1-4; table 2 *	1,3	
X	GB-A-2 198 141 (NIPPON) * page 19 - page 20; example 4 * * page 22; example 4; table 2 *	1	
X	EP-A-0 333 498 (MITSUBISHI) * page 13 - page 14; examples COM.EX.1,3; table 3 *	1	TECHNICAL FIELDS SEARCHED (Int.Cl.6) G03G
A	EP-A-0 241 160 (TOSHIBA) * claim 1 * -----	9,10	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	20 November 1995	Vogt, C

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

EPO FORM 1503 03.82 (P04C01)