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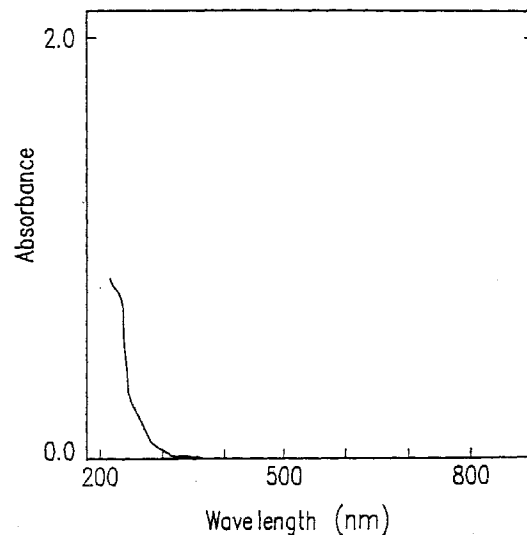
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(54) **Image forming method**

(57) The invention provides an image forming method for allowing toner for a two-component developer to be recycled, wherein toner includes toner particles which contain a binding resin and particles of a magnetic powder dispersed in the binding resin, the magnetic powder being contained in a ratio of 0.1 to 5 parts by weight with respect to 100 parts of the binding resin; the binding resin is formed of a composition containing a resin having an anionic group; and an extracted solution obtained by extracting the toner with methanol has substantially no absorption peak in the range of 280 to 350 nm, and has a substantially zero absorbance in the range of 400 to 700 nm.

*FIG. 1*



**EP 0 701 178 A1**

**Description**

## 1. Field of the Invention:

5 The present invention relates to an image forming method which allows toner to be recycled. In particular, the present invention relates to an image forming method which uses toner having a satisfactory transfer efficiency and providing a long life to the developer to reproduce images at a desired density for a long period of time despite absence of a charge control agent, and is preferably used for an electrophotographic image forming apparatus such as an electrostatic copying machine and a laser beam printer. Even more particularly, the present invention relates to an image forming method for stably forming high quality images even in the state where such toner is recycled.

## 2. Description of the Related Art:

15 In electrophotography, an image is generally formed in the following manner. An electrostatic charge is applied uniformly to a photosensitive body having a photoconductive layer formed of a photoconductive material, and thus an electrostatic latent image corresponding to an original image is formed on a surface of the photosensitive body by light reflected by the original image. The electrostatic latent image is developed into a toner image. The toner image is transferred to a transfer medium such as a transfer paper sheet, and the resultant image is bound by applying heat or pressure to the transfer paper sheet.

20 In the transfer step, the toner forming the toner image is not entirely transferred to the transfer medium, instead, a part of the toner remains on the photosensitive body. Accordingly, it is economically advantageous to recover and recycle the residual toner after the transfer step. An image forming apparatus for recovering such toner during the cleaning step after the transfer step and re-supplying the recovered toner to the developing device has been proposed.

25 Toner to be recycled is required to have a satisfactory chargeability. Conventional toner generally contains a charge control agent situated on the surfaces of the toner particles and the vicinity thereof contributes to the generation of a charge by friction. Toner of a type to be negatively charged contains a negative charge control agent such as a dye of a complex containing a metal such as chromium (for example, an dye of an azo compound -chromium complex.) or an oxycarboxylic acid - metal complex (for example, a salicylic acid - metal complex) as described in Japanese Laid-Open Patent Publication No. 3-67268. Toner of a type to be positively charged contains a positive charge control agent such as an oil soluble dye such as nigrosine or an amine-type control agent as described in Japanese Laid-Open Patent Publication No. 56-106249.

35 The charge control agent situated on the surfaces of the toner particles and the vicinity thereof generally comes off easily from the surfaces of the toner particles due to friction with, for example, the carrier particles. The recycled toner is easily affected by various external forces applied in the cleaning step of scraping off the residual toner from the surface of the photosensitive body by a blade and in the transportation step of transporting the recovered toner to the developing device as well as by friction caused while the toner is mixed and stirred with the carrier. Thus, the charge control agent is removed from the toner particles at an excessively high frequency.

40 Accordingly, in a toner recycle system, the developer is formed of unused toner having a sufficient amount of charge control agent on the surfaces of the toner particles and recycled toner without the charge control agent. Since toner without the charge control agent does not have a sufficient charge control function, the entire developer does not have a stable chargeability. As the content of the recycled toner with respect to the developer increases, the quality of the reproduced image is deteriorated.

45 **SUMMARY OF THE INVENTION**

The image forming method for allowing toner for a two-component developer to be recycled of this invention, which overcomes the above-discussed and numerous other disadvantages and deficiencies of the prior art, wherein toner includes toner particles which contain a binding resin and particles of a magnetic powder dispersed in the binding resin, the magnetic powder being contained in a ratio of 0.1 to 5 parts by weight with respect to 100 parts of the binding resin; the binding resin is formed of a composition containing a resin having an anionic group; and an extracted solution obtained by extracting the toner with methanol has substantially no absorption peak in the range of 280 to 350 nm, and has a substantially zero absorbance in the range of 400 to 700 nm.

55 In a preferred embodiment, the magnetic powder is contained in a ratio of 0.5 to 3 parts by weight with respect to 100 parts of the binding resin.

In a preferred embodiment, the toner particles have a volume-based average particle diameter of 5 through 15  $\mu\text{m}$ , and spacer particles having a volume-based average particle diameter of 0.05 through 1.0  $\mu\text{m}$  are attached onto surfaces of the toner particles.

Thus, the invention described herein makes possible the advantages of (1) providing an image forming method which maintains the developing characteristic of the developer even when the toner is recycled; (2) providing an image forming method for stably forming a satisfactory image even when the content of the recycled toner with respect to the developer increases; (3) providing an image forming method for extending the life of the developer; and (4) providing an image forming method for stably forming images having no fog with a sufficient density and a satisfactory transfer efficiency for a long period of time.

These and other advantages of the present invention will become apparent to those skilled in the art upon reading and understanding the following detailed description with reference to the accompanying figures.

## BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a graph showing absorbance of a methanol extracted solution of toner used in the present invention in the range of 200 to 700 nm;

Figure 2 is a graph showing absorbance of a methanol extracted solution of toner having an azo dye - chrome complex as a charge control agent in the range of 200 to 700 nm;

Figure 3 is a graph showing absorbance of a methanol extracted solution of toner having a salicylic acid - metal complex as the charge control agent in the range of 200 to 700 nm;

Figure 4 is a graph showing absorbance of a methanol extracted solution of carrier in a two-component magnetic developer used for a long time in which toner has an azo dye - chrome complex as the charge control agent and chargeability of carrier is unstabilized by a spent in the range of 200 to 700 nm;

Figure 5 is a graph showing a relationship between shaking time and a spent ratio obtained with regard to two kind of a two-component magnetic developer, one comprising toner having a charge control agent and magnetic carrier and another comprising toner having no charge control agent and magnetic carrier;

Figure 6 is a graph showing a relationship between shaking time and quantity of charge of toner obtained with regard to two kind of a two-component magnetic developer, one comprising toner having a charge control agent and magnetic carrier and another comprising the toner having no charge control agent and magnetic carrier;

Figure 7 is a graph showing a relationship between an amount of spent of carrier and content of a charge control agent in a toner particle;

Figure 8 is a graph showing a relationship between shaking time and amount of spent obtained in the case where each component contained in a toner particle and magnetic carrier are individually mixed and shaken;

Figure 9 illustrates a mechanism of a charge failure caused by a spent in a conventional two-component magnetic developer;

Figure 10 is a schematic view of an image forming apparatus for forming an image using a method according to the present invention;

Figure 11 is a schematic view of a toner recycle system used in the present invention.

## DESCRIPTION OF THE PREFERRED EMBODIMENTS

Toner used in the present invention has no charge control agent, such as a dye of an azo compound - metal complex and an oxycarboxylic acid - metal complex, at all. Therefore, a spent caused by a charge control agent, which will be described in detail below, scarcely occurs in the toner used in the method of the present invention, resulting in realizing a high quality copied image for a long period of time.

Since the toner used in the method of the present invention has no charge control agent, it is impossible to detect any charge control agent, i.e., a dye type compound, from the toner by any chemical or physical method. For example, such a compound cannot be detected in the toner used in the method of the present invention by any chemical reaction. Alternatively, absorption peaks owing to such a compound cannot be detected in an organic solvent extracted solution of the toner used in the method of the present invention. For example, when the toner used in the method of the present invention is extracted with an organic solvent such as methanol, the extracted solution has substantially no absorption

peak in the range of 280 to 350 nm, and has substantially zero absorbance in the range of 400 to 700 nm. Herein, "to have substantially no absorption peak" means, in an extracted solution obtained by extracting 0.1 g of the toner used in the method of the present invention with 50 ml of methanol, absorption peaks are not detected at all, or if detected, values of the absorbance peaks are 0.05 or less. Similarly, "to have substantially zero absorbance" means that values of the absorbance of the extracted solution obtained by extracting 0.1 g of the toner used in the method of the present invention with 50 ml of methanol are 0.05 or less.

In the present invention, instability of the charge of the toner due to a lack of a charge control agent is compensated for as follows. First, a polymer having an anionic group is used as a binder resin of a toner particle; and secondly, magnetic powder is contained in the toner particle at a predetermined proportion. In the toner used in the method of the present invention, in order to further enhance the function of the toner, the binder resin is made of a composition containing a resin including a low molecular weight polymer and a high molecular weight polymer, and both the polymers have an anionic group. This results in further decreasing charge failure of the toner. Furthermore, spacer particles having a desired particle diameter are attached on the surfaces of the toner particles, if necessary, thereby increasing the transfer efficiency of the toner.

The above-mentioned characteristics of the toner used in the method of the present invention will be described in detail.

Figure 1 shows an UV-visible spectrum of a methanol extracted solution of the toner used in the method of the present invention in the range of 200 to 700 nm. As is shown in this spectrum, the extracted solution has no peak, which is otherwise formed because of a charge control agent. Specifically, the solution has substantially no absorption peak in the range of 280 to 350 nm, and the absorbance in the range of 400 to 700 nm is substantially zero. To the contrary, in an absorbance curve of a methanol extracted solution of toner having an azo dye - chrome complex as a charge control agent shown in Figure 2, absorption peaks are found in the range of 400 to 700 nm, in particular, 550 to 570 nm. Further, in the UV-visible spectrum of a methanol extracted solution of toner having a salicylic acid - metal complex as a charge control agent shown in Figure 3, an absorption peak is found in the range of 280 to 350 nm.

It is because the charge control agent is present on the surfaces of the toner particles at a rather high concentration that the methanol extracted solution of the toner having the charge control agent has absorption peaks due to the charge control agent.

A carrier included in a developer which has insufficient chargeability owing to occurrence of a spent is extracted with methanol, and then the UV-visible spectrum of the extracted solution is measured to find absorption peaks in the range of 400 to 700 nm derived from a charge control agent. For example, the developer, comprising the toner having an azo dye - chrome complex, whose UV-visible spectrum is shown in Figure 2, was used for a long period of time to cause a spent therein. Then, UV-visible spectrum of a methanol extracted solution of the carrier in this developer was measured to give the spectrum shown in Figure 4. As is shown in Figure 4, absorption peaks are found at the same position as the spectrum in Figure 2. It is conventionally understood that a spent is caused because a binder resin in the toner is attached to the surface of a carrier particle to form a resin film. The comparison between the absorbance curves in Figures 2 and 4, however, reveals that one of the major causes of a spent is the transfer of the charge control agent from the toner particles to the carrier particles.

The present inventors conducted the following experiments in order to find out more about the relationship between a charge control agent and a spent: First, toner comprising toner particles containing 1.5 wt% of the azo dye - chrome complex was mixed with a carrier to obtain a developer. The toner and the carrier was shaken for a predetermined period of time. Figure 5 shows a relationship between the shaking time and amount of an attachment on the surfaces of the carrier particles. In Figure 5, the amount of attachment is indicated as a spent ratio, that is, a percentage based on a total weight of the carrier particles bearing the attachment. Furthermore, Figure 6 shows the relationship between the shaking time and the amount of charge of the toner. The same procedure was repeated with regard to a developer comprising toner having no charge control agent and carrier. The experimental results of this developer are also shown in Figures 5 and 6, wherein the results obtained by the developer including the toner having the charge control agent are plotted with black circles, and those by the developer including the toner having no charge control agent are plotted with white circles. It is apparent from Figures 5 and 6 that a larger amount of attachment is formed on the carrier particles as the spent and the charge amount of the toner has a greater decrease in the developer including the toner particle having the charge control agent than in the developer including the toner particle having no charge control agent.

Next, the weight of toner components attached on the surfaces of the carrier particles as the spent was measured with time. The results are shown in a graph of Figure 7, wherein the abscissa indicates a measured amount of the spent and the ordinate indicates the content of the charge control agent in the toner particle. The broken line in Figure 7 indicates the amount of the charge control agent calculated in assuming that the toner components attached as the spent are identical to the components in the toner particles. Figure 7 reveals that a large amount of the charge control agent is deposited to be attached on the surfaces of the carrier particles at the initial stage. In Figure 7, as amount of the spent increases, the measured values approximate the calculated values. This is because they are experimental results obtained in a close system having no supply of fresh toner. Therefore, when toner is exchanged as in a copying

machine, the difference between the measured values and the calculated values would be much larger.

Furthermore, the present inventors measured the weight of the attachment on the surfaces of the carrier particles resulting from mixing the carrier with each of the toner components, that is, a charge control agent, a binder resin, carbon black as a coloring agent and wax, so as to find out the relationships between the respective toner components and the spent. The results are shown in Figure 8 as a variation with time in the amount of the attachment (i.e., amount of the spent), wherein the results obtained from the mixture with the charge control agent is plotted with white circles, those from the carbon black with black circles, those from the binder resin with squares, and those from the wax with triangles. It is apparent from Figure 8 that the charge control agent causes the largest amount of attachment due to the spent.

Based on the above-mentioned facts, the charge failure caused by the spent in a conventional two-component magnetic developer is explained as follows referring to Figure 9. In the initial stage of the usage of a developer, a carrier particle 1 is positively charged and a toner particle 2 is negatively charged as is shown in an upper portion of Figure 9. In this case, the toner particle works as a negative toner particle 21. When this developer is continued to be used, a component including the charge control agent as a main component in the toner particle is attached on the surface of the carrier particle 1. Attachment 201, which is the spent, is negatively charged. The negatively charged attachment 201 leads to the formation of a toner particle having positive charge, that is, a reversely charged toner particle 22. The reversely charged toner particle 22 is formed on the surface of the carrier particle 1 as is shown in a lower portion of Figure 9, resulting in scattering of the toner and decreasing the transfer efficiency of the toner.

As described above, preferably, the toner does not have a charge control agent not only because the agent can include a heavy metal but also because the agent is the main cause of the spent, scatter of the toner and of a decrease in the transfer efficiency of the toner. Accordingly, the toner used in the method of the present invention has no charge control agent at all.

The instability of charge of the toner due to the lack of the charge control agent, in particular, the insufficiency in charge amount of the toner is compensated by using a binder resin having an anionic group as mentioned above. The insufficiency in charge amount of the toner particles can be supplemented because the binder resin has a negative charge in itself owing to the anionic group included therein. Since the anionic group is bonded to the main chain of the binder resin, it would never move onto the surface of the carrier particle as the charge control agent does, and hence it never causes the spent. On the contrary, charge around the surface of the toner particle caused by the anionic group of the binder resin is not so large that the electrostatic attraction between the toner particle and the carrier particle owing to the Coulomb force is insufficient when they are conveyed as a magnetic brush for development. Therefore, in a rapid copying operation, the toner cannot be sufficiently prevented from scattering because of insufficient coupling with the carrier particles. The scattered toner stains the inner wall of the copying machine, and can cause so-called a fog on a copied image.

In order to overcome such disadvantages, the toner used in the method of the present invention includes magnetic powder at a predetermined proportion, that is, 0.1 to 5 parts by weight on the basis of 100 parts by weight of the binder resin. The insufficiency in the charge amount of the toner particles can be thus compensated for. The magnetic powder contained in the toner particle causes magnetic attraction between the toner particle and the carrier particle. This magnetic attraction between the toner particle and the carrier particle together with electrostatic attraction prevents the toner from scattering.

The content of the magnetic powder in toner particles is in the range of 0.1 to 5 parts by weight per 100 parts by weight of the binder resin as described above. When the content is less than 0.1 parts by weight, the magnetic attraction between the toner particle and the carrier particle is insufficient, resulting in insufficient coupling with the carrier particle and causing toner scattering or fog forming on a copied image. Furthermore, the density of the copied image is low because of the insufficient charge amount. When the contents exceeds 5 parts by weight, the magnetic attraction between the carrier particle and the toner particle becomes so strong that the toner is not sufficiently attached onto an electrostatic latent image, resulting in decreasing the density of the copied image.

Several attempts have been made to improve the resolution of a copied image and the like by including (inclusively adding) magnetic powder as a toner component. For example, Japanese Laid-Open Patent Publication No. 56-106249 discloses a toner particle including 10 wt% of ferrite, and Japanese Laid-Open Patent Publication No. 59-162563 discloses a toner particle including 5 through 35 wt% of a magnetic fine particle. In either case, however, the content of the magnetic powder is excessive, and hence, the density of the copied image is low. Japanese Laid-Open Patent Publication No. 3-67268 discloses toner to which 0.05 to 2 wt% of magnetic powder is externally added. In this case, since the magnetic powder is not included in the toner particle, the powder is likely to be ununiformly attached onto the surface of the toner particle, resulting in insufficient magnetic attraction between the toner particle and the carrier particle. Furthermore, in either of the above-mentioned toners, the spent can be disadvantageously caused because a charge control agent is contained therein.

As described above, the toner used in the present invention has a stable chargeability although containing no charge control agent. By using such toner in a toner recycle system, separation of the charge control agent from the toner particles by an external force or the like is avoided. Thus, the deterioration in quality of the recycled toner is minimized;

namely, the recycled toner has substantially no difference in quality from the unused toner. Accordingly, a satisfactory image quality can be maintained even when a mixture of the recycled toner and the unused toner is used.

In the present invention, spacer particles having a particle diameter of 0.05 through 1.0  $\mu\text{m}$  are attached preferably onto the surfaces of the toner particles in order to increase the transfer efficiency of the toner image.

The spacer particles can work to enhance fluidity of the toner, and in addition, form a gap between the photosensitive body and the toner particles when the toner is attached onto the electrostatic latent image formed on the photosensitive body. Therefore, the toner can be transferred from the photosensitive body onto the transfer paper with ease even when the toner attains a large quantity of charge through a long copying operation, resulting in a high transfer efficiency of the toner.

When the spacer particle is similar to the particle of the magnetic powder included in the toner particle, the magnetic attraction between the toner particle and the carrier particle can be further enhanced, thereby further preventing toner scattering and a fog.

A fine particle having a particle diameter of approximately 0.015  $\mu\text{m}$  is used to enhance fluidity of a conventional toner. Such a small particle cannot form a sufficient gap between the photosensitive body and the toner particles, and cannot work as the spacer particle for the aforementioned purposes.

Now, preferable resins to be used as the binder resin in the toner used in the method of the present invention will be described. Herein, a "lower alkyl group" indicates alkyl having 1 to 5 carbon atoms.

(Binder resin of a toner particle included in the present invention)

The binder resin of the toner particle used in the present invention comprises a composition including a polymer having an anionic group. Such a binder resin is obtained by polymerizing a monomer having an anionic group or a mixture of the monomer having an anionic group with other monomers. The obtained resin can be a homopolymer or a copolymer.

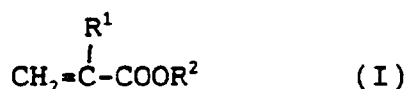
The binder resin used in the toner is preferably a copolymer, such as a random copolymer, a block copolymer and a grafted copolymer, obtained from a monomer having an anionic group and other monomers.

Examples of the monomer having an anionic group include monomers having a carboxylic acid group, a sulfonic acid group or a phosphoric acid group, and a monomer having a carboxylic acid group is generally used. Examples of the monomer having a carboxylic acid group include ethylenically unsaturated carboxylic acids such as acrylic acid, methacrylic acid, crotonic acid, maleic acid and fumaric acid; monomers that can form a carboxylic acid group such as maleic anhydride; and lower alkyl halfester of dicarboxylic acid such as maleic acid and fumaric acid. Examples of the monomer having a sulfonic acid group include styrene sulfonic acid and 2-acrylamido-2-methylpropane sulfonic acid. Examples of the monomer having a phosphoric acid group include 2-phosphono(oxy)propylmethacrylate, 2-phosphono(oxy) ethylmethacrylate, 3-chloro-2-phosphono(oxy) propylmethacrylate.

Such a monomer having an anionic group can be a free acid, a salt of an alkaline metal such as sodium and potassium, a salt of an alkaline earth metal such as calcium and magnesium, and a salt such as zinc.

The monomer having no anionic group used to prepare the binder resin is selected so that the resultant binder resin has a sufficient fixability and chargeability required of toner, and is one or a combination of an ethylenically unsaturated monomer. Examples of such a monomer include ethylenically unsaturated carboxylic acid ester, monovinyl arene, vinyl ester, vinyl ether, diolefin and monoolefin.

The ethylenically unsaturated carboxylic acid esters are represented by the following Formula (I):



wherein  $\text{R}^1$  is a hydrogen atom or a lower alkyl group; and  $\text{R}^2$  is a hydrocarbon group having 11 or less carbon atoms or a hydroxyalkyl group having 11 or less carbon atoms.

Examples of such ethylenically unsaturated carboxylic acid esters include methyl acrylate, ethyl acrylate, butyl acrylate, 2-ethylhexyl acrylate, cyclohexyl acrylate, phenyl acrylate, methyl methacrylate, hexyl methacrylate, 2-ethylhexyl methacrylate,  $\beta$ -hydroxyethylacrylate,  $\gamma$ -hydroxypropylacrylate,  $\delta$ -hydroxybutylacrylate and  $\beta$ -hydroxyethylmethacrylate.

The monovinyl arenes are represented by the following Formula (II):



wherein  $\text{R}^3$  is a hydrogen atom, a lower alkyl group or a halogen atom;  $\text{R}^4$  is a hydrogen atom, a lower alkyl group, a halogen atom, an alkoxy group, an amino group or a nitro group; and  $\phi$  is a phenylene group.

EP 0 701 178 A1

Examples of such monovinyl arene include styrene,  $\alpha$ -methylstyrene, vinyltoluene,  $\alpha$ -chlorostyrene, o-chlorostyrene, m-chlorostyrene, p-chlorostyrene and p-ethylstyrene.

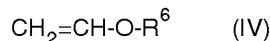
The vinyl esters are represented by the following Formula (III):



wherein R<sup>5</sup> is a hydrogen atom or a lower alkyl group.

Examples of such vinyl esters include vinyl formate, vinyl acetate and vinyl propionate.

10 The vinyl ethers are represented by the following Formula (IV):



wherein R<sup>6</sup> is a monovalent hydrocarbon group having 11 or less carbon atoms.

15 Examples of such vinyl ethers include vinyl methyl ether, vinyl ethyl ether, vinyl n-butyl ether, vinyl phenyl ether and vinyl cyclohexyl ether.

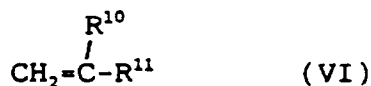
The diolefins are represented by the following Formula (V):



wherein R<sup>7</sup>, R<sup>8</sup> and R<sup>9</sup> are independently a hydrogen atom, a lower alkyl group or a halogen atom.

Examples of such diolefins include butadiene, isoprene and chloroprene.

25 The monoolefins are represented by the following Formula (VI):



30 wherein R<sup>10</sup> and R<sup>11</sup> are independently a hydrogen atom or a lower alkyl group.

Examples of such monoolefins include ethylene, propylene, isobutylene, 1-butene, 1-pentene and 4-methyl-1-pentene.

35 Specific examples of the polymer having an anionic group, that is, a (co)polymer obtained through the polymerization of the aforementioned monomers, include styrene-acrylic acid copolymers, styrene-maleic acid copolymers and ionomer resins. Furthermore, a polyester resin having an anionic group can be also used. The polymer having an anionic group preferably includes the anionic group at a proportion for attaining an acid value of 2 through 30, and preferably 5 through 15, when the anionic group is present as a free acid. When part or the entire anionic group is neutralized, the anionic group is preferably contained at such a proportion that the acid value would be in the aforementioned range in assuming that it is present as a free acid. When the acid value, i.e., the concentration of the anionic group, of the polymer or the composition is below the aforementioned range, the chargeability of the resultant toner is insufficient. When it exceeds 40 the range, the resultant toner disadvantageously has a hygroscopic property. A preferable binder resin is a copolymer obtained from the monomer having an anionic group and at least one of the ethylenically unsaturated carboxylic acid ester represented by Formula (I) as an indispensable components, and any of the monomers represented by Formulae (II) through (VI) as an optional component to be used if necessary. One or a combination of two or more of the aforementioned monomers is used for preparing the binder resin.

45 The binder resin used in the invention is made of the composition including the aforementioned polymers, and the composition can further include a polymer having no anionic group as well. In this case, the proportion of the anionic group in the entire composition is preferably within the aforementioned range.

50 (Magnetic powder)

The magnetic powder contained in (inclusively added to) the toner particles can be any magnetic powder used in a conventional one-component type developer. Examples of the material for the magnetic powder include triiron tetroxide (Fe<sub>3</sub>O<sub>4</sub>), maghemite ( $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>), zinc iron oxide (ZnFe<sub>2</sub>O<sub>4</sub>), yttrium iron oxide (Y<sub>3</sub>Fe<sub>5</sub>O<sub>12</sub>), cadmium iron oxide (CdFe<sub>2</sub>O<sub>4</sub>), gadolinium iron oxide (Gd<sub>3</sub>Fe<sub>5</sub>O<sub>12</sub>), copper iron oxide (CuFe<sub>2</sub>O<sub>4</sub>), lead iron oxide (PbFe<sub>12</sub>O<sub>19</sub>), nickel iron oxide (NiFe<sub>2</sub>O<sub>4</sub>), neodyum iron oxide (NdFeO<sub>3</sub>), barium iron oxide (BaFe<sub>12</sub>O<sub>19</sub>), magnesium iron oxide (MgFe<sub>2</sub>O<sub>4</sub>), manganese iron oxide (MnFe<sub>2</sub>O<sub>4</sub>), lanthanum iron oxide (LaFeO<sub>3</sub>), iron (Fe), cobalt (Co) and Nickel (Ni). Particularly preferable magnetic powder is made from triiron tetroxide (magnetite) in the shape of fine particles. The particle of 55

preferable magnetite is in the shape of a regular octahedron with a particle diameter of 0.05 through 1.0  $\mu\text{m}$ . Such a magnetite particle can be subjected to a surface treatment with a silane coupling agent or a titanium coupling agent. The particle diameter of the magnetic powder contained in the toner particle is generally 1.0  $\mu\text{m}$  or smaller, and preferably in the range between 0.05 and 1.0  $\mu\text{m}$ .

The content of the magnetic powder in the toner particle is in the range of 0.1 to 5 parts by weight, more preferably 0.5 to 4 parts by weight, and most preferably 0.5 to 3 parts by weight per 100 parts by weight of the binder resin. When the content is too small, the toner can be scattered during the development or a fog can be formed on a copied image.

(Inner additives in the toner particle)

The toner particle contains, as described above, the binder resin and the magnetic powder as indispensable components, and can optionally include some inner additive generally used for a toner, if necessary.

Examples of such additives include a coloring agent and a release agent.

As the coloring agent, the following pigments can be used:

- Black pigment:  
carbon black, acetylene black, lampblack, aniline black;
- Extender:  
barite powder, barium carbonate, clay, silica, white carbon, talc, alumina white.

Such a pigment is contained in the toner particle in the range of 2 to 20 parts by weight, and preferably 5 to 15 parts by weight per 100 parts by weight of the binder resin.

As the release agent, various wax and olefin resins can be used as in a conventional toner. Examples of the olefin resin include polypropylene, polyethylene, and propylene-ethylene copolymers, and polypropylene is particularly preferred.

(Preparation of the toner)

The toner particles in the toner included in a two-component type developer of the present invention can be produced by any ordinary method for toner particles such as crushing and classification, fusing granulation, spray granulation and polymerization, and are generally produced by the crushing and classification method.

For example, the components for the toner particles are previously mixed in a mixer such as a Henschel mixer, kneaded with a kneader such as a biaxial extruder, and then cooled. The resultant is crushed and classified to give toner particles. The particle diameter of the toner particle is generally in the range between 5 and 15  $\mu\text{m}$  and preferably between 7 and 12  $\mu\text{m}$  in the volume-base averaged particle diameter (a medium size measured with a Coulter counter).

It is possible to improve the fluidity of the toner by attaching, as an outer additive, a fluidity enhancer such as hydrophobic vapor deposited silica particles onto the surfaces of the toner particles, if necessary. The primary particle diameter of the fluidity enhancer such as the silica particles is generally approximately 0.015  $\mu\text{m}$ , and such a fluidity enhancer is added to the toner in the range of 0.1 to 2.0 percent by weight on the basis of the weight of the entire toner, i.e., the total weight of the toner particles and the fluidity enhancer.

Furthermore, spacer particles having a larger particle diameter than that of the fluidity enhancer are preferably added in the present invention. As the spacer particles, any of organic and inorganic inactive particles with a particle diameter of 0.05 through 1.0  $\mu\text{m}$ , more preferably 0.07 through 0.5  $\mu\text{m}$  can be used. Examples of the material for such inactive particles include silica, alumina, titanium oxide, magnesium carbonate, an acrylic resin, a styrene resin and magnetic materials. The spacer particle can not only work as a fluidity enhancer but also increase the transfer efficiency as described above. As the spacer particle, the same type of magnetic powder as included in the toner particle, in particular, triiron tetroxide (magnetite) in the shape of fine particle is preferably used. The magnetic powder, when used as the spacer particles, effectively suppresses the scattering of the toner as described above. The content of the spacer particles is 10 percent by weight or less, more preferably in the range of 0.1 to 10 percent by weight, and most preferably 0.1 to 5 percent by weight on the basis of the total weight of the toner. When the spacer particles are excessively included in toner, the density of a copied image is insufficient. When the magnetic powder is used as the spacer particles, the total amount of the magnetic powder together with that contained in the toner particles is preferably 10 parts by weight or less per 100 parts by weight of the binder resin. When it is excessively included, the density of a copied image can be decreased.

When the fluidity enhancer and the spacer particles are added to the toner particles, the following production method is preferred. The fluidity enhancer and the spacer particles are first sufficiently mixed with each other, and then the obtained mixture is added to the toner particles, and then is sufficiently unbound. Thus, the spacer particles can be

attached onto the surfaces of the toner particles. To "be attached" herein means both to be held in contact with the surface of the toner particle and to be partly embedded in the toner particle. In this manner, the toner used in the method of the present invention is produced.

5 (Preparation of the developer)

A two-component type developer is prepared by mixing the above-mentioned toner and magnetic carrier.

10 Ferrite particle, in particular spherical soft ferrite particle which contains at least one metal selected from the group of Cu, Mg, Mn and Ni in addition to Fe, such as sintered Cu-Zn-Mg-ferrite particle, is preferably used as the magnetic carrier. A surface of the carrier particle may be coated or not coated with organic materials. Preferably, the surface of the carrier is coated with silicone resin (polysiloxane), fluorine contained resin, epoxy resin, amino resin, urethane resin. The particle diameter of the carrier particle is in the range of 30 to 200  $\mu\text{m}$ , and preferably 50 to 150  $\mu\text{m}$ . The carrier particle has a saturation magnetization in the range between 30 and 70 emu/g, and preferably 45 and 65 emu/g. The mixing ratio of the carrier and the toner is generally 98:2 through 90:10, and preferably 97:3 through 94:6, by weight.

15 (Image forming method)

Next, an image forming method according to the present invention will be described.

20 Figure 10 is a schematic view of an image forming apparatus preferably used for effecting an image forming method according to the present invention.

The image forming apparatus includes an image carrier (photosensitive body) 32 on which an electrostatic latent image is to be formed. The image carrier 32 is formed of a rotatable drum and is surrounded by a corona charger 35, an exposure optical system 36, a developing device 34, an electrostatic transfer device 37, and a cleaning device 31 having a blade provided in this order in the direction of arrow A. The image forming apparatus further includes a binding device 39 formed of a pair of heating rollers for binding the image by heat in contact with the transfer paper sheet.

The image forming apparatus having the above-described structure operates in the following manner.

30 A surface of the image carrier 32 is uniformly charged by the corona charger 35 and exposed by the exposure optical system 36, thus forming an electrostatic latent image corresponding to an original document (not shown). The electrostatic latent image is developed into a toner image by the developing device 34. The toner image is transferred on a transfer paper sheet 38 by the electrostatic transfer device 37, and the image on the transfer paper sheet 38 is bound with heat by the binding device 39. After the image carrier 32 passes the electrostatic transfer device 37, the blade of the cleaning device 31 slides on the surface of the image carrier 32 to scrape off the residual toner. Then, the surface of the image carrier 32 is again charged by the corona charger 35.

35 The image forming apparatus further includes a toner recycle system B for recycling the toner recovered by the cleaning device 31. The toner recycle system B supplies the recovered toner to a tank 34b of the developing device 34 together with toner which is newly supplied from a toner tank 33. In Figure 10, the dashed line indicates the flow of the toner.

40 Figure 11 shows an example of a toner recycle system. The toner recycle system includes a developing device 41, a cleaning device 42, a toner distributor 43, a magnetic brush 44, an image carrier 45, a screw conveyor 46, a first screw 47, and a second screw 48. In such a structure, toner from the screw conveyor 48 is supplied to the toner distributor 43 by the first screw 47 and the second screw 48. In detail, the first and the second screws 47 and 48 each have a rotating shaft and a spiral blade provided along the shaft. The toner supplied by the screw conveyor 46 is sequentially pushed up by the blade in accordance with the rotation of the shaft and thus is sent to the second screw 48. The second screw 48 horizontally conveys the toner sequentially to the toner distributor 43 by the same principle with the first screw 47. In this manner, the recovered toner is supplied to the developing device 41 and is used for the development of an electrostatic latent image on the image carrier 45.

### Examples

50 The present invention will now be described by way of examples. It is noted that the invention is not limited to these examples.

55

(Example 1)

Table 1 Components of toner particle

component	Parts by weight
Binder resin <sup>a)</sup>	100
Coloring agent: Carbon black	8
Magnetic powder: Magnetite	2

<sup>a)</sup> The binder resin used in this example was a styrene-acrylic copolymer having a carboxyl group (wherein the weight ratio among styrene, butyl methacrylate, acrylic acid was 70:28:2).

The above listed components were fused and kneaded with a biaxial extruder, and the resultant was crushed with a jet mill, and classified with a pneumatic classifier to give toner particles with an average particle diameter of 10.0  $\mu\text{m}$ .

To the obtained toner particles were added 0.3 part by weight of hydrophobic silica fine powder with an average particle diameter of 0.015  $\mu\text{m}$  as a fluidity enhancer on the basis of 100 parts by weight of the toner particles. The resultant mixture was mixed with a Henschel mixer for two minutes to give toner.

(Example 2)

To the toner particle obtained in Example 1 were added 0.5 parts by weight of acrylic resin particles with an average particle diameter of 0.3  $\mu\text{m}$  and 0.3 part by weight of hydrophobic silica fine powder with an average particle diameter of 0.015  $\mu\text{m}$  on the basis of 100 parts by weight of the toner particles. The resultant mixture was mixed with a Henschel mixer for two minutes to give toner.

(Comparative Example 1)

The same procedure was repeated as in Example 1 except that an azo dye - chrome complex was further added to components listed in Table 1 of Example 1.

[Evaluation of the method for developing an electrostatic latent image]

Obtained toners in Examples 1, 2 and Comparative example 1 and carrier were homogeneously mixed to give a two-component type developer having a toner concentration of 3.5 wt%. Then, the obtained developers were evaluated with regard to the following items.

For the tests described below, a copying machine (manufactured by Mita Industrial Co., Ltd.; brand name: DC-4685) was used after being modified to include a toner recycle system as shown in Figure 10.

(a) Image density (I.D.):

A copying operation was continued by using an original bearing characters with a black area ratio of 8% until 50,000 copies were made with regard to the developers of Examples 1 and 2 and Comparative Example 1. The density of a black portion in a copied image on every 5000 copies was measured by a reflection densitometer (manufactured by Tokyo Denshoku Co., Ltd.; TC-6D), and the average density was taken as an image density (I.D.). An original used for sampling every 5000 copies had a black area ratio of 15% including a black solid portion. The results obtained from the developers of Examples 1 and 2 and Comparative Example 1 are listed in Table 2.

(b) Fog density (F.D.):

A copying operation was continued by using an original bearing characters with a black area ratio of 8% until 50,000 copies were made with regard to the developers of Examples 1 and 2 and Comparative Example 1. The

## EP 0 701 178 A1

density of a white portion in a copied image on every 5000 copies was measured by the reflection densitometer (manufactured by Tokyo Denshoku Co., Ltd.; TC-6D). A difference between the thus measured density and the density of paper to be used for the copying operation (base paper) measured by the reflection densitometer was calculated, and the maximum difference was taken as a fog density (F.D.). An original used for sampling every 5000 copies had a black area ratio of 15% including a black solid portion. The results obtained from the developers of Examples 1 and 2 and Comparative Example 1 are listed in Table 2.

(c) Charge amount:

A copying operation was continued by using an original bearing characters with a black area ratio of 8% until 50,000 copies were made with regard to the developers of Examples 1 and 2 and Comparative Example 1. During this copying operation, after making every 5,000 copies, the charge amount of 200 mg of the developer was measured by a blowoff type powder charge amount measuring device (manufactured by Toshiba Chemical Co., Ltd.), and the average of the charge amount per 1 g of the toner was calculated based on the measured value. The results obtained from the developers of Examples 1 and 2 and Comparative Example 1 are listed in Table 2.

(d) Amount of attachment on the surface of the carrier particle due to the spent:

A copying operation was conducted by using an original bearing characters with a black area ratio of 8%. After making 50,000 copies, the developer was tested as follows: The developer was placed on a screen of 400 mesh, and sucked from the below with a blower, thereby separating the toner and the carrier. Five g of the carrier remained on the screen was charged in a beaker, to which toluene was added. Thus, the toner component attached onto the surfaces of the carrier particles due to the spent was dissolved. Then, the toluene solvent was discarded with the carrier attracted upon the bottom of the beaker with a magnet. This procedure was repeated several times until the resultant toluene solution became transparent. Then, the resultant carrier was heated with an oven to evaporate the toluene attached thereto, and the weight of the obtained residue was measured. A difference between the weight of the carrier charged in the beaker at first (i.e., 5 g in this case) and the weight of the residue after evaporating the toluene was taken as the amount of the toner components attached onto the surfaces of the carrier particles due to the spent (i.e., the spent amount). The spent amount is indicated as the weight in mg of the toner components attached to 1 g of the carrier. The results obtained from the developers of Examples 1 and 2 and Comparative Example 1 are listed in Table 2.

(e) Toner scattering:

A copying operation was continued by using an original bearing characters with a black area ratio of 8% until 50,000 copies were made. Then, the toner scattering state in the copying machine was visually observed and evaluated. The results obtained from the developers of Examples 1 and 2 and Comparative Example 1 are listed in Table 2. In these tables, ○ indicates that the toner was not scattered; and × indicates that the toner was scattered.

Table 2

Toner component and Evaluation of developers of Example 1 and 2 and Comparative Examples.			
	Example 1	Example 2	Comparative Example 1
Toner component (parts by weight)			
Bainder resin	100	100	100
Carbon black	8	8	8
Magnetic powder	2	2	2
Charge control agent	none	none	2
Additive 1 (silica;0.015μm)	0.3	0.3	0.3
Additive 2 (acrylic resin;0.30μm)	none	0.5	none
Results of evaluation			
I.D.	1.373	1.382	1.371
F.D.	0.005	0.005	0.021
Toner scattering	○	○	×
Spent amount (mg)	0.69	0.65	1.92
Charge amount (μC/g)	-20.5	-20.3	-15.1

[Review of the evaluation]

5 The toners produced in Examples 1 and 2 were stable in a satisfactory state in the image density, the fog density, and the charge amount, from the start of the copying until after 30,000 images were reproduced. In the case of the toner produced in comparative example 1, generation of a spent, toner scattering due to the reduction in the charge amount, and increase of the fog occurred.

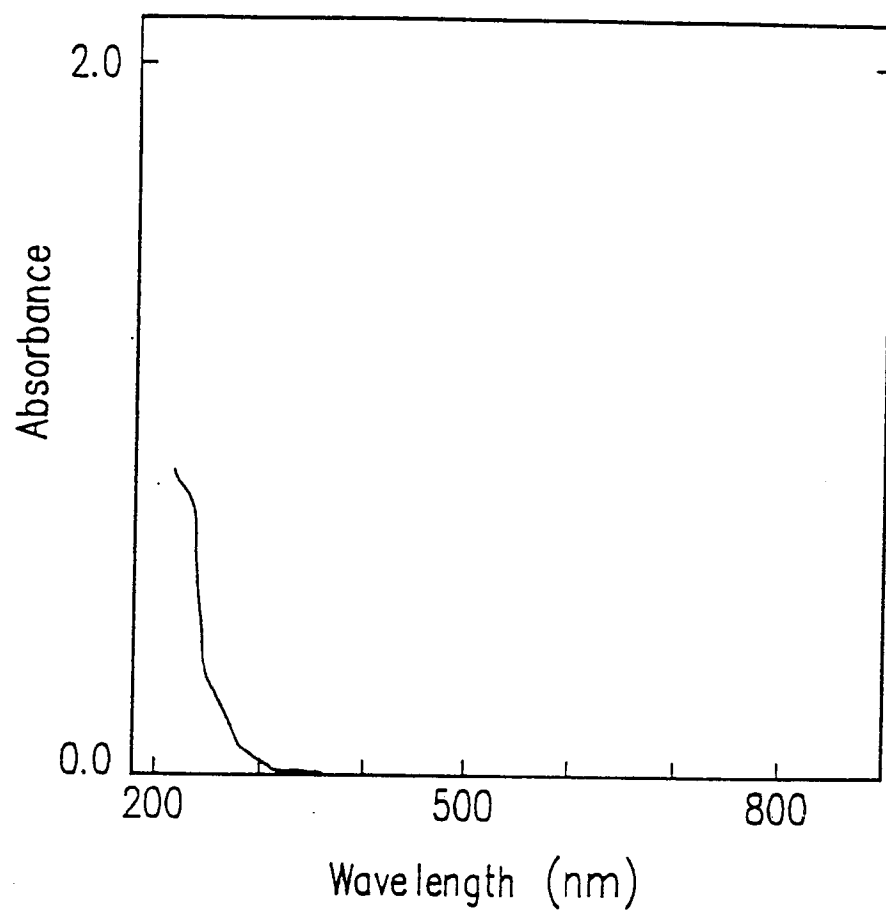
10 According to the present invention, an image forming method using toner containing no charge control agent which is a main cause of the spent during copying is provided. Toner particles of the toner according to the present invention contain a binder resin having an anionic group and also contain a magnetic powder at a predetermined ratio. As necessary, spacer particles having a predetermined particle diameter are attached to the surfaces of the toner particles. Accordingly, the toner has a sufficient chargeability, does not scatter during copying, and has a sufficient transfer efficiency. Due to such advantages, images having a necessary density can be reproduced stably in a long period of time even when the toner is recycled. Such toner for a two-component developer is preferably used in an electrophotographic image forming apparatus including a toner recycle system such as an electrostatic copying machine and a laser printer.

15 Various other modifications will be apparent to and can be readily made by those skilled in the art without departing from the scope and spirit of this invention. Accordingly, it is not intended that the scope of the claims appended hereto be limited to the description as set forth herein, but rather that the claims be broadly construed.

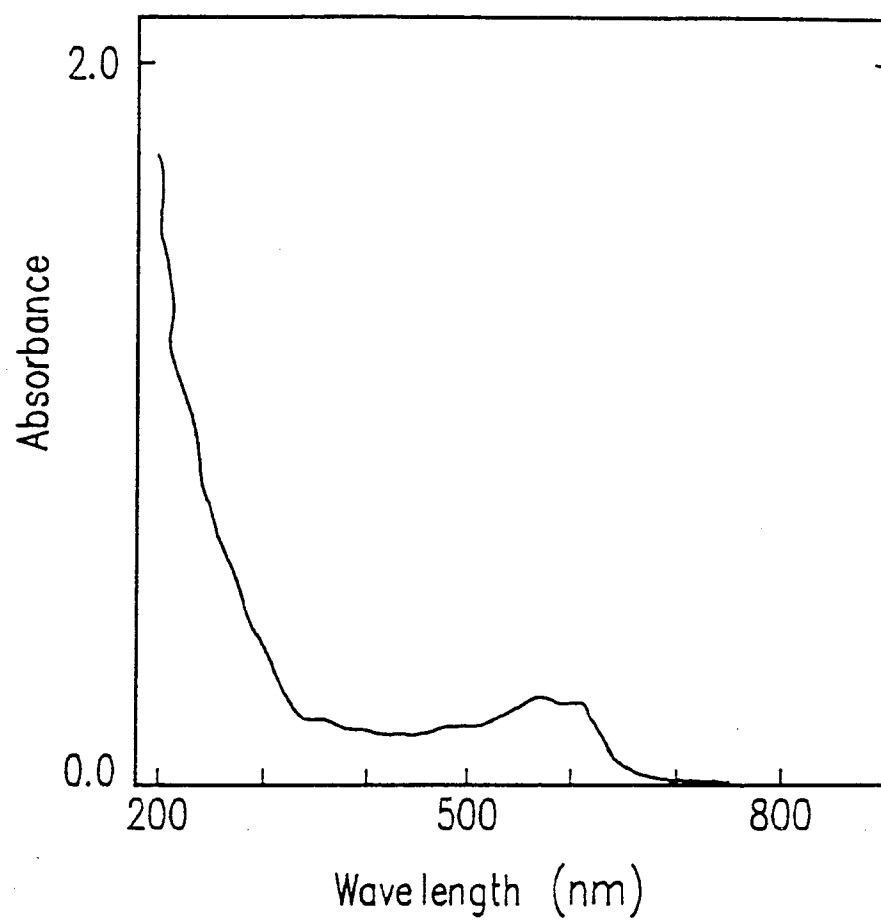
## 20 Claims

- 25 1. An image forming method for allowing toner for a two-component developer to be recycled, wherein:  
toner includes toner particles which contain a binding resin and particles of a magnetic powder dispersed in the binding resin, the magnetic powder being contained in a ratio of 0.1 to 5 parts by weight with respect to 100 parts of the binding resin;  
the binding resin is formed of a composition containing a resin having an anionic group; and  
an extracted solution obtained by extracting the toner with methanol has substantially no absorption peak in the range of 280 to 350 nm, and has a substantially zero absorbance in the range of 400 to 700 nm.
- 30 2. An image forming method according to claim 1, wherein the magnetic powder is contained in a ratio of 0.5 to 3 parts by weight with respect to 100 parts of the binding resin.
- 35 3. An image forming method according to claim 1, wherein the toner particles have a volume-based average particle diameter of 5 through 15  $\mu\text{m}$ , and spacer particles having a volume-based average particle diameter of 0.05 through 1.0  $\mu\text{m}$  are attached onto surfaces of the toner particles.

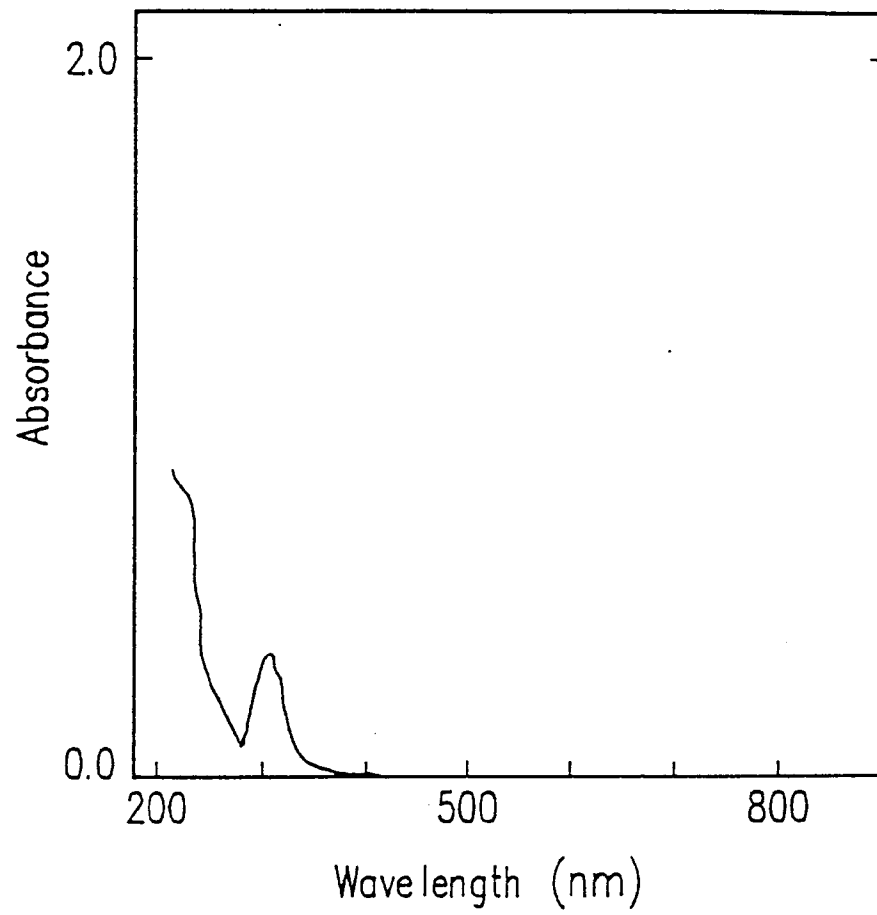
*FIG. 1*



*FIG. 2*



*FIG. 3*



*FIG. 4*

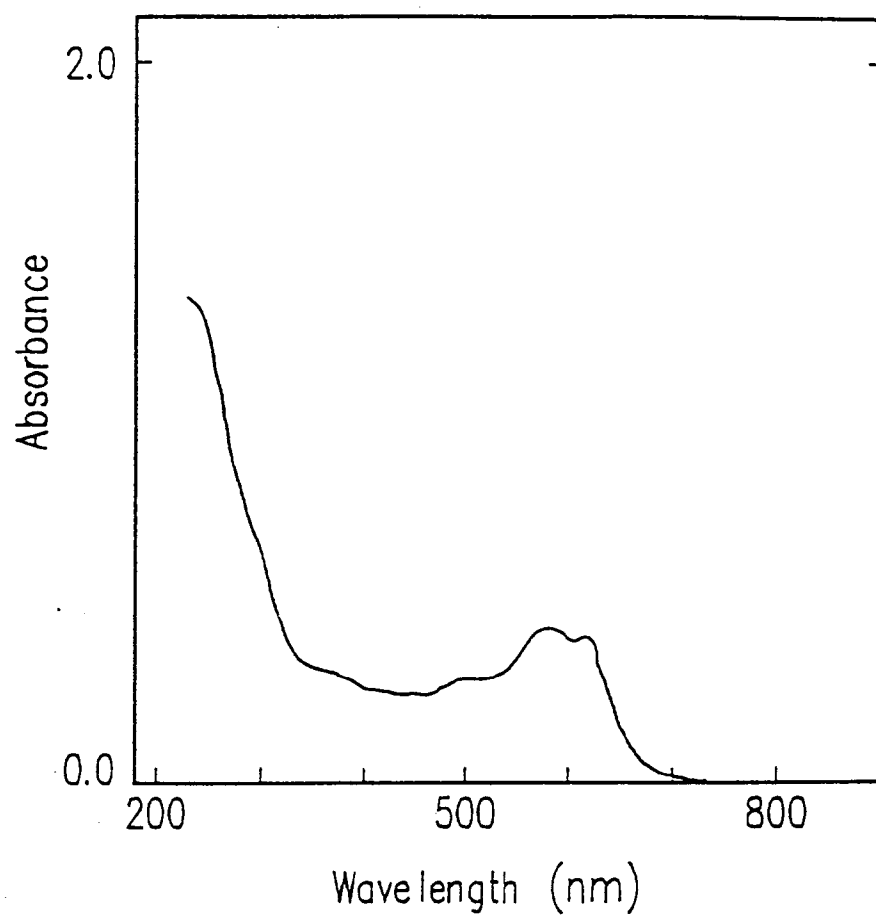


FIG. 5

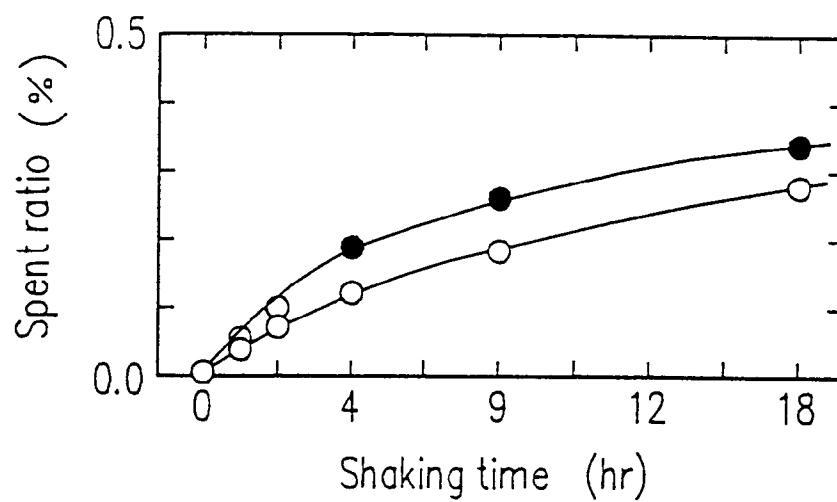


FIG. 6

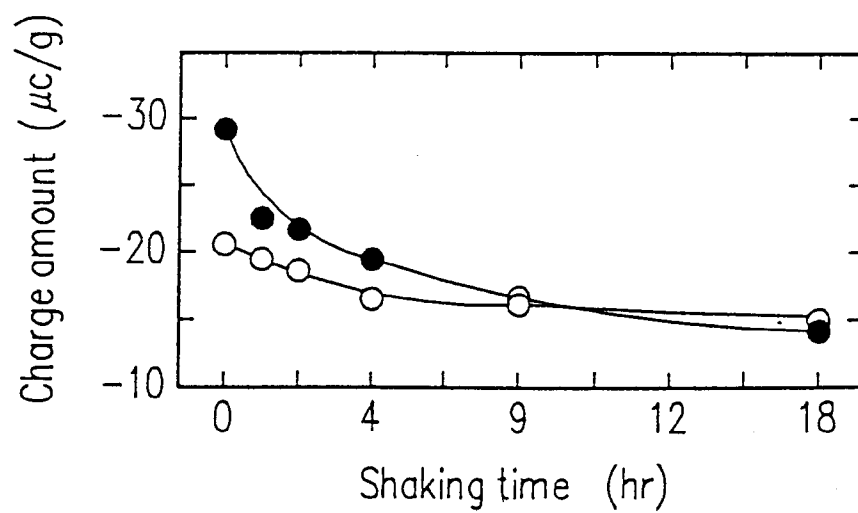


FIG. 7

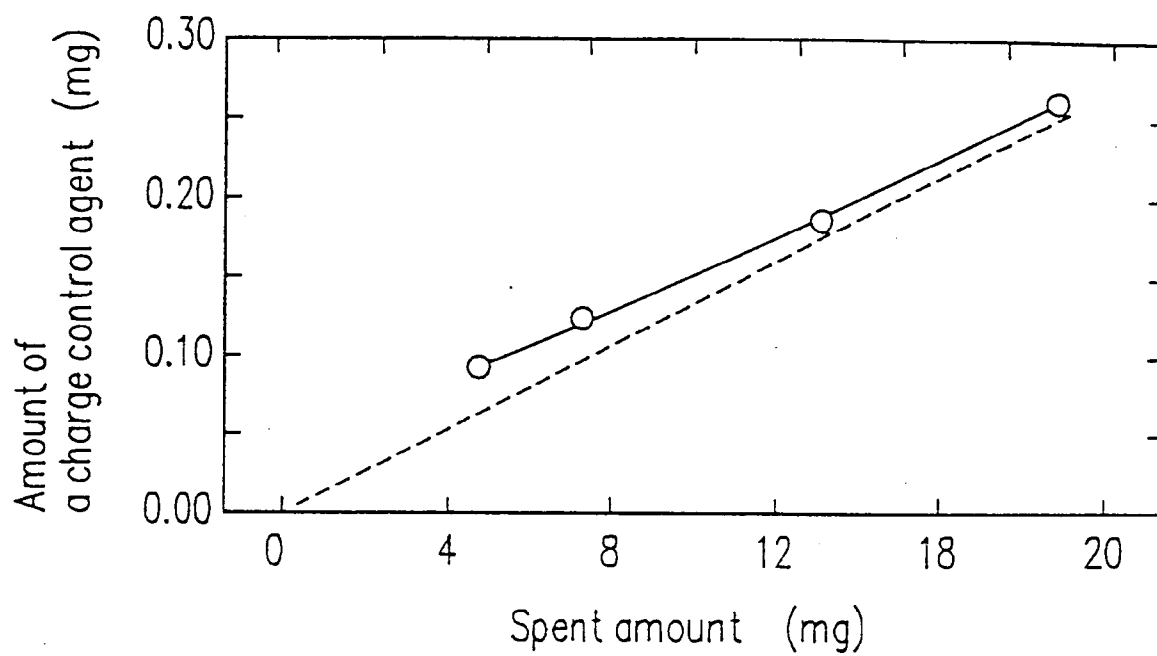


FIG. 8

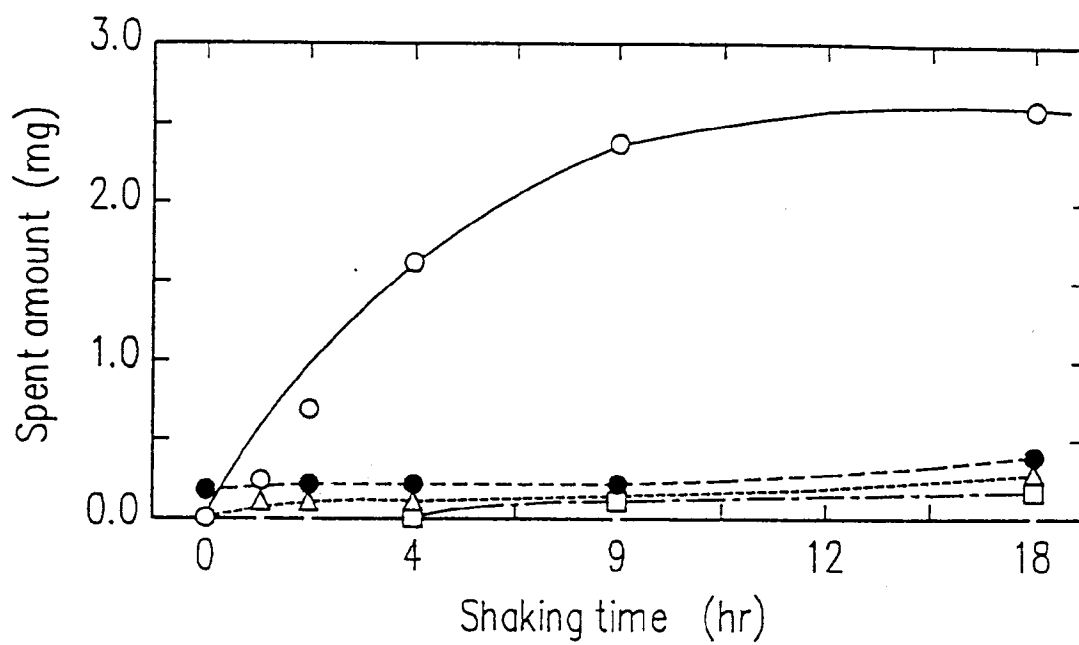


FIG. 9

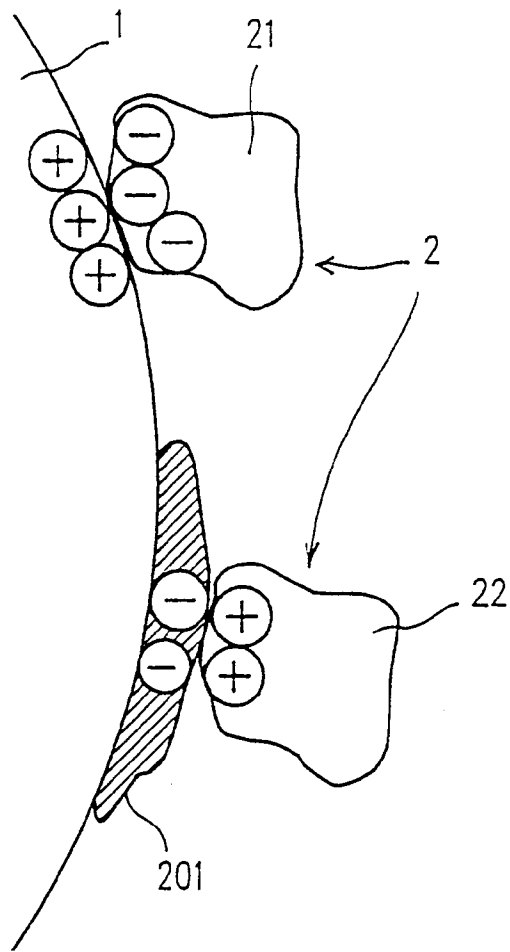


FIG. 10

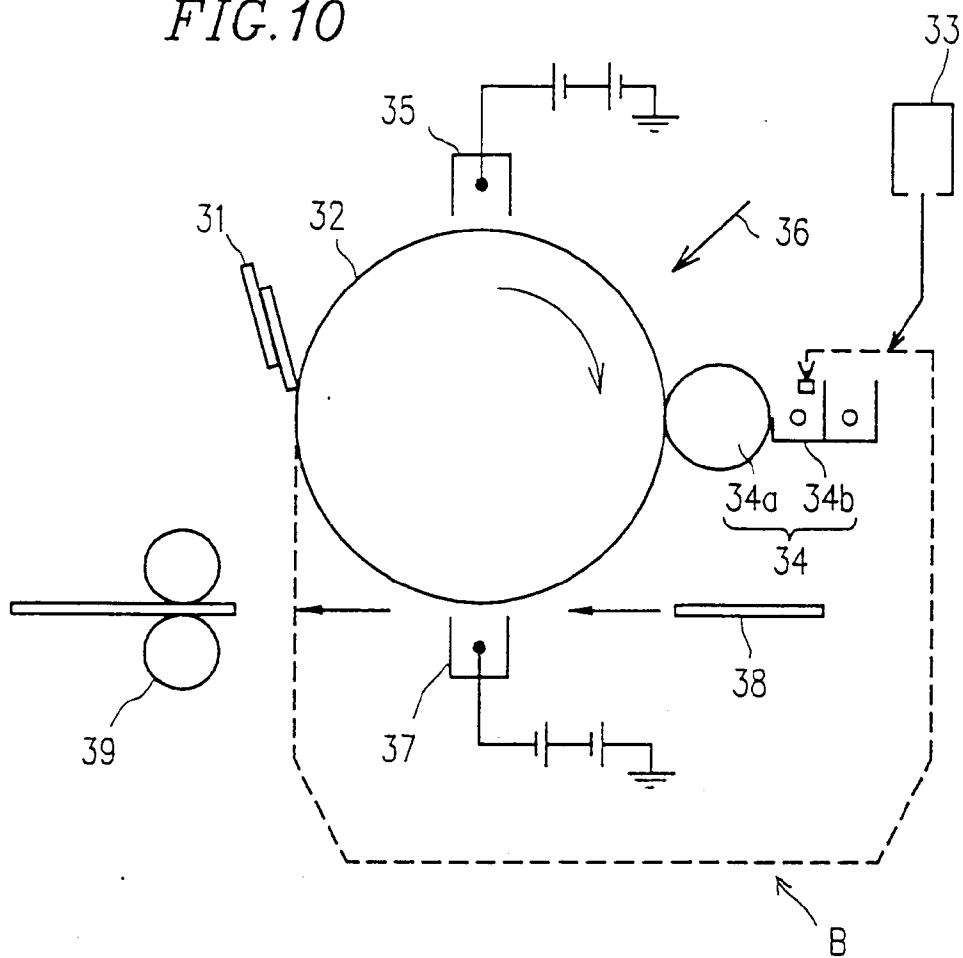
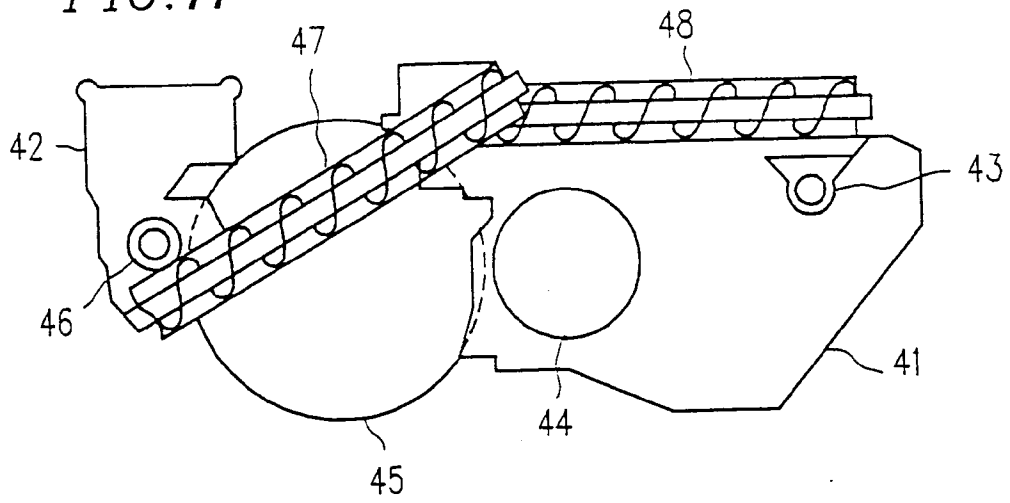


FIG. 11





European Patent  
Office

EUROPEAN SEARCH REPORT

Application Number  
EP 95 30 6127

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)
A	EP-A-0 357 042 (TDK CORP.) * claims 1-6; examples 1-4 * ---	1-3	G03G9/087 G03G9/083 G03G21/10
A	PATENT ABSTRACTS OF JAPAN vol. 9 no. 120 (P-358) [1843] ,24 May 1985 & JP-A-60 004950 (CANON) 11 January 1985, * abstract *	1-3	
A	EP-A-0 407 604 (MITA) * page 12, line 7 - page 17, line 10; claim 4 * * page 26, line 11 - line 22; examples 1-6 *	1-3	
A	EP-A-0 573 933 (CANON) * page 15, line 35 - line 38; figure 3 *	1-3	
P,X	EP-A-0 643 337 (MITA) * claims 1,2 *	1-3	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			G03G
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 21 December 1995	Examiner Vanhecke, H
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	

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