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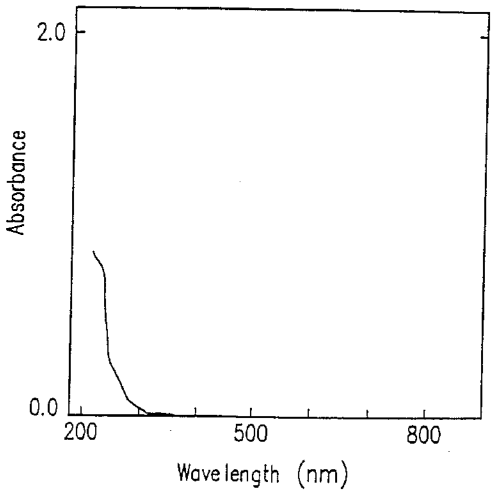
(54) Toner for a two-component type developer

(57) The invention provides toner for a two-component type developer containing toner particles including a fixing resin, magnetic powder dispersed in the fixing resin and a releasing agent. The fixing resin contained in the toner is made of a composition including at least one of the following: (1) a copolymer obtained from a monomer having an anionic group and a monomer having an alkyl group containing 12 or more carbon atoms at the side chain, or a mixture thereof with other monomers; and (2) a mixture of a polymer obtained from a monomer having an anionic group or a a mixture of the monomer having an anionic group with other monomers, and a polymer obtained from a monomer having an alkyl group containing 12 or more carbon atoms at the side chain or an a mixture of the monomer having an alkyl group containing 12 or more carbon atom with other monomers. The magnetic powder is contained in the toner particles in the range between 0.1 and 5 parts by weight per 100 parts by weight of the fixing resin.

FIG.1



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Description

1. Field of the Invention:

The present invention relates to toner for a two-component type developer used for electrophotography. More particularly, the present invention relates to toner, which does not include a charge control agent, suitably used in an electrophotographic image forming apparatus such as an electrostatic copying machine and a laser beam printer.

2. Description of the Related Art:

A two-component type developer is used as one of the developers used for developing an electrostatic latent image on a photosensitive body in an electrophotographic image forming apparatus. The two-component type developer includes toner comprising a binder resin and a coloring agent such as carbon black, and magnetic carrier such as iron powder and ferrite particles.

An electrostatic latent image is developed by the following steps. The developer forms a magnetic brush shape on a developing roller by a magnetic field thereof and is carried out to the photosensitive body. In this step, the toner is charged by friction with the carrier so as to have a desired charge and polarity of charge. Then, the developer is contacted with the photosensitive body by the developing roller, resulting in attaching the toner onto the electrostatic latent image formed thereon. Generally, the toner includes a charge control agent which controls and stabilizes the charge of the toner so as to attach a constant amount of the toner on the electrostatic latent image and provide a good developed image for a long period of time. Negatively charged toner includes a negative charge control agent such as a dye of a metal complex including a metal ion such as chrome(III) (for example, an azo compound - chrome(III) complex), and an oxycarboxylic acid - metal complex (for example, a salicylic acid - metal complex) (Japanese Laid-Open Patent Publication No. 3-67268). Positively charged toner includes a positive charge control agent such as an oil soluble dye including nigrosine and an amine type charge control agent (Japanese Laid-Open Patent Publication No. 56-106249).

Many metal complexes, including a heavy metal ion such as a chrome ion, are used as a conventional charge control agent. They are carefully selected, in terms of environmental safety, so that only those having passed various toxicity tests and safety tests alone are used. Therefore, although they would be safe in themselves or when included in toner, it is more preferable to refrain from using the metal complexes including a heavy metal as the charge control agent. In addition, the charge control agent is expensive as compared with the other materials for toner such as a binder resin and a coloring agent, for example, carbon black. Therefore, although the charge control agent has a content of merely several %, this results in increasing the price of the resultant toner. Accordingly, it is desired to develop toner having no charge control agent of a metal complex.

Furthermore, when conventional toner is used for a long period of time, the toner components tend to attach on a surface of the carrier particle. The attached components are called a spent. The spent makes the carrier charge with the same polarity as the toner, resulting in the disadvantages that the toner can be scattered and transfer efficiency of toner image is decreased.

SUMMARY OF THE INVENTION

The toner for a two-component type developer of the present invention, which overcomes the above-discussed and numerous other disadvantages and deficiencies of the prior art, comprises toner particles including a binder resin, magnetic powder dispersed in the binder resin and a releasing agent. The binder resin is made of a composition including at least one of the following:

(1) a copolymer obtained from a monomer having an anionic group and a monomer having an alkyl group containing 12 or more carbon atoms at the side chain, or a mixture thereof with other monomers; and

(2) a mixture of a polymer obtained from a monomer having an anionic group or a mixture of the monomer having an anionic group with other monomers, and a polymer obtained from a monomer having an alkyl group containing 12 or more carbon atoms at the side chain or a mixture of the monomer having an alkyl group containing 12 or more carbon atoms with other monomers. The magnetic powder is contained in the toner particles in the range between 0.1 and 5 parts by weight per 100 parts by weight of the binder resin.

In one embodiment, an extracted solution obtained by extracting the toner with methanol has substantially no absorption peak in the range between 280 and 350 nm, and has a substantially zero absorbance in the range between 400 and 700 nm.

In one embodiment, the magnetic powder is contained in the range between 0.5 and 3 parts by weight per 100 parts by weight of the binder resin.

In one embodiment, the toner particles have a volume-based average particle diameter of 5 through 15 µm, and spacer particles with a volume-based average particle diameter of 0.05 through 1.0 µm are attached onto surfaces of the toner particles.

Thus, the invention described herein makes possible the advantages of (1) providing toner with excellent chargeability including no charge control agent at all; (2) providing toner little scattered in development for realizing a copied image with a high quality; and (3) providing toner in which a spent is not caused even when used for a long period of time, and hence, by which an excellent image quality can be maintained and transfer efficiency can be stabilized.

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 according to 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 a dye of an azo compound - 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 a dye of an azo compound - 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 kinds of 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 kinds of 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; and

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

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Toner for a two-component type developer according to 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 present toner, resulting in realizing a high quality copied image for a long period of time. Since the toner 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 present toner by any chemical reaction. Alternatively, absorption peaks owing to such a compound cannot be detected in an organic solvent extracted solution of the present toner. For example, when the present toner 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 present toner 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 present toner with 50 ml of methanol are 0.05 or less.

In the present toner, instability of charge of toner due to a lack of a charge control agent is compensated 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 present toner, in order to further enhance the function of the toner, a polymer obtained from a monomer having an alkyl group containing 12 or more carbon atoms as the side chain is used as the binder resin. Therefore, the wax, that is, a release agent is well dispersed and prevented from attaching onto the surfaces of the carrier particles to cause the spent, thereby elongating the life time of the carrier. Furthermore, spacer particles having a desired particle diameter are attached on the surfaces of the toner particles, if necessary, thereby increasing transfer efficiency of the toner.

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

Figure **1** shows an UV-visible spectrum of a methanol extracted solution of the present toner 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 a dye of an azo compound - 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. Furthermore, 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 a dye of an azo compound - 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 dye of the azo compound - 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 present toner 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 present toner 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. Moreover, since the number of the toner particles to be attached onto an electrostatic latent image is increased as the charge amount of one toner particle is smaller, apparent development sensitivity is increased.

The content of the magnetic powder in the 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 charge amount of the toner particle is insufficient, resulting in insufficient coupling with the carrier particle and causing toner scattering. In this case, a fog can be disadvantageously formed 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.

In the present toner, the binder resin for the toner particles is made of a polymer obtained from a monomer having an alkyl group containing 12 or more carbon atoms at the side chain. This polymer can be any of the aforementioned resins having an anionic group or another polymer. When transferred image is thermally fixed with heat rollers, the toner particles generally include a releasing agent for preventing the offset of the image onto the transfer paper. Various types of wax and olefin resins can be used as the releasing agent. Such a releasing agent is heated and kneaded together with the binder resin and the magnetic powder in the production process of the toner. A SP value of the releasing agent, however, is different (a solubility parameter value) from that of the generally used binder resin, and hence, the compatibility between the releasing agent and the binder resin is poor. Therefore, the releasing agent cannot be sufficiently dispersed in the resin in the heating and kneading process. As a result, the releasing agent is ununiformly present on the resultant toner particles in the shape of a comparatively large particle, and the particle of the releasing agent is also present on the surface of the toner particle. Accordingly, when such toner particles are used with carrier, the releasing agent is attached onto the surfaces of carrier particles, thereby causing a spent. In the present invention, however, since the binder resin is made of the polymer obtained from a monomer having an alkyl group containing 12 or more carbon atoms at the side chain as described above, the compatibility between the releasing agent and the binder resin is improved. Thus, the problem of the spent can be overcome.

In the present invention, spacer particles having a particle diameter of 0.05 through 1.0 μm 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 μm 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 present toner will be described. Herein, a "lower alkyl group" indicates alkyl group having 1 to 5 carbon atoms.

(Binder resin)

The binder resin contained in the toner particles of the present invention is made of a composition including at least one of the following: (1) a copolymer obtained from a monomer having an anionic group and a monomer having an alkyl group containing 12 or more carbon atoms at the side chain, or a mixture thereof with other monomers; and (2) a mixture of a polymer obtained from a monomer having an anionic group or a mixture of the monomer having an anionic group with other monomers, and a polymer obtained from a monomer having an alkyl group containing 12 or more carbon atoms at the side chain or a mixture of the monomer having an alkyl group containing 12 or more carbon atom with other monomers. The "side chain" of a monomer herein indicates a portion where a side chain of a (co)polymer obtained from the monomer can be formed.

The copolymer including an anionic group and an alkyl group containing 12 or more carbon atoms at the side chain can be obtained through copolymerization using a monomer having an anionic group and a monomer having an alkyl group containing 12 or more carbon atoms at the side chain. The copolymer can be a copolymer obtained from a monomer having an anionic group and a monomer having an alkyl group containing 12 or more carbon atoms at the side chain, or can be a copolymer obtained from these monomers and other monomers. Alternatively, the copolymer can be a mixture of these copolymers.

In the mixture of the polymer obtained from a monomer having an anionic group or a mixture of the monomer having an anionic group with other monomers and the polymer obtained from a monomer having an alkyl group containing 12 or more carbon atoms or a mixture of the monomer having an alkyl group containing 12 or more carbon atom with other monomers, the former polymer can be a homopolymer obtained from the monomer having an anionic group or a copolymer obtained from a monomer having an anionic group and other monomers, or a mixture of such polymers. The latter polymer can be a polymer obtained from the monomer having an alkyl group containing 12 or more carbon atoms at the side chain or a mixture of the monomer having an alkyl group containing 12 or more carbon atom with other monomers or a copolymer obtained from a monomer having an alkyl group containing 12 or more carbon atoms and other monomers, or a mixture of such polymers. Such copolymers can be a random copolymer, a block copolymer or a graft copolymer.

The binder resin used in the present toner preferably comprises the polymer of item (1), that is, a copolymer obtained from a monomer having an anionic group and a monomer having an alkyl group containing 12 or more carbon atoms at the side chain. More preferably, the binder resin used in the present toner comprises the copolymer prepared by polymerizing a monomer having an anionic group, a monomer having an alkyl group containing 12 or more carbon atoms at the side chain 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.

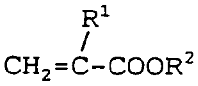
Such a monomer having an anionic group can be a free acid, a salt of an alkaline metal such as sodium and potassium, a salt of an alkaline earth metal such as calcium and magnesium, and a salt such as zinc.

Next, the monomer having an alkyl group containing 12 or more carbon atoms at the side chain will be described in detail. The alkyl group containing 12 or more carbon atoms herein includes an acyclic linear hydrocarbon group, an acyclic branched hydrocarbon group and a cyclic hydrocarbon group.

Examples of the monomer having an alkyl group containing 12 or more carbon atoms at the side chain include an ethylenically unsaturated carboxylic acid ester such as acrylic acid ester and methacrylic acid ester having an alkyl group containing 12 or more carbon atoms linked through an ester bond; a vinyl ester having an alkyl group containing 12 or more carbon atoms linked through an ester bond; a vinyl ether having an alkyl group containing 12 or more carbon atoms linked through an ether bond; a 1-alkene having 14 or more carbon atoms; a monovinyl arene having at least one substituent having an alkyl group containing 12 or more carbon atoms; and a 1,3-alkadiene having at least one alkyl group containing 12 or more carbon atoms. One or a combination of two or more can be used.

The ethylenically unsaturated carboxylic acid ester having an alkyl group containing 12 or more carbon atoms at the side chain is represented by the following Formula (I):

Formula (I):



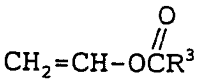
$$CH_2=C(R^1)-COOR^2$$

wherein R^1 is a hydrogen atom or a lower alkyl group; and R^2 is an alkyl group containing 12 or more carbon atoms.

Examples of such an ethylenically unsaturated carboxylic acid ester having an alkyl group containing 12 or more carbon atoms include lauryl acrylate, tridecyl acrylate, stearyl acrylate, docosyl acrylate, dicyclohexylmethyl acrylate, dicyclohexylpropyl acrylate, cyclododecyl acrylate, cycloundecanemethyl acrylate, lauryl methacrylate, tridecyl methacrylate, stearyl methacrylate, docosyl methacrylate, dicyclohexylmethyl methacrylate, dicyclohexylpropyl methacrylate, cyclododecyl methacrylate and cycloundecanemethyl methacrylate.

The vinyl ester having an alkyl group containing 12 or more carbon atoms at the side chain is represented by the following Formula (II):

Formula (II):



$$CH_2=CH-OC(=O)R^3$$

wherein R^3 is an alkyl group containing 12 or more carbon atoms.

Examples of such a vinyl ester include vinyl laurate, vinyl tridecanoate, vinyl stearate, vinyl docosanoate, vinyl triacontanoate, vinyl pentylcyclohexanoate and vinyl dicyclohexylacetate.

The vinyl ether having an alkyl group containing 12 or more carbon atoms at the side chain is represented by the following Formula (III):

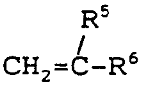
Formula (III): $CH_2=CH-O-R^4$

wherein R^4 is an alkyl group containing 12 or more carbon atoms.

Examples of such a vinyl ether include vinyl lauryl ether, vinyl stearyl ether, vinyl docosyl ether and vinyl cyclododecyl ether.

The 1-alkene having 14 or more carbon atoms is represented by the following Formula (IV):

Formula (IV):



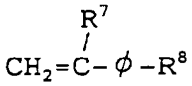
$$CH_2=C(R^5)-R^6$$

wherein R^5 and R^6 are independently a hydrogen atom or an alkyl group containing 12 or more carbon atoms.

Examples of such a 1-alkene include 1-tetradecene and 1-eicocene.

The monovinyl arene having at least one substituent having an alkyl group containing 12 or more carbon atoms is represented by the following Formula (V):

Formula (V):



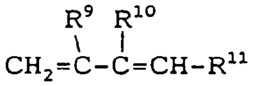
$$CH_2=\overset{R^7}{C}-\phi-R^8$$

wherein R^7 is a hydrogen atom, a lower alkyl group, an alkyl group containing 12 or more carbon atoms or a halogen atom; R^8 is an alkoxy group, an amino group, a nitro group or an alkyl group containing 12 or more carbon atoms; and ϕ is a phenylene group. The phenylene group can include another substituent such as a lower alkyl group, a halogen atom, an alkoxy group, an amino group, a nitro group and an alkyl group containing 12 or more carbon atoms. The alkyl group containing 12 or more carbon atoms can be linked via an ester bond, a (thio)ether bond or an amido bond.

Examples of such a monovinyl arene include m-raulylstyrene, p-raulylstyrene, m-stearylstyrene, p-stearylstyrene, α-methyl-3-stearylstyrene, m-stearoxystyrene, p-stearoxystyrene, stearyl 4-vinylbenzoate and 4-stearoylaminostyrene.

The 1,3-alkadiene having an alkyl group containing 12 or more carbon atoms is represented by the following Formula (VI):

Formula (VI):



$$CH_2=\overset{R^9}{C}-\overset{R^{10}}{C}=CH-R^{11}$$

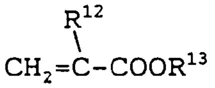
wherein R^9, R^{10} and R^{11} are independently a hydrogen atom, a lower alkyl group, an alkyl group containing 12 or more carbon atoms or a halogen atom.

Examples of such a 1,3-alkadiene include 1,3-hexadecadiene, 1,3-docosadiene and 2-methyl-1,3-docosadiene.

The other monomer that is polymerized with the monomer having an anionic group and/or the monomer having an alkyl group containing 12 or more carbon atoms at the side chain, if necessary, is selected so that the resultant polymer can attain a sufficient fixability and chargeability required of toner, and is prepared from one or a combination of two or more of monomers including an ethylenically unsaturated bond. Examples of such a monomer include ethylenically unsaturated carboxylic acid esters, monovinyl arenes, vinyl esters, vinyl ethers, diolefins and monoolefins.

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

Formula (VII):



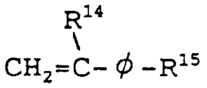
$$CH_2=\overset{R^{12}}{C}-COOR^{13} \qquad (VII)$$

wherein R^{12} is a hydrogen atom or a lower alkyl group; and R^{13} 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, β-hydroxyethylacrylate, γ-hydroxypropylacrylate, δ-hydroxybutylacrylate and β-hydroxyethylmethacrylate.

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

Formula (VIII):



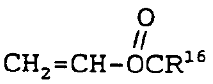
$$CH_2=\overset{R^{14}}{C}-\phi-R^{15} \qquad (VIII)$$

wherein R^{14} is a hydrogen atom, a lower alkyl group or a halogen atom; R^{15} is a hydrogen atom, a lower alkyl group, a halogen atom, an alkoxy group, an amino group or a nitro group; and ϕ is a phenylene group.

Examples of such monovinyl arenes include styrene, α-methylstyrene, vinyltoluene, α-chlorostyrene, o-chlorostyrene, m-chlorostyrene, p-chlorostyrene and p-ethylstyrene.

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

Formula (IX):



$$CH_2=CH-O\overset{O}{\overset{\|}{C}}R^{16} \qquad (IX)$$

wherein R^{16} is a hydrogen atom or a lower alkyl group.

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

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

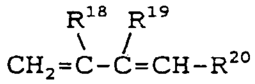
Formula (X): $CH_2=CH\text{-}O\text{-}R^{17}$ (X)

wherein R^{17} is a monovalent hydrocarbon group having 11 or less carbon atoms.

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 (XI):

Formula (XI):



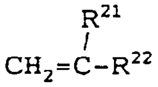
$$CH_2=\overset{R^{18}}{C}-\overset{R^{19}}{C}=CH-R^{20} \qquad (XI)$$

wherein R^{18}, R^{19} and R^{20} are independently a hydrogen atom, a lower alkyl group or a halogen atom.

Examples of such diolefins include butadiene, isoprene and chloroprene.

The monoolefins are represented by the following Formula (XII):

Formula (XII):



$$CH_2=\overset{R^{21}}{C}-R^{22} \qquad (XII)$$

wherein R^{21} and R^{22} 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.

Examples of the polymer obtained from a monomer having an anionic group and/or a monomer having an alkyl group containing 12 or more carbon atoms at the side chain or a mixture of the monomer having an alkyl group containing 12 or more carbon atom with other monomers include (meth)acrylic acid-stearyl (meth)acrylate copolymers, styrene-stearyl (meth)acrylate-(meth)acrylic acid copolymers, styrene-(meth)acrylate-stearyl (meth)acrylate-(meth)acrylic acid copolymers, styrene-stearyl (meth)acrylate-maleic acid copolymers, maleic acid-stearyl (meth)acrylate copolymers, styrene-tridecyl (meth)acrylate-(meth)acrylic acid copolymers, and styrene-lauryl (meth)acrylate-(meth)acrylic acid copolymer. Further more, a polyester resin having an anionic group can be also used. It is preferable that such a composition includes the anionic group preferably at a proportion for attaining an acid value of 2 through 30, 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 contained preferably at such a proportion that the acid value would be within the aforementioned range in assuming that it is present as a free acid. When the acid value of the polymer, i.e., the concentration of the anionic group, is below the aforementioned range, the chargeability of the resultant toner is insufficient. When it exceeds the range, the resultant toner disadvantageously has a hygroscopic property. Furthermore, the monomer having an alkyl group containing 12 or more carbon atoms at the side chain is contained in the range of 0.1 to 20 parts by weight, more preferably 0.5 to 10 parts by weight, and most preferably 1 to 5 parts by weight per 100 parts by weight of the entire monomers. When the content of the monomer having an alkyl group containing 12 or more carbon atoms is below the aforementioned range, the compatibility between the releasing agent and the binder resin is so poor that the spent is caused with ease. When it exceeds the range, the Tg of the binder resin is too low to achieve sufficient storage stability.

A preferable binder resin is obtained from any of the aforementioned monomers having an anionic group and at least one of the ethylenically unsaturated carboxylic acid esters represented by Formula (I), and any of the monomers represented by Formulae (II) through (VI) can be optionally copolymerized, if necessary. Other monomers can be coplymerized, if necessary. The resin is obtained from one or a combination of two or more of the aforementioned monomers.

The binder resin used in the present toner is made of a composition including one of the aforementioned copolymers or the mixture of the copolymers, and can further include a polymer having neither an anionic group nor an alkyl group containing 12 or more carbon atoms as well. In this case, the contents of the anionic group and the alkyl group containing 12 or more carbon atoms are preferably within the aforementioned ranges, respectively.

(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_3O_4), maghemite (γ-Fe_2O_3), zinc iron oxide ($ZnFe_2O_4$), yttrium iron oxide ($Y_3Fe_5O_{12}$), cadmium iron oxide ($CdFe_2O_4$), gadolinium iron oxide ($Gd_3Fe_5O_{12}$), copper iron oxide ($CuFe_2O_4$), lead iron oxide ($PbFe_{12}O_{19}$), nickel iron oxide ($NiFe_2O_4$), neodyum iron oxide ($NdFeO_3$), barium iron oxide ($BaFe_{12}O_{19}$), magnesium iron oxide ($MgFe_2O_4$), manganese iron oxide ($MnFe_2O_4$), lanthanum iron oxide ($LaFeO_3$), 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 preferable magnetite is in the shape of a regular octahedron with a particle diameter of 0.05 through 1.0 µm. 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 µm or smaller, and preferably 0.05 through 1.0 µm.

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 and the transfer efficiency of the toner can be decreased as described above.

(Releasing agent)

A releasing agent is one of an additive included in toner particles. In the present toner, for example, various types of natural or synthetic wax and olefin resins having a molecular weight of 2,000 through 16,000, preferably 3,000 through 6,000 can be used as the releasing agent. Examples of the olefin resin include polypropylene, polyethylene, and propylene-ethylene copolymers, and polypropylene is particularly preferred. The content of the releasing agent is in the range of 0.01 to 6 parts by weight, more preferably 0.1 to 5 parts by weight on the basis of 100 parts by weight of the binder resin. Such a releasing agent works to prevent the offset of an image in the thermal fixing process. When the content is smaller than 0.01 part by weight, the preventive effect on offset in the thermal fixing process can be insufficient, and when it exceeds 6 parts by weight, a spent is likely to be caused.

(other additives in the toner particles)

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 percent by weight, and preferably 5 to 15 parts by weight per 100 parts by weight of the binder resin.

(Preparation of the toner)

The toner particles in the present toner 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 of 5 to 15 µm and preferably 7 to 12 µm in the volume-based average 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 depositioned 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 µm, 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 µm, more preferably 0.07 through 0.5 µm 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 of the present invention is produced.

(Carrier particle)

In the present invention, generally used magnetite or ferrite can be used as a carrier for the two-component type developer. In such a compound, the electrical resistance is little varied with time or by the change of the environment, and hence, it can provide the resultant developer with a stable chargeability. Furthermore, such a compound is formed into a soft spicated shape in the developing apparatus when a magnetic field is applied. This prevents the turbulence of a toner image formed on the photosensitive body, thereby suppressing the formation of a white stripe in a copied image.

In the present invention, the carrier is charged preferably by allowing a resin having a cationic group to be contained in a coating layer of the carrier particle. Therefore, when this carrier is combined with toner including no charge control agent, the chargeability of the toner is remarkably improved, thereby stabilizing the chargeability of the toner. Furthermore, since the present toner does not include a charge control agent as the conventional developer does, the resultant developer can attain a longer life time by effectively preventing the spent from occurring on the carrier particles.

The carrier particle in the carrier used in the present invention is more preferably formed from a particle having a two-layered structure including a core particle and a coating layer over the core particle. The core particle comprises a magnetic material represented by the following Formula (A):

$$MOFe_2O_3 \qquad (A)$$

wherein M is at least one metal selected from the group consisting of Cu, Zn, Fe, Ba, Ni, Mg, Mn, Al and Co.

The compound represented by Formula (A) is magnetite (wherein M is Fe) or ferrite (wherein M is one of the metals other than Fe), and ferrite, wherein M is Cu, Zn, Mn, Ni or Mg, is preferably used. Change of the electrical resistance of such magnetite and ferrite is little for a long time, and the magnetite and ferrite can be formed into a soft spicated shape in the developing apparatus when a magnetic field is applied. The core particle comprising such a magnetic material has a particle diameter between 30 and 200 μm, and preferably between 50 and 150 μm. The core particles are obtained by granulating the fine particles of the magnetic material by spray granulation and the like, and then heating the resultant particles. The core particle has a volume specific resistivity between 10^5 and 10^9 Ω·cm, and preferably between 10^6 and 10^8 Ω·cm. The saturation magnetization of the core particle is in the range of 30 to 70 emu/g, and preferably between 45 and 65 emu/g.

The resin having a cationic group included in the resin composition, which forms the coating layer of the carrier particle, can be a thermoplastic resin and a thermosetting resin, and is preferably a thermosetting resin or a mixture of a thermosetting resin and a thermoplastic resin in terms of the heat resistance and the durability. Examples of the cationic group include a basic nitrogen containing group such as primary, secondary and tertiary amino groups, a quaternary ammonium group, an amido group, an imino group, an imido group, a hydrazino group, a guanidino group and an amidino group, among which an amino group and a quaternary ammonium group are particularly preferred.

Examples of the thermoplastic resin having a cationic group include thermoplastic acrylic resins, thermoplastic styrene-acrylic resins, polyester resins, polyamide resins and olefin copolymer, each of which includes a cationic group. Examples of the thermosetting resin include modified and unmodified silicone resins, thermosetting acrylic resins, thermosetting styrene-acrylic resins, phenol resins, urethane resins, thermosetting polyester resins, epoxy resins and amino resins, each of which includes a cationic group. Such a resin including a cationic group is obtained by polymerizing a monomer having a cationic group or a mixture containing the monomer having a cationic group. Alternatively, such a resin is obtained by linking a compound having a cationic group with a resin having no cationic group. Furthermore alternatively, a monomer having a cationic group and/or other monomers are (co)polymerized by using a polymerization initiator having a cationic group, thereby introducing the cationic group into the resultant resin.

When a resin prepared from alkoxysilane or alkoxytitanium is used, it is possible to produce the resin having a cationic group by allowing a silane coupling agent having a cationic group to react with the resin during or after the preparation of the resin. Examples of the silane coupling agent include N-(2-aminoethyl)-3-aminopropyltrimethoxysilane, N-(2-aminoethyl)-3-aminopropylmethyldimethoxysilane, γ-aminopropyltriethoxysilane and N-phenyl -3-aminopropyltrimethoxysilane. This type of silane coupling agent can be linked onto the surface of the core particle via a hydroxyl group generally present on the surface of the core particle. Therefore, such a silane coupling agent can form the coating layer by itself. Examples of the polymerization initiator having a cationic group include amidine type compound, e.g., azobis compounds.

The resin having a cationic group for forming the coating layer is used singly or together with any other of the aforementioned resins, or together with another resin having no cationic group.

The content of the cationic group in the resin having a cationic group is generally in the range of 0.1 to 2000 mmole, and preferably of 0.5 to 1,500 mmole per 100 g of the resin. When the resin having a cationic group is used with a resin having no cationic group, the cationic group is preferably contained in the entire resins forming the coating layer of the carrier particle at a proportion in the aforementioned range.

The resin composition forming the coating layer of the carrier particle includes at least one of the above-mentioned resins having a cationic group, together with another resin having no cationic group, if necessary. Examples of a mixture of the resin having a cationic group and the resin having no cationic group include a mixture of an alkylated melamine resin and a styrene-acrylic copolymer, and a mixture of an alkylated melamine resin and an acryl-modified silicone resin. The resin composition can further comprise an additive such as silica, alumina, carbon black, fatty acid metal salt, a silane coupling agent and silicone oil. These additives work for regulating physical properties of the coating layer.

(Preparation of the carrier)

The resin composition including a cationic group is applied to the surface of the core particle by a known method to form the coating layer. For example, the core particle is coated with a solution or a dispersion of the resin composition and dried, thereby forming the coating layer. Alternatively, when a thermosetting resin or a reactive resin oligomer is used, the core particle is coated with an uncured resin, or a solution or a dispersion of the oligomer, and then heated to cure the resin. The coating layer can be formed by any of the generally used methods such as immersion, spray, a fluidized bed method, a moving bed method and a tumbling layer method. As a solvent used to dissolve or disperse the resin composition, any of the ordinary organic solvents can be used. Examples of the solvent include aromatic hydrocarbons such as toluene and xylene; ketones such as acetone, methyl ethyl ketone, methyl isobutyl ketone and cyclohexanone; cyclic ethers such as tetrahydrofuran and dioxane; alcohols such as ethanol, propanol and butanol; cellosolves such as ethyl cellosolve and butyl cellosolve; esters such as ethyl acetate and butyl acetate; and amide type solvents such as dimethylformamide and dimethylacetoamide. The solvent is appropriately selected in accordance with the chemical properties of the resin such as the solubility.

The particle diameter of the thus obtained carrier particle is in the range of 30 to 200 μm, and preferably of 50 to 150 μm. The weight ratio of the coating layer on the carrier particle is in the range of 0.001 to 2.5 parts by weight, and preferably of 0.005 to 2.0 parts by weight per 100 parts by weight of the core particle. The obtained carrier particle has a volume specific resistivity in the range between 10^5 and 10^{13} Ω·cm, and preferably between 10^7 and 10^{12} Ω·cm, and a saturation magnetization in the range between 30 and 70 emu/g, and preferably between 45 and 65 emu/g.

(Preparation of a developer)

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

A copying operation is conducted using the present toner by a general electrophotographic method. Specifically, for example, a photoconductive layer on a photosensitive body is uniformly charged, and an image is exposed to form an electrostatic latent image thereon. Then, a magnetic brush made of the two-component magnetic developer is allowed to come in contact with the photosensitive body, thereby developing the electrostatic latent image with ease into a toner image. The thus obtained toner image is transferred onto transfer paper to form a transfer image, which is then applied with heat and pressure by a heat roller to fix the image thereon.

Examples

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

(Example 1)

<Preparation of toner>

Components of toner	Parts by weight
Fixing resin [a)]	100
Polypropylene (an average molecular weight of 4,000)	3
Coloring agent: Carbon black	10
Magnetic powder: Magnetite	2

[a)] The binder resin used in this example was a styrene-acrylic copolymer having a carboxyl group and an alkyl group containing 12 or more carbon atoms as the side chain (wherein the weight ratio among styrene, stearyl methacrylate, acrylic acid and butyl methacrylate was 75:4:5:16).

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 μm.

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 μm as a fluidity enhancer and 0.6 part by weight of hydrophobic alumina fine particles with an average particle diameter of 0.3 μm as spacer particles, on the basis of 100 parts by weight of the toner particles. The resultant mixture was mixed with a Henschel mixer for 2 minutes to give toner.

<Preparation of a developer>

The thus produced toner was homogeneously mixed with a ferrite carrier with an average particle diameter of 100 μm to give a two-component type developer with a toner concentration of 3.5 wt%.

(Comparative Example 1)

Toner was prepared in the same manner as in Example 1 except that a styrene-acrylic copolymer including no alkyl group containing 12 or more carbon atoms at the side chain (wherein the weight ratio among styrene, acrylic acid and butyl methacrylate was 75:20:5) was used as a binder resin, and a developer was prepared by using the thus obtained toner.

(Example 2.1)

<Preparation of a carrier>

Spherical ferrite particles with an average particle diameter of 100 μm were used as the magnetic core particles. To 1000 parts by weight of the ferrite particles was added a coating agent with components as listed in Table 1, and the resultant was mixed with a thermal stirrer. The solvent was removed from the resultant mixture, and the residue was subjected to a heat treatment at a temperature of 200°C for 1 hour to give carrier particles each having a coating layer.

<Preparation of a developer>

The toner produced in Example 1 and the thus obtained carrier were homogeneously mixed to give a two-component type developer having a toner concentration of 3.5 wt%.

(Example 2.2)

The same procedure was repeated as in Example 2.1 except that a coating agent with components as listed in Table 1 was used, thereby preparing a developer.

(Example 2.3)

The same procedure was repeated as in Example 2.1 except that a coating agent with components as listed in Table 1 was used, thereby preparing a developer.

(Example 2.4)

The same procedure was repeated as in Example 2.1 except that a coating layer is not formed on a carrier particle without using any coating agent, thereby preparing a developer.

Table 1

Coating Agents of Examples 1-3 and Comparative Example 1.

component	Example 1	Example 2	Example 3	Comparative Example 1
Resin 1	Acryl-modified silicone	Metylphenyl silicone	Styrene-acrylic polymer	none
parts by weight	2.5	4.8	3.5	
Resin 2	Metylated melamine	γ-aminopropyltriethoxysilane	Methylated melamine	none
parts by weight	2.5	0.2	1.5	
Solvent: toluene (parts by weight)	200	200	200	none

[Evaluation of the developers]

The developers obtained in the above described examples and comparative example were evaluated with regard to the following items. An electric copying machine (manufactured by Mita Industrial Co., Ltd.; brand name: DC-4685) was modified so as to make easier evaluation sampling, and the modified copying machine was used in the evaluation.

(a) Transfer efficiency:

The amount of toner in a toner hopper in the copying machine was measured at first, and a predetermined number of copies were made. Then, the amount of the toner left in the toner hopper was measured. From a difference between the amounts of the toner before and after the copying operation, a consumed amount of the toner was calculated. At the same time, the amount of the toner collected in a cleaning process during the copying operation was also measured as a collected amount. Based on these amounts, the transfer efficiency of the toner was calculated by using Equation (i) below. An original used in the copying operation bore characters with a black area ratio of 8%. This evaluation was conducted to perform various evaluation tests described in the following items (b) through (h).

$$\text{Equation (i): Transfer efficiency (\%)} = \frac{\text{(Consumed amount)-(Collected amount)}}{\text{(Consumed amount)}}$$

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

A copying operation was continued by using an original bearing characters with a black area ratio of 8% until the transfer efficiency became less than 70%. 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 produced in Example 1 and Comparative Example 1 are listed in Table 2, and those of Examples 2.1 through 2.4 are listed in Table 3.

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

A copying operation was continued by using an original bearing characters with a black area ratio of 8% until the transfer efficiency became less than 70%. The density of a white portion in a copied image on every 5000 copies was measured by a 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 produced in Example 1 and Comparative Example 1 are listed in Table 2, and those of Examples 2.1 through 2.4 are listed in Table 3.

(d) Resolution:

A copying operation was conducted by using an original bearing characters with a black area ratio of 8%. When 50,000 copies were made (in the case where the transfer efficiency became less than 70% before making 50,000 copies, at that time), a normal chart original (an original bearing a plurality of patterns in each of which a predetermined number of parallel lines are drawn per 1 mm) was copied, and the obtained copied image was visually evaluated. The results obtained from the developers produced in Example 1 and Comparative Example 1 are listed in Table 2, and those of Examples 2.1 through 2.4 are listed in Table 3.

(e) Charge amount:

A copying operation was continued by using an original bearing characters with a black area ratio of 8% until the transfer efficiency became less than 70%. 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 produced in Example 1 and Comparative Example 1 are listed in Table 2, and those of Examples 2.1 through 2.4 are listed in Table 3.

(f) Toner scattering:

A copying operation was continued by using an original bearing characters with a black area ratio of 8% until the transfer efficiency became less than 70%. Then, the toner scattering state in the copying machine was visually observed and evaluated. The results obtained from the developers produced in Example 1 and Comparative Example 1 are listed in Table 2, and those of Examples 2.1 through 2.4 are listed in Table 3, wherein ○ indicates that the toner was not scattered; and × indicates that the toner was scattered.

(g) Durability:

After making every 10,000 copies, the transfer efficiency was calculated based on the consumed amount and the collected amount of the toner to find the number of copies that had been made before the transfer efficiency became less than 70%. The number was taken as an indicator for the durability of the developer. The results obtained from the developers produced in Example 1 and Comparative Example 1 are listed in Table 2, and those of Examples 2.1 through 2.4 are listed in Table 3.

(h) 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 (in the case where the transfer efficiency became less than 70% before making 50,000 copies, at that time), the developer was tested as follows. The developer was placed on a screen of 400 mesh, and sucked from below with a blower, thereby separating the toner and the carrier. Five grams of the carrier remained on the screen and 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 remaining 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 produced in Example 1 and Comparative Example 1 are listed in Table 2, and those of Examples 2.1 through 2.4 are listed in Table 3.

Table 2 Toner component and Evaluation of Example 1 and Comparative Example 1.

	Example 1	Comparative Example 1
Toner component (parts by weight)		
Binder resin	100	100
;Long-chain alkyl*	present	none
Releasing agent (Wax)	3	3
Carbon black	10	10
Magnetic powder	2	2
Charge control agent	none	none
External additive 1 (silica; 0.015 μm)	0.3	0.3
External additive 2 (almina; 0.3 μm)	0.6	0.6
Evaluation		
I.D.	1.375	1.371
F.D.	0.002	0.003
Resolution	5	5
Charge amount (μC/g)	-21.4	-22.2
Spent amount (mg)	0.59	0.69
Toner scattering	○	○
Durability (copies)	90,000	60,000

* Alkyl group having 12 or more carbon atoms at the side chain.

Table 3

Evaluation of Examples 2.1-2.4.

	Example 2.1	Example 2.2	Example 2.3	Example 2.4
I.D.	1.384	1.320	1.377	1.363
F.D.	0.002	0.003	0.003	0.004
Resolution	5	5	5	5

Continuation of the Table on the next page

Table 3 (continued)

Evaluation of Examples 2.1-2.4.				
	Example 2.1	Example 2.2	Example 2.3	Example 2.4
Charge amount (µC/g)	-23.8	-25.9	-24.1	-22.0
Toner scattering	○	○	○	○
Durability (copies)	140, 000	140, 000	130, 000	70, 000
Spent amount (mg) at 50, 000 copies	0.32	0.31	0.35	0.58

[Review of the evaluation]

The developer produced in Example 1 containing the toner including the binder resin including an alkyl group containing 12 or more carbon atoms at the side chain had a smaller spent amount and was improved in the durability as compared with the developer of Comparative Example 1 containing the toner including the binder resin including no alkyl group containing 12 or more carbon atoms.

The developers produced in Examples 2.1 through 2.4 were excellently stable in resolution and charge amount. Furthermore, when these developers were used, no toner scattering was observed. The developers of Examples 2.1 through 2.3 containing the carrier having a coating layer had a further lower fog density and a further smaller spent amount and were improved in durability as compared with the developer of Example 2.4 containing the carrier having no coating layer.

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.

Claims

1. Toner for a two-component type developer, comprising: toner particles including a binder resin, magnetic powder dispersed in said binder resin and a releasing agent,

wherein said binder resin is made of a composition including at least one of the following;

(1) a copolymer obtained from a monomer having an anionic group and a monomer having an alkyl group containing 12 or more carbon atoms at the side chain, or a mixture thereof with other monomers; and

(2) a mixture of a polymer obtained from a monomer having an anionic group or a mixture of the monomer having an anionic group with other monomers, and a polymer obtained from a monomer having an alkyl group containing 12 or more carbon atoms at the side chain or a mixture of the monomer having an alkyl group containing 12 or more carbon atoms with other monomers, and

said magnetic powder is contained in said toner particles in the range between 0.1 and 5 parts by weight per 100 parts by weight of said binder resin.

2. Toner for a two-component type developer according to claim 1,

wherein an extracted solution obtained by extracting said toner with methanol has substantially no absorption peak in the range between 280 and 350 nm, and has a substantially zero absorbance in the range between 400 and 700 nm.

3. Toner for a two-component type developer according to claim 1,

wherein said magnetic powder is contained in the range between 0.5 and 3 parts by weight per 100 parts by weight of said binder resin.

4. Toner for a two-component type developer according to claim 1,

wherein said toner particles have a volume-based an average particle diameter of 5 through 15 µm, and spacer particles with a volume-based average particle diameter of 0.05 through 1.0 µm are attached onto surfaces of said toner particles.

FIG.1

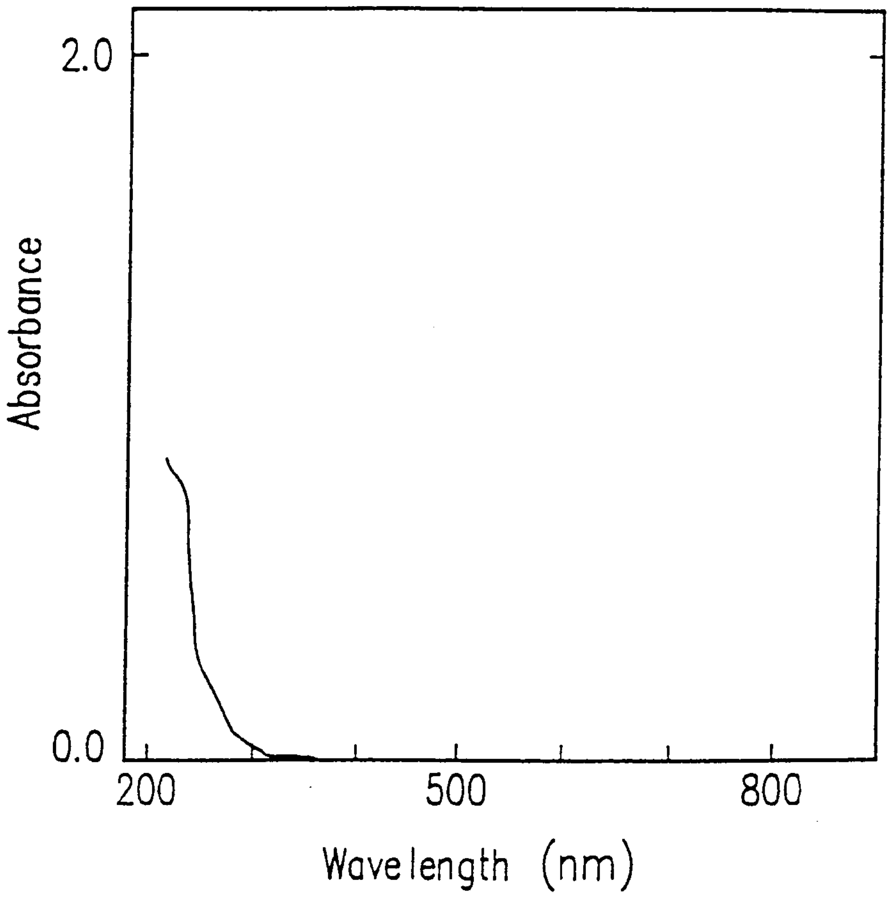


FIG. 2

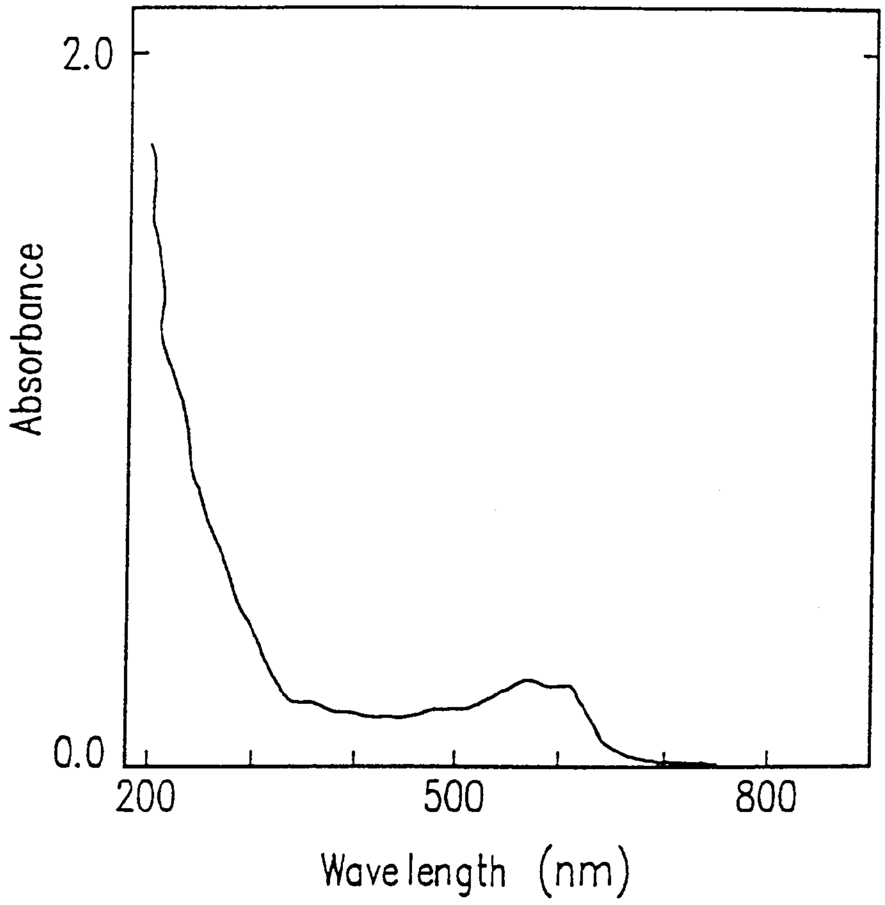


FIG. 3

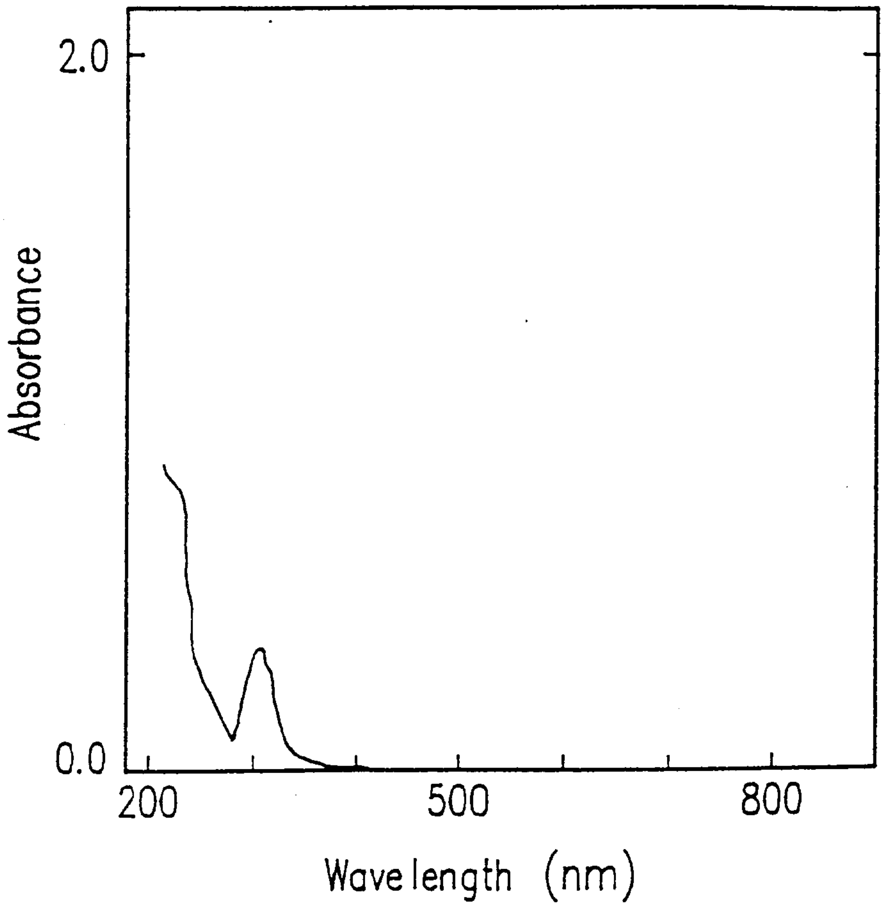


FIG. 4

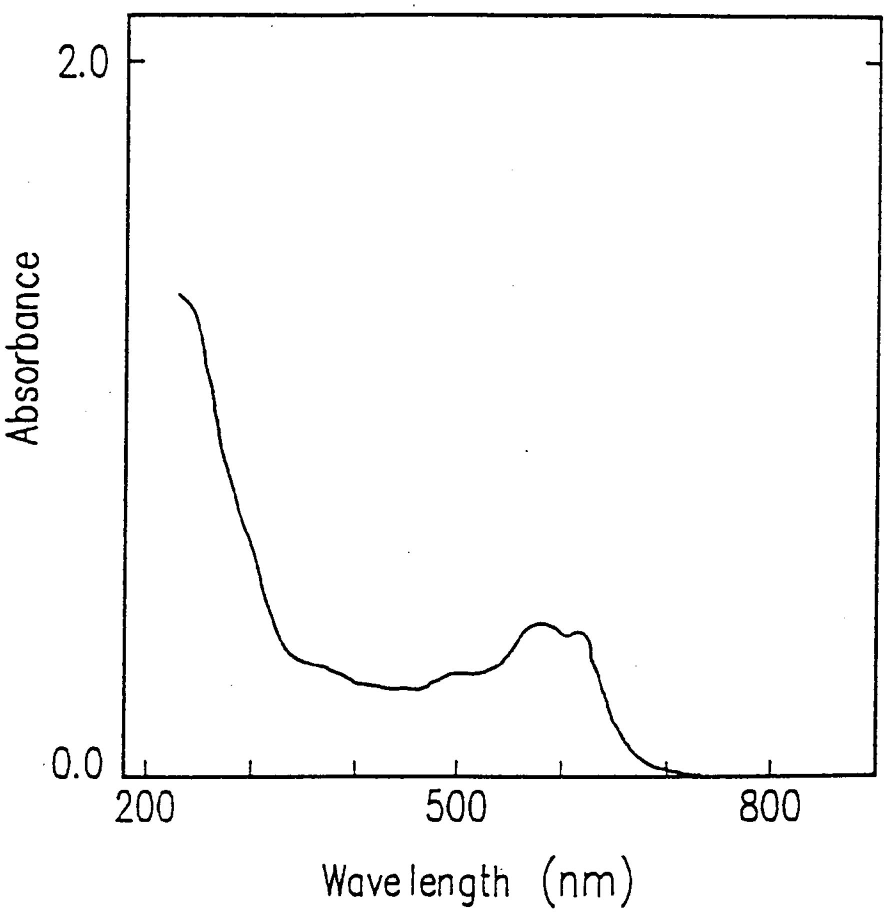


FIG. 5

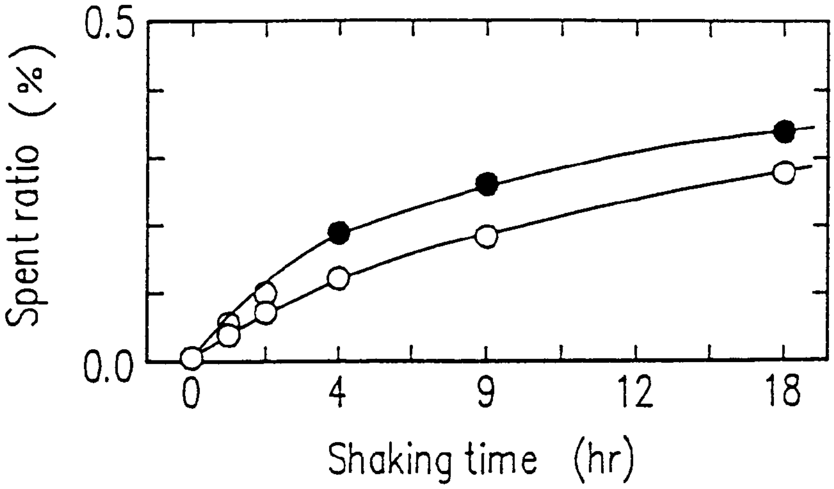

0.5
0.0
Spent ratio (%)
0
4
9
12
18
Shaking time (hr)

FIG. 6

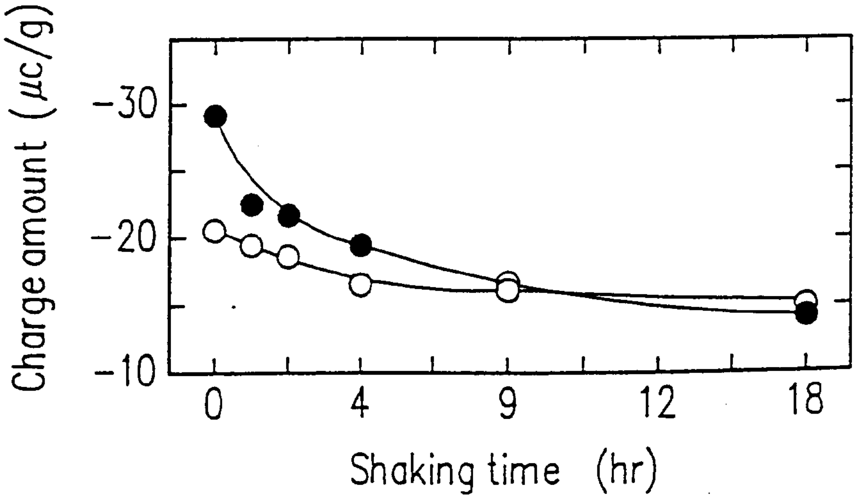

Charge amount (μc/g)
-30
-20
-10
0
4
9
12
18
Shaking time (hr)

FIG.7

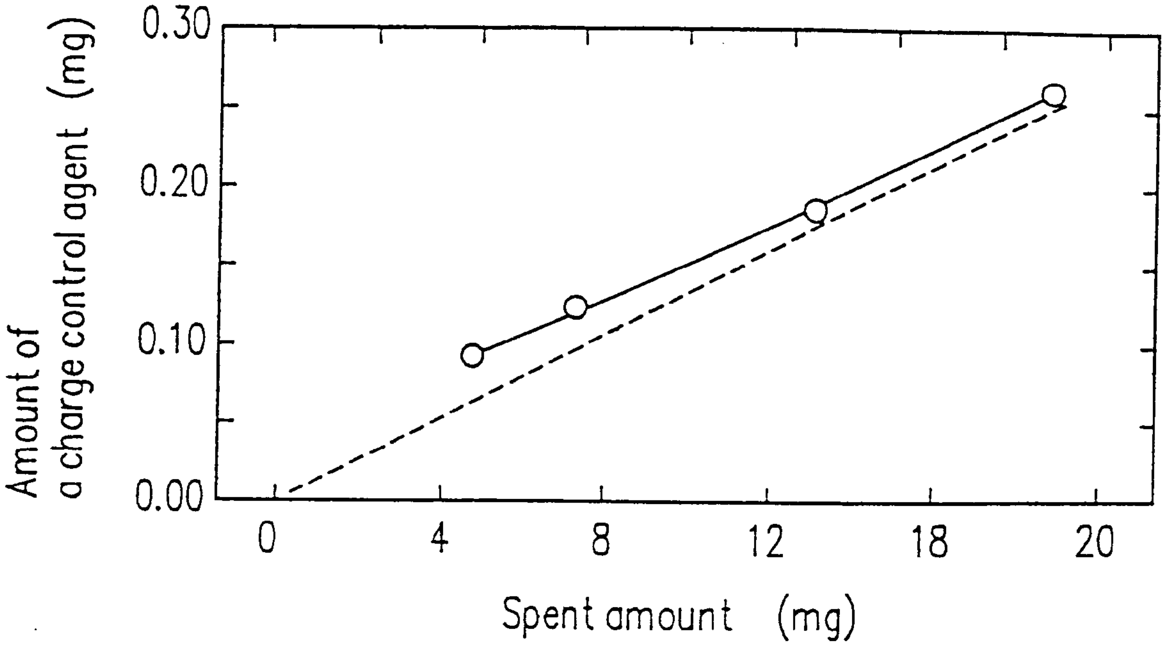

Amount of
a charge control agent (mg)
0.30
0.20
0.10
0.00
0
4
8
12
18
20
Spent amount (mg)

FIG. 8

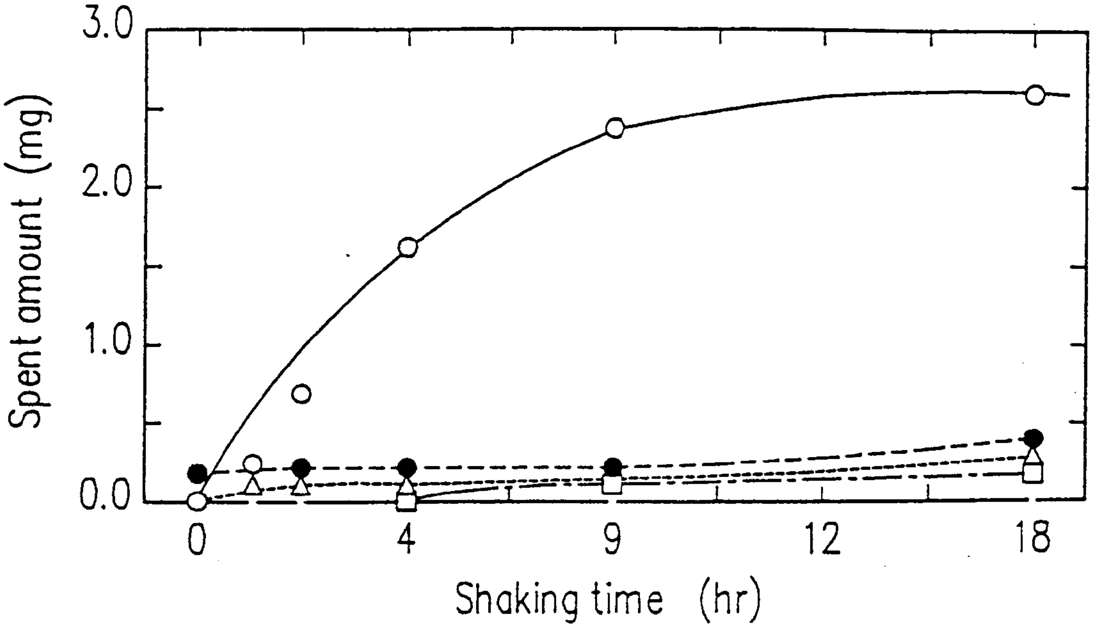
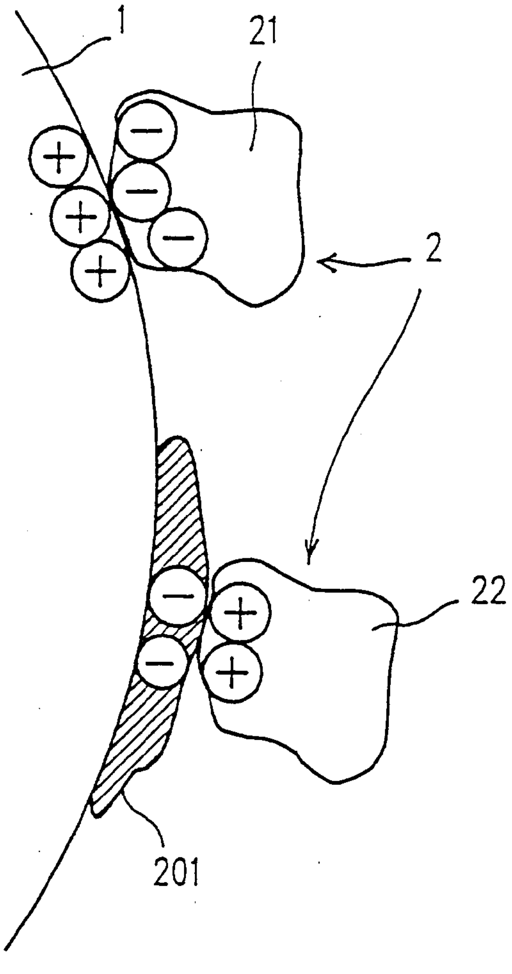


FIG.9



European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 95 30 5610

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-0 407 604 (MITA) * page 12, line 8 - page 18, line 6; claim 4; examples 2-6 * ---	1	G03G9/087 G03G9/083
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-0 357 042 (TDK) * claims 1-4 * ---	1,2	
A	DATABASE WPI Section Ch, Week 7932 Derwent Publications Ltd., London, GB; Class G06, AN 79-58841b & JP-A-54 080 752 (TOKYO SHIBAURA) , 27 June 1979 * abstract * ---	1	**TECHNICAL FIELDS SEARCHED (Int.Cl.6)**
A	PATENT ABSTRACTS OF JAPAN vol. 18 no. 457 (P-1792) ,25 August 1994 & JP-A-06 148936 (NIPPON SHOKUBAI) 27 May 1994, * abstract * ---	1	G03G
A	PATENT ABSTRACTS OF JAPAN vol. 14 no. 138 (P-1022) ,15 March 1990 & JP-A-02 005071 (FUJI XEROX) 9 January 1990, * abstract * ---		
A	PATENT ABSTRACTS OF JAPAN vol. 9 no. 207 (P-382) ,24 August 1985 & JP-A-60 069659 (CANON) 20 April 1985, * abstract * -----		

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	5 January 1996	Vanhecke, H

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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