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(54) **Toner for two-component magnetic developing agent**

(57) A negatively chargeable toner for a two-component magnetic developing agent obtainable by dispersing carbon black in a fixing resin medium wherein the fixing resin medium is a copolymerized resin or a resin composition comprising anionic polar groups and having an acid value from 4 to 30, and the carbon black has a pH less than 7, a ratio (7-pH)/specific surface area (m<sup>2</sup>/g) from 0.010 to 0.050 and is present in an amount from 4 to 15% by weight relative to the fixing resin. The toner maintains an electric charge in an amount sufficient for developing in the absence of a negative charge control agent. Hence, charge control agent does not migrate onto the carrier surfaces and hence the deterioration of charging properties by spent toner is reduced.

**EP 0 744 668 A2**

**Description****BACKGROUND OF THE INVENTION**

## 1. Field of the Invention

The present invention relates to a toner for a two-component magnetic developing agent having excellent resistance against being spent. More specifically, the invention relates to a toner for a two-component magnetic developing agent without containing charge control agent that has a property to migrate onto the carrier surfaces.

## 2. Description of the Prior Art

A so-called two-component magnetic developing agent has been widely used for developing static charge image formed on an electrophotosensitive material.

The two-component magnetic developing agent is constituted by a mixture of a magnetic carrier comprising iron powder, ferrite particles, etc. and an electrosopic toner comprising a colored resin composition. The magnetic carrier and the toner are mixed together so that the toner particles are electrically charged to a predetermined polarity. To effect the developing, the mixture is conveyed in the form of a magnetic brush up to the photosensitive material, the surface of the photosensitive material is rubbed with the magnetic brush, and the charged toner is adsorbed and held by the charge image on the surface of the photosensitive material so as to form a visible image.

Generally, a charge control agent is contained in the toner particles so that the toner particles will be frictionally charged to a predetermined polarity. A negatively charging toner uses a negative charge control agent such as a metal-containing complex salt dye or a metal complex of oxycarboxylic acid (e.g., Japanese Laid-Open Patent Publication No. 67268/1991), and a positively charging toner uses a positively charging control agent such as an oil-soluble dye, for example, Nigrosine or an amine-type control agent (e.g., Japanese Laid-Open Patent Publication No. 106249/1981).

A magnetic toner has long been used as a toner for the two-component magnetic developing agent. For instance, the above-mentioned Japanese Laid-Open Patent Publication No. 106249/1981 and Japanese Laid-Open Patent Publication No. 162563/1984 disclose toners to which a magnetic power is internally added, i.e., disclose toners containing a magnetic powder, and the above-mentioned Japanese Laid-Open Patent Publication No. 67268/1991 discloses a toner to which a magnetic powder is externally added, i.e., discloses a toner to which is added and mixed a silica powder and a magnetic powder.

It has been known that the two-component magnetic developing agent exhibits satisfactory charging property in its early stage of use upon mixing the magnetic carrier and the toner together, but loses its charging property due to the occurrence of a so-called spent toner causing its life to be shortened.

The spent toner is a phenomenon in which the toner component adheres like a film onto the surfaces of the magnetic carrier. That is, the surfaces of the magnetic carrier become close to those of the toner, and the frictional series of the two become close to each other, so that predetermined charging property is no longer maintained. When the spent occurs, therefore, the magnetic carrier must be discarded and must be replaced by the new magnetic carrier.

**SUMMARY OF THE INVENTION**

The object of the present invention therefore is to provide a heat-fixing toner for a two-component magnetic developing agent having excellent resistance against being spent and featuring extended life of toner and carrier.

Another object of the present invention is to provide a heat-fixing toner for a two-component magnetic developing agent without containing charge control agent (CCA) that has a property to migrate onto the carrier surfaces, the toner without scattering at the time of developing and being capable of increasing apparent developing sensitivity.

A further object of the present invention is to provide a heat-fixing toner for a two-component magnetic developing agent, which enables the image to be efficiently transferred onto the paper from the surface of the photosensitive material though it does not contain the charge control agent having migrating property.

According to the present invention, there is provided a negatively charging toner for a two-component magnetic developing agent obtained by dispersing carbon black in a fixing resin medium, wherein:

said fixing resin medium is a copolymerized resin or a resin composition having a free or neutralized anionic polar group and has an acid value of from 4 to 30 by measuring said anionic polar group in the form of a free acid; and

said carbon black has a pH of smaller than 7 and a ratio (7-pH)/specific surface area (m<sup>2</sup>/g) of from 0.010 to 0.050, and is blended in an amount of from 4 to 15% by weight per said resin fixing medium.

According to the present invention, furthermore, there is provided a two-component magnetic developing agent comprising the above-mentioned toner and a magnetic carrier coated with a resin or a magnetic carrier obtained by dispersing a magnetic powder in a resin.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a graph showing a curve of absorbancy at wavelengths of from 200 to 700 nm of an extract obtained by extracting with methanol a toner that contains a chromium complex salt dye (2:1 type) as a charge control agent;  
 Fig. 2 is a graph showing a curve of absorbancy at wavelengths of from 200 to 700 nm of an extract obtained by extracting with methanol a toner that contains a metal salicylate complex as a charge control agent;  
 Fig. 3 is a graph showing a curve of absorbancy at wavelengths of from 200 to 700 nm of an extract obtained by extracting with methanol a carrier, which is poorly charged due to the occurrence of spent toner, in a two-component magnetic developing agent containing the toner used in the measurement of Fig. 1;  
 Fig. 4 is a graph plotting relationships between the mixing time and the spent amount of when there are used a mixture of a toner containing a positive charge control agent and a magnetic carrier, and a mixture of a toner without containing charge control agent and the magnetic carrier;  
 Fig. 5 is a graph plotting relationships between the mixing time and the amount of charge of when there are used a mixture of a toner containing a negative charge control agent and a magnetic carrier, and a mixture of a toner without containing charge control agent and the magnetic carrier;  
 Fig. 6 is a graph illustrating relationships between the spent amount of the carrier on which the spent toner is adhered and the amount of the charge control agent in the spent toner;  
 Fig. 7 is a graph illustrating relationships between the mixing time and the spent amount of when each of the components in the toner and the magnetic carrier are mixed together;  
 Fig. 8 is a diagram illustrating the mechanism of poor charging due to the occurrence of spent toner in the conventional two-component magnetic developing agent;  
 Fig. 9 is a graph showing a curve of absorbancy at wavelengths of from 200 to 700 nm of an extract obtained by extracting with methanol a negatively charging toner of the present invention;  
 Fig. 10 is a diagram of an apparatus for measuring the resistivity of a carrier;  
 Fig. 11 is a diagram of a curve representing the distribution of GPC molecular weights of a low molecular polymer synthesized for the preparation of a fixing resin medium according to Example 1; and  
 Fig. 12 is a diagram of a curve representing the distribution of GPC molecular weights of a fixing resin medium used for the toner of the present invention prepared according to Example 1.

DETAILED DESCRIPTION OF THE INVENTION

The present inventors have forwarded the study in an effort to prevent the occurrence of spent toner and have found an interesting fact.

Fig. 1 is a graph showing a curve of absorbancy at wavelengths of from 200 to 700 nm of an extract obtained by extracting with methanol a toner that contains a chromium complex salt dye (2:1 type) as a charge control agent among toners for the conventional two-component magnetic developing agent used for developing positively charged image, the peaks lying over a region of wavelengths of from 400 to 700 nm. Fig. 2 is a graph showing a curve of absorbancy at wavelengths of from 200 to 700 nm of an extract obtained by extracting with methanol a toner that contains a metal salicylate complex as a charge control agent, the peaks lying over a region of wavelengths of from 280 to 350 nm.

From these results, the two extracts exhibit characteristic absorption peaks due to the charge control agents. This means that the charge control agent is contained at a considerably high concentration in the surfaces of the toner particles.

Fig. 3 is a graph showing a curve of absorbancy at wavelengths of from 200 to 700 nm of an extract obtained by extracting with methanol a carrier which is poorly charged due to the occurrence of spent toner. The carrier is contained in a two-component magnetic developing agent containing the toner used in the measurement of Fig. 1. In the curve, the peaks lying over a region of wavelengths of from 400 to 700 nm.

The result of the measurement reveal an astonishing fact that the charge control agent is adhered and deposited at a high concentration even on the carrier surfaces, and poor charging due to the spent toner is not caused by a simple filming of the toner resin on the carrier surfaces that was so far considered but is caused by the migration of the charge control agent onto the carrier surfaces.

This fact becomes even more obvious with reference to Figs. 4 and 5. Figs. 4 and 5 are graphs plotting relationships between the mixing time and the spent amount, and relationships between the mixing time and the amount of charge of when there are used a mixture of a toner containing a positive or negative charge control agent and a magnetic carrier, and a mixture of a toner without containing charge control agent and the magnetic carrier. From these results, the fact becomes obvious in that when the charge control agent is contained, the spent amount increases with an increase in the mixing time, and the amount of charge decreases to a large extent.

Fig. 6 is a graph illustrating relationships between the spent amount of the carrier to which the spent toner is adhered and the charge control agent in the spent toner, wherein a dotted line is drawn by plotting estimated values calculated from the toner recipe. These results reveal the fact that the charge control agent selectively migrates and

adheres onto the carrier surfaces in an early stage of occurrence of the spent toner. In Fig. 6, the amount of the charge control agent approaches the values estimated from the toner composition with an increase in the spent amount due to the fact that the mixture system is a closed system where no toner is replenished. When the toner is exchanged in the copying machine, it is estimated that the difference further increases depending upon whether the charge control agent is used or not used.

Fig. 7 illustrates relationships between the mixing time and the spent amount of when each of the components in the toner and the magnetic carrier are mixed together. These results tell the fact that among the components of the toner, the charge control agent migrates overwhelmingly onto the carrier surfaces, giving rise to the occurrence of spent toner.

From the foregoing results, the conventional two-component magnetic developing agent becomes poorly charged due to the occurrence of spent toner as explained in Fig. 8. That is, in an early stage of use of the mixture, the carrier has been positively charged and the toner has been negatively charged. As the charge control agent selectively migrates onto the carrier surface to form spent toner, however, the spent layer is negatively charged and whereby a toner of a reverse polarity (positively charged) is formed.

According to the present invention, there is used no charge control agent having property to migrate onto the toner particles, and, hence, no charge control agent migrates onto the surfaces of the magnetic carrier. As represented by a curve of absorbancy of Fig. 9, therefore, in the extract of the negatively charging toner of the present invention extracted with methanol, the absorbancy is substantially zero over wavelengths of from 400 to 700 nm. The toner of the present invention is not, as a matter of course, blended with a positive charge control agent such as metal salicylate complex, and its extract with methanol exhibits no peak of absorbancy over the wavelengths of from 280 to 350 nm.

In this specification, the absorbancy which is substantially zero stands for that no absorption peak is quite detected in the above-mentioned wavelength region from an extract obtained by extracting 0.1 g of toner with 50 ml of methanol or the absorbancy at the peak is not larger than 0.05 if it is detected.

Here, as shown in Fig. 5, the toner without containing charge control agent is electrically charged in an amount which is inevitably smaller than that of the toner containing the charge control agent. To overcome this inconvenience according to the present invention, use is made of a copolymerized resin composition having anionic polar group as a fixing resin medium, and use is further made of carbon black having a pH on the acidic side as a coloring agent. Use of such a fixing resin medium and carbon black enables the toner to be electrically charged in an amount large enough for effecting the developing.

That is, the anionic polar group possessed by the fixing resin medium gives a negatively charging property to the toner and exists in the molecular skeleton of the resin. Therefore, the anionic polar group does not migrate onto the carrier surfaces and does not become a cause of spent toner unlike the charge control agent.

As described above, the fixing resin medium used in the present invention has an acid value in connection with the possession of an anionic polar group. Here, however, the acid value must lie within a range of from 4 to 30. When the acid value is larger than 30, the amount of anionic groups increases whereby the toner exhibits increased hygroscopic property making it difficult to frictionally charge the toner maintaining stability. When the acid value becomes smaller than 4, on the other hand, the amount of anionic groups is so small that it becomes difficult to maintain the electric charge of the toner in an amount large enough for the developing. The anionic polar group may exist in a free form (in the form of a free acid) or may exist in the form of a metal salt such as sodium salt or the like salt, i.e., may exist in a neutralized form. The acid value is measured in the form of a free acid. That is, in the present invention, if the anionic polar groups at least partly exist in the neutralized form, the acid value stands for a value that is found by hydrolyzing the groups to form free acids.

In the present invention, furthermore, carbon black which is a coloring agent must have a pH which lies on the acidic side (i.e., smaller than 7) and a ratio  $(7-\text{pH})/\text{specific surface area (m}^2/\text{g)}$  that lies within a range of from 0.010 to 0.050.

In general, the carbon black has a pH of about 8 which is on the neutral to alkaline side. In order to control the electrically conducting property, furthermore, there has been used the carbon black which is treated with an acid so that it has a pH of smaller than 7. The present invention selectively uses the carbon black having a pH of smaller than 7 which, however, does not mean that the invention uses the carbon black of which the electrically conducting property is controlled.

The present inventors have confirmed through their study that the carbon black is negatively charged when the carbon black and the magnetic carrier are mixed together and are stirred. That is, according to the present invention which uses the acid-treated carbon black having a pH of smaller than 7, the fixing resin medium having the anionic polar group exhibits reinforced negatively charging property, and the drop of the charging property is effectively prevented despite the negative charge control agent is not blended.

In the present invention, the ratio  $(7-\text{pH})/\text{specific surface area}$  is an index representing the degree of treatment with acid, i.e., representing the density of acidic functional groups existing on the surfaces of the carbon black. When this value is smaller than the aforementioned range, the negatively charging property is not reinforced to a sufficient degree and the charging property inevitably drops. When this value is larger than the aforementioned range, on the other hand,

the toner exhibits increased hygroscopic property and it becomes difficult to stably maintain the amount of charge by friction.

The pH of carbon black is measured in the following way. Five grams of a sample is put into 100 ml of ion-exchanged water and is boiled for 5 minutes. After left to cool, water is replenished by an amount that has vaporized and is filtered using a paper. Then, the filtrate is measured by using a commercially available glass-electrode pH measuring instrument.

(Resin Medium)

The fixing resin medium used in the present invention is a copolymerized resin having an anionic polar group. The anionic polar group may be any polar group such as of carboxylic acid, sulfonic acid or phosphonic acid. Among them, however, the anionic polar group of carboxylic acid is particularly preferred. The copolymerized resin having such an anionic polar group is obtained by incorporating a monomer having a polar group into a resin relying upon random copolymerization, block-copolymerization or graft-copolymerization. Preferred examples of the monomer are as described below. In the following description, a lower alkyl group stands for the one having not more than 5 carbon atoms, and a higher alkyl group stands for the one having not less than 12 carbon atoms.

Examples of those of the carboxylic acid type include ethylenically unsaturated carboxylic acid, such as acrylic acid, methacrylic acid, crotonic acid, maleic acid, maleic anhydride, fumaric acid, lower alkyl half ester of maleic acid, lower alkyl half ester of fumaric acid and the like.

Examples of those of the sulfonic acid type include styrenesulfonic acid, 2-acrylamide-2-methylpropanesulfonic acid and the like.

Examples of those of the phosphonic acid type include 2-acid phosphoxypropyl methacrylate, 2-acid phosphoxyethyl methacrylate, 3-chloro-2-acid phosphoxypropyl methacrylate and the like.

These anionic polar group-containing monomer units may be incorporated in the form of free acids or in the form neutralized with an alkali metal such as sodium or potassium, an alkaline earth metal such as calcium or magnesium, or zinc.

Another monomer which is a chief component of the copolymerized resin composition exhibits fixing property and charging property required for the toner when it is polymerized, and may be one or two or more kinds of monomers having an ethylenically unsaturated bond.

Preferred examples of the monomer include acrylic ester type monomer, aromatic monovinyl monomer, vinyl ester type monomer, vinyl ether type monomer, diolefin type monomer and monoolefin type monomer. Described below are concrete examples.

The acrylic ester type monomer is represented by, for example, the following general formula (1),



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

Preferred examples include methyl acrylate, ethyl acrylate, butyl acrylate, 2-ethylhexyl acrylate, cyclohexyl acrylate, phenyl acrylate, methyl methacrylate, hexyl methacrylate, 2-ethylhexyl methacrylate,  $\beta$ -hydroxyethyl acrylate,  $\gamma$ -hydroxypropyl acrylate,  $\delta$ -hydroxybutyl acrylate,  $\beta$ -hydroxyethyl methacrylate, 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, cycloundecanemethyl methacrylate, etc.

The aromatic monovinyl monomer is represented by the following general formula (2),



wherein  $\text{R}^3$  is a hydrogen atom, a lower alkyl group, a halogen atom or a higher alkyl group,  $\text{R}^4$  is a hydrogen atom, a lower alkyl group, a higher alkyl group, a halogen atom, an alkoxy group, an amino group or a nitro group,  $\Phi$  is a phenylene group which may have, as a substituent, a lower alkyl group, a higher alkyl group, a halogen atom, an alkoxy group, an amino group or a nitro group.

Preferred examples include styrene,  $\alpha$ -methylstyrene, vinyltoluene,  $\alpha$ -chlorostyrene, o-, m- or p-chlorostyrene, p-ethylstyrene, m- or p-laurylstyrene, m- or p-stearylstyrene,  $\alpha$ -methyl-3-stearylstyrene, m- or p-stearoxystyrene, 4-vinyl-stearyl benzoate and 4-stearoylaminostyrene.

The other monomer is represented by the following general formula (3), (4), (5) or (6),



wherein  $R^5$  is a hydrogen atom, a lower alkyl group or a higher alkyl group, like such vinyl esters as vinyl formate, vinyl acetate, vinyl propionate, vinyl laurate, vinyl tridecanoate, vinyl stearate, vinyl docosanoate, vinyl triacontanoate, vinyl pencylcyclohexanoate, vinyl dicyclohexyl acetate, etc.,



wherein  $R^6$  is a monovalent hydrocarbon group having up to 11 carbon atoms or a higher alkyl group, like such vinyl ethers as methyl vinyl ether, ethyl vinyl ether, vinyl-n-butyl ether, vinylphenyl ether, vinylcyclohexyl ether, vinylauryl ether, vinylstearyl ether, vinyldocosyl ether, vinylcyclododecyl ether, etc.,



wherein  $R^7$ ,  $R^8$  and  $R^9$  are each a hydrogen atom, a lower alkyl group, a higher alkyl group or a halogen atom, like such diolefins as butadiene, isoprene, chloroprene, 1,3-hexadecadiene, 1,3-docosadiene, 2-methyl-1,3-docosadiene, etc.,



wherein  $R^{10}$  and  $R^{11}$  are each a hydrogen atom, a lower alkyl group or a higher alkyl group, like such monoolefins as ethylene, propylene, isobutylene, butene-1, pentene-1, 4-methylpentene-1, 1-tetradecene, 1-eicosene, etc.

In the copolymerized resin having anionic polar groups used as a fixing resin medium of the present invention, the anionic polar groups exist in such an amount that the acid value is from 4 to 30 and, particularly, from 5 to 15. When the anionic polar groups of the copolymerized resin are partly or wholly neutralized, the anionic polar groups inclusive of the neutralized polar groups are contained in an amount that corresponds to the above-mentioned acid value. As described earlier, when the acid value of the copolymerized resin is smaller than the above-mentioned range, charging property of the toner becomes unsatisfactory. When the acid value of the copolymerized resin is greater than the above-mentioned range, on the other hand, the toner becomes susceptible to humidity, and charging property of the toner becomes insufficient, too.

A preferred copolymerized resin contains a monomer having anionic polar groups and one or two or more kinds of acrylic monomers of the formula (1) and, further, contains monomers of the formulas (2) to (6) and, particularly, the styrene monomer of the formula (2).

In the present invention, the copolymerized resin containing anionic polar group can be used as a fixing resin medium in a single kind as described above and can be further used as a composition containing two or more kinds of anionic polar group-containing copolymerized resins or as a composition containing an anionic polar group-containing copolymerized resin and a copolymerized resin without having anionic polar group. Even in this case, the content of the anionic polar groups in the whole resin composition should be such that the acid value lies within the range specified above for the copolymerized resin.

In the present invention, it is preferred that the fixing resin medium has a weight average molecular weight over a range of from 70,000 to 200,000 to maintain a property of being pulverized and a granulating property. In particular, it is desired that the fixing resin medium contains low molecular components having peak molecular weights over a range of from 4,000 to 30,000 and high molecular components having a molecular weight distribution in a high molecular weight region. The low molecular components help increase toner transfer efficiency and heat-fixing property, and high molecular components help improve resistance against the offset.

When the developing is carried out for extended periods of time using the toner obtained by using the above-mentioned fixing resin medium containing low molecular components and high molecular components, the low molecular components in the resin medium tend to selectively adhere onto the carrier surfaces to form a spent toner. That is, even when the charge control agent is not used, it was found through experiment that the occurrence of spent toner is not perfectly prevented; i.e., the spent toner is formed by the low molecular components as the developing is executed for extended periods of time though the amount of the spent toner is small. When the anionic polar groups exist in the low molecular components adhered onto the carrier surfaces, however, the carrier itself tends to be negatively charged giving rise to the formation of a toner charged to an opposite polarity. When the developing is repeated for extended periods of time, therefore, the scattering of toner and fogging become no longer negligible due to the toner charged to the opposite polarity.

In order to effectively prevent the occurrence of the toner charged to an opposite polarity due to the spent toner of low molecular components according to the present invention, it is desired that the acid value of the low molecular components in the fixing resin medium is set to be lower than the acid value of the whole resin medium, i.e., set to lie within a range of from 3 to 15. When the acid value of the low molecular components is larger than the above-mentioned range, the amount of the anionic polar groups in the spent toner becomes so large that it becomes difficult to effectively prevent the occurrence of the toner charged to the opposite polarity. When the acid value is smaller than the above-

mentioned range, on the other hand, difference in the acid value from that of the high molecular components becomes so large that compatibility decreases between the high molecular components and the low molecular components, giving rise to the occurrence of such inconvenience as nonuniformity in the charge.

From the standpoint of compatibility between the high molecular components and the low molecular components and the transfer efficiency, furthermore, it is desired that the acid value of the low molecular components is within a range of from 10 to 95% with respect to the acid value of the whole fixing resin medium. It is further desired that the low molecular components are contained in an amount of from 40 to 75% by weight per the fixing resin medium.

The fixing resin medium can be easily produced by using monomer components mentioned earlier and by radical polymerizing with a widely known polymerization initiator. In this case, the fixing resin medium containing low molecular components and high molecular components is obtained by preparing, in advance, the low molecular components having a predetermined low acid value and blending them with high molecular components having a high acid value that are separately prepared, or by preparing the high molecular components by effecting the radical polymerization in the presence of the low molecular components. From the standpoint of compatibility between the high molecular components and the low molecular components, in general, it is desired that the high molecular components are prepared in the presence of low molecular components.

A preparation method will now be described.

Monomers for low molecular components and the polymerization initiator are mixed together and stirred in an organic solvent such as toluene or xylene capable of dissolving both the monomer components and the resin that is to be formed. The mixture solution is introduced into a reaction oven and is polymerized with sufficient stirring. After the polymerization, the solution is deaerated and is dried to obtain a polymer that serves as a low molecular component. Here, the time and temperature of polymerization are usually from 60 to 250°C and from about 3 to about 10 hours, though they may vary depending upon the kind and amount of the polymerization initiator.

Next, monomers for high molecular components, the polymer for low molecular component obtained above and the polymerization initiator are mixed together and stirred in a solvent capable of dissolving both the monomer components and the resin. The mixture solution is introduced into an oven and is polymerized with sufficient stirring. After the polymerization, the solution is deaerated and is dried to obtain a desired fixing resin medium containing low molecular components and high molecular components. In this case, the temperature and time of polymerization are set depending upon the kind and amount of the polymerization initiator so that there is obtained a polymer having a molecular weight in a desired range. Usually, however, the temperature and time of polymerization is from 60 to 200°C and from about 5 to about 24 hours.

The acid value can be easily adjusted by adjusting the amount of feeding the anionic polar group-containing monomers.

In order to improve resistance against the offset, furthermore, a parting agent such as wax is usually blended in the toner. However, the wax that is blended as a parting agent has an SP value (solubility parameter) greatly different from that of the fixing resin medium and cannot be uniformly dispersed in the medium causing the amount of wax to vary depending upon the individual toner particles or causing the wax to be distributed in deviated amounts on the surfaces of the toner particles. That is, when the developing is effected using such a toner, the wax tends to adhere as spent on the surfaces of the carrier particles. When the developing agent of a mixture of the toner particles and the carrier particles is used for extended periods of time, therefore, charging property of the carrier particles drops due to the spent arousing a problem from the standpoint of durability. When the toner is blended with such a parting agent according to the present invention, it is desired that the fixing resin medium contains a polymer component that has a higher alkyl group with not less than 12 carbon atoms on a side chain thereof. Use of the polymer component having such a higher alkyl group makes it possible to effectively solve the above-mentioned problem that stems from nonuniform dispersion of the parting agent. Though the reason has not yet been clarified, the present inventors consider it as described below.

A polymer having a higher alkyl group on a side chain thereof has an SP value close to that of the wax, and is, hence, compatible with the wax. It is therefore considered that the fixing resin medium containing such a polymer permits the parting agent to be uniformly dispersed therein.

The polymer having a higher alkyl group may be the aforementioned polymer having an anionic polar group and having a higher alkyl group on a side chain thereof. Or, the polymer having an anionic polar group may be used as a separate polymer. Generally, the former polymer is preferably used. The fixing resin medium is prepared by using, for example, a monomer for introducing anionic groups, a monomer for introducing higher alkyl groups and, as required, other monomers, and polymerizing these monomers based upon the block-polymerization, random polymerization or graft-polymerization. The monomer for introducing higher alkyl groups will be the one having a higher alkyl group selected from the aforementioned monomers of the formulas (1) to (6).

Preferred examples of the fixing resin medium include the following copolymers, i.e., (meth)acrylic acid-stearyl (meth)acrylate copolymer, styrene-stearyl (meth)acrylate-(meth)acrylic acid copolymer, (meth)acrylic acid ester-stearyl (meth)acrylate-(meth)acrylic acid copolymer, styrene-(meth)acrylic acid ester-stearyl (meth)acrylate-(meth)acrylic acid copolymer, styrene-stearyl (meth)acrylate-maleic acid copolymer, maleic acid-stearyl(meth)acrylate copolymer, styrene-tridecyl (meth)acrylate-(meth)acrylic acid copolymer, styrene-lauryl (meth)acrylate-(meth)acrylic acid copolymer.

Even in these fixing resin media composed of the above-mentioned copolymers, the acid values should lie within the aforementioned range. It is desired that the higher alkyl group on the side chain of the polymer exists in an amount of from 0.1 to 20 parts by weight and, particularly, from 0.5 to 10 parts by weight per 100 parts by weight of the fixing resin medium on the basis of the monomer having the higher alkyl group. When the amount of the higher alkyl group is smaller than the above-mentioned range, compatibility drops between the parting agent and the fixing resin medium, and durability is not improved to a satisfactory degree. When the amount of the higher alkyl group is larger than the above-mentioned range, on the other hand, the fixing resin medium exhibits decreased Tg and the toner loses preservation stability.

#### (Carbon Black)

In the present invention, any carbon black can be dispersed in the fixing resin medium provided it has a pH of smaller than 7 and, preferably, from 2 to 5 and has a ratio (7-pH)/specific area ( $\text{m}^2/\text{g}$ ) of from 0.010 to 0.050 and, particularly, from 0.015 to 0.040. Generally, however, it is desired to use furnace black treated with acid so as to have a pH value satisfying the above-mentioned conditions.

The treatment with acid can be carried out by using an inorganic acid such as hydrochloric acid, sulfuric acid, nitric acid, or phosphoric acid or by using an organic acid such as acetic acid, citric acid, propionic acid, benzoic acid, salicylic acid or toluenesulfonic acid. Due to this treatment, an acidic group such as carboxylic group is introduced into the surfaces of the carbon black to reinforce the negatively charging property of the toner. As will be obvious from the pH conditions mentioned above, the acid is used in a very small amount in the treatment and does not adversely affect electric properties of the toner.

It is desired that the carbon black has a specific surface area of usually not smaller than  $50 \text{ m}^2/\text{g}$  and, particularly, from 100 to  $300 \text{ m}^2/\text{g}$  from the standpoint of dispersion property in the resin.

The carbon black is blended in an amount of from 4 to 15% by weight and, particularly, from 6 to 12% by weight per the fixing resin medium. When the blending amount is smaller than the above-mentioned range, negatively charging property of the toner is not satisfactory causing fogging to occur. When the carbon black is used in an amount larger than the above range, on the other hand, the toner exhibits decreased fixing property.

#### (Other Blending Agents)

The toner for a two-component magnetic developing agent of the present invention may be blended with various additives in addition to the above-mentioned carbon black like the conventional toners but without being blended with the charge control agent. Such additives may include parting agent, body, fixing improving agent, magnetic powder, etc.

#### Parting Agent;

According to the present invention which uses, as a fixing resin medium, a resin composition containing the above-mentioned low molecular components and high molecular components, it is allowed to increase resistance against the offset during the heat-fixing. By being blended with a parting agent, furthermore, resistance against the offset can be further improved.

Such a parting agent may be natural or synthetic waxes. In general, it is desired to use a polyolefin wax such as polypropylene wax, polyethylene wax, propylene-ethylene random copolymer wax and, particularly, polypropylene wax. Among them, it is desired to use the one having an average molecular weight of from 2,000 to 16,000 and, particularly, from 3,000 to 6,000.

Such a parting agent is used in an amount of from 0.01 to 10 parts by weight and, particularly, from 0.1 to 6 parts by weight per 100 parts by weight of the fixing resin medium. When the amount is smaller than the above-mentioned range, resistance against the offset is not satisfactory. When the amount is larger than the above-mentioned range, on the other hand, charging property of the toner decreases and the toner scatters and develops fogging due to poor electric charge.

To improve resistance against the offset by using the parting agent, it is desired to use a fixing resin medium containing a polymer that has a higher alkyl group on a side chain thereof as mentioned earlier.

The above-mentioned wax can be blended in the toner by being graft-fixed to a suitable polymer such as the polymer constituting the fixing resin medium. The wax that is blended by the graft-fixing is very advantageous from the standpoint of uniformly dispersing the wax in the fixing resin medium.

The wax can be easily graft-fixed relying upon the radical polymerization in the presence of wax at the time of synthesizing the copolymerized resin having anionic polar group based on the radical polymerization. That is, the wax is graft-fixed to part of the copolymer having anionic polar group; i.e., the wax is graft-fixed simultaneously with the preparation of the copolymerized resin for fixing. Moreover, a resin or a copolymerized resin containing a polymer to which the wax is graft-fixed is obtained by subjecting a monomer without anionic polar group, for example, by subjecting at



least one of the monomers (preferably, having a higher alkyl group) of the formulas (2) to (6), to the radical polymerization in the presence of wax. This resin or copolymerized resin may be blended with a copolymerized resin containing an anionic polar group.

#### 5 Extender Pigment;

The extender pigment is blended to adjust physical properties such as bulk density, etc., and its examples include barite powder, barium carbonate, clay, silica, white carbon, talc, and alumina white. Such a pigment is used in an amount of from 2 to 20 parts by weight and, particularly, from 5 to 15 parts by weight per 100 parts by weight of the fixing resin medium.

#### Magnetic Powder;

According to the present invention, the fixing resin medium may be blended with a magnetic powder in addition to the above-mentioned blending agents. By being blended with such a magnetic powder, the toner particles in the magnetic brush during the developing is held on the carrier by the coulomb force as well as the magnetic attractive force. Accordingly, the toner is more reliably prevented from scattering, which is very desirable from the standpoint of preventing the copying machine from being contaminated with toner and preventing the copy from developing fogging. Such advantages are desired as the copying speed increases. By being blended with the magnetic powder, furthermore, the amount of charge can be decreased per a toner particle. Therefore, developing sensitivity can be increased and image of a high density can be obtained.

Examples of the magnetic powder include those magnetic powders that have heretofore been used for the magnetic toners such as tri-iron tetroxide ( $\text{Fe}_3\text{O}_4$ ), iron sesquioxide ( $\gamma\text{-Fe}_2\text{O}_3$ ), zinc iron oxide ( $\text{ZnFe}_2\text{O}_4$ ), yttrium iron oxide ( $\text{Y}_3\text{Fe}_5\text{O}_{12}$ ), cadmium iron oxide ( $\text{CdFe}_2\text{O}_4$ ), gadolinium iron oxide ( $\text{Gd}_3\text{Fe}_5\text{O}_{12}$ ), copper iron oxide ( $\text{CuFe}_2\text{O}_4$ ), lead iron oxide ( $\text{PbFe}_{12}\text{O}_{19}$ ), nickel iron oxide ( $\text{NiFe}_2\text{O}_4$ ), neodymium iron oxide ( $\text{NdFeO}_3$ ), barium iron oxide ( $\text{BaFe}_{12}\text{O}_{19}$ ), magnesium iron oxide ( $\text{MgFe}_2\text{O}_4$ ), manganese iron oxide ( $\text{MnFe}_2\text{O}_4$ ), lanthanum iron oxide ( $\text{LaFeO}_3$ ), iron powder (Fe), cobalt powder (Co), nickel powder (Ni), etc. Particularly preferred magnetic powder is that of a fine particulate tri-iron tetroxide (magnetite).

The preferred magnetite is of a regular octahedral shape having particle sizes of from 0.05 to 1.0  $\mu\text{m}$ . The magnetite particles may be treated for their surfaces with a silane coupling agent or a titanium coupling agent.

The magnetic powder may be blended in an amount as small as from 0.1 to 5 parts by weight and, particularly, from 0.5 to 3.0 parts by weight per 100 parts by weight of the resin medium. In the magnetic toner used for the conventional one-component magnetic developing agent, the magnetic powder is used in an amount larger than 10 parts by weight per 100 parts by weight of the resin medium. In the present invention, however, the magnetic powder is used in an amount considerably smaller than the above-mentioned amount. The internal addition of the magnetic powder even in such a small amount makes it possible to form an image of a high density yet preventing the toner from scattering.

#### Fixing Improvent Agent;

In the present invention, it is desired to blend a polyethylene having a number average molecular weight of from 1000 to 7000 as a fixing improving agent. That is, the anionic polar group contained in the fixing resin medium gives negatively charging property to the toner but tends to increase the heat-melting temperature of the resin medium due to association among the polar groups. Such a rise in the heat-melting temperature is not desirable from the standpoint of fixing. According to the present invention, the polyethylene having the above-mentioned number average molecular weight that is blended makes it possible to prevent a drop in the fixing property caused by the presence of anionic polar groups but rather helps increase the fixing property. Though the reason is not yet obvious why the polyethylene that is blended helps improve the fixing property, the present inventors consider it in the following way.

That is, the polyethylene having a number average molecular weight over the above-mentioned range has a softening point lower than that of the fixing resin medium, and loses the viscosity abruptly near its softening point and melts. When the toner is heat-fixed, therefore, the polyethylene melts, first, and infiltrates into the paper. As a result, the fixing resin medium loses wettability for the paper and exhibits improved permeability. The fixing resin medium that is melted does not diffuse but infiltrates into the paper enabling the fixing property to be improved.

It is desired that the polyethylene is used in an amount of from 0.5 to 5 parts by weight per 100 parts by weight of the fixing resin medium from the standpoint of improving fixing property of the toner without impairing other properties.

#### (Toner)

The toner of the present invention can be prepared by a widely known method such as pulverization-classification method, melt-granulation method, spray-granulation method or polymerization method. Generally, however, the toner is

prepared by the pulverization-classification method. That is, the above-mentioned fixing resin medium and various blending agents are pre-mixed together in a mixer such as Henschel's mixer and are kneaded using a kneader such as biaxial extruder. The kneaded composition is cooled, pulverized and is classified to obtain a toner.

It is desired that the particle diameter of the toner is generally from 5 to 15  $\mu\text{m}$  and, particularly, from 7 to 12  $\mu\text{m}$  in terms of a volume-based average particle diameter (median diameter using the Coulter counter).

As required, a fluidity improving agent such as silica obtained by the hydrophobic vapor-phase method is externally adhered onto the surfaces of the toner particles to improve fluidity of the toner. The fluidity improving agent is a very fine powder having a primary particle size of usually as small as from 0.005 to 0.050  $\mu\text{m}$ , and is externally added in an amount of from 0.1 to 2.0% by weight with respect to the whole weight of the toner (total amount of the toner particles and the externally added agents).

According to the preferred embodiment of the present invention, furthermore, spacer particles having a diameter of from 0.05 to 1.0  $\mu\text{m}$  and, particularly, from 0.07 to 0.5  $\mu\text{m}$  larger than the particle diameter of the fluidity improving agent are externally added to the toner particles together with the fluidity improving agent. With such spacer particles being externally added, bonding is weakened between the toner image and the latent image on the surface of the photosensitive member, enabling the toner image to be easily peeled and the transfer efficiency to be improved in the step of transferring the toner image.

As the spacer particles, use is made of organic or inorganic inert particles of a definite shape having the aforesaid particle diameter. When the particle diameter is larger than the above-mentioned range, the bonding force becomes weak between the toner image and the latent image on the surface of the photosensitive material, and it becomes difficult to form a favorable image. When the particle diameter is smaller than the above-mentioned range, on the other hand, a sufficiently large gap is not formed between the toner image and the latent image (photosensitive material), whereby the bonding force is not weakened between the two and the transfer efficiency is not improved to a satisfactory degree.

Concrete examples of the inert particles having a definite shape may include silica, alumina, titanium oxide, magnesium carbonate, acrylic resin powder, styrene resin powder and magnetic powder. They should be externally added in an amount of not larger than 10% by weight, preferably, from 0.1 to 10% by weight and, most preferably, from 0.1 to 5% by weight with respect to the whole weight of the toner (total amount of the toner particles and externally added materials). When they are used in excess amounts, the density of the image decreases. When a magnetic powder is used as the spacer particles, it is desired that the total amount of the magnetic powder inclusive of the magnetic powder that has been internally added to the toner particles is not larger than 10% by weight with respect to the fixing resin medium. When the total amount becomes too large, the density of the image decreases, too.

In the present invention, furthermore, it is desired to use, as the above-mentioned spacer particles, first spacer particles having a resistivity of from  $10$  to  $10^5 \Omega \cdot \text{cm}$  and, particularly from  $10^3$  to  $10^5 \Omega \cdot \text{cm}$  and second spacer particles having a resistivity of from  $10^8$  to  $10^{13} \Omega \cdot \text{cm}$  and, particularly, from  $10^9$  to  $10^{12} \Omega \cdot \text{cm}$  in combination. Use of two kinds of spacer particles having different resistivities makes it possible to enhance the transfer efficiency of the toner image from the photosensitive material onto the transfer paper as well as to divide the resistance on the surfaces of the toner particles into two. From the viewpoint of exchange of electric charge of the toner, therefore, the function is divided for generating the electric charge and for leaking the electric charge. As a result, the toner maintains desired amount of electric charge efficiently and more stably, so that image is formed maintaining stable density.

The resistivity can be easily adjusted by treating the surfaces to be electrically conducting, i.e., doping the surfaces with, for example, tin. That is, the spacer particles that are usually used have a relatively large resistivity like the second spacer particles and are treated to become electrically conducting and to exhibit a decreased resistivity, and are used as the first spacer particles. In the present invention, in particular, titanium oxide or magnesium oxide of which the surfaces are doped with tin is favorably used as the first spacer particles, and titanium oxide or magnesium oxide which is not doped with tin is favorably used as the second spacer particles.

The first spacer particles and the second spacer particles are used at a weight ratio of from 1:7 to 7:1 and, particularly, from 1:4 to 4:1, and in a total amount as described earlier.

The resistivity of the spacer particles can be measured by using, for example, a resistivity measuring device 4 shown in Fig. 10.

That is, 8 g of a sample of spacer particles (203) is introduced into a vinyl chloride tube (41) having an inner diameter ( $H_1$ ) of 1 inch and is sandwiched by electrodes (421) made of a steel. Teflon plates (43) having a thickness of 2 mm are arranged on both outer sides of the electrodes (421), and a pressure  $P_r$  of 200  $\text{kg}/\text{cm}^2$  is applied from one side of the Teflon plates (43) by using a hydraulic pressing machine, in order to measure a resistance  $r$  ( $\Omega$ ) at 500 V using an ultra-insulation resistance tester (42) (Model SM-5 manufactured by Toa Denpa Kogyo Co.). Overall length ( $H_2$ ) (cm) of the resistor is measured, the thickness of the pressurized sample is calculated relying upon a difference from the overall length (11.35 cm) of when no sample is charged, and the resistivity ( $\Omega \cdot \text{cm}$ ) is calculated from the following formula (7),

$$R = [(2.54/2)^2 \cdot \pi / (H_2 - 11.35)] \times r \quad (7)$$

In the present invention, furthermore, it is desired that the surfaces of the toner particles onto which the spacer particles will be adhered or the surfaces of the spacer particles are treated with a metal stearate or amide, i.e., it is desired that the metal stearate is adhered onto the surfaces of either of these particles. In this case, parting property is not adversely affected between the toner particles and the surface of the photosensitive material and, besides, the resistance of the toner suitably decreases, which is advantageous for forming image maintaining a high density. In this case, furthermore, the melting temperature of the toner decreases giving another advantage in that infiltration of the toner into the transfer paper is promoted during the heat-fixing by using a heat roll, and fixing property of the transferred toner image is enhanced. Besides, since the melting temperature of the metal stearate is lower than the melting temperature of the fixing resin medium, the surface of the image exhibits improved smoothness when the transferred toner image is heat-fixed, making it possible to obtain image with luster.

Examples of the metal stearate or amide include zinc stearate, magnesium stearate, aluminum stearate, calcium stearate, chromium stearate, mercury stearate, cerium stearate, ferric stearate, sodium stearate, lead stearate, barium stearate and stearic acid amide, which may be used in a single kind or in a combination of two or more kinds. Generally, it is desired to use zinc stearate or magnesium stearate. Most desirably, zinc stearate is used in a single kind.

It is desired that these metal stearates are used in an amount of from 0.001 to 3% by weight, preferably, from 0.003 to 1% by weight and, most preferably, from 0.005 to 0.2% by weight per the whole weight of the toner. Moreover, the metal stearates may be adhered on the surfaces of the toner particles or on the surfaces of the spacer particles.

(Magnetic Carrier)

Any widely known magnetic carrier can be used in combination with the above-mentioned toner. Desirably, there can be used magnetite ( $M = Fe$ ) or ferrite ( $M$  is other than  $Fe$ ) represented by the following formula (7),



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

Particularly, there can be used sintered ferrite particles and, especially, spherical particles of soft ferrite such as copper-zinc-magnesium ferrite in which  $M$  includes at least one and, preferably, two or more of  $Cu$ ,  $Zn$ ,  $Mg$ ,  $Mn$  and  $Ni$ .

The magnetic carrier particles permit electric resistance to change little depending upon the environment or aging, and exhibit stable charging property. Besides, the magnetic brush has a soft ear and does develop white streaks such as sweeping traces of magnetic brush on the formed image.

It is desired that the magnetic carrier has an average particle diameter of generally from 30 to 200  $\mu\text{m}$  and, particularly, from 50 to 150  $\mu\text{m}$ , a saturation magnetization of from 30 to 80  $\text{emu/g}$  and, particularly, from 45 to 70  $\text{emu/g}$ , and a volume resistivity of from  $10^5$  to  $10^9 \Omega \cdot \text{cm}$  and, particularly from  $10^6$  to  $10^8 \Omega \cdot \text{cm}$ .

Moreover, the magnetic carrier particles serving as cores may be coated with a variety of thermoplastic resins and thermosetting resins. Examples of the thermoplastic resin include thermoplastic acrylic resin, thermoplastic styrene-acrylic resin, polyester resin, polyamide resin and olefin-type copolymer resin, and examples of the thermosetting resin include modified or unmodified silicone resin, thermosetting acrylic resin, thermosetting styrene-acrylic resin, phenol resin, urethane resin, thermosetting polyester resin, epoxy resin, amino resin, fluorine-containing resin and melamine resin. Such resin coatings make it possible to more effectively avoid the occurrence of spent toner. Generally speaking, it is desired that the amount of resin coating is from 0.001 to 2.5 parts by weight and, particularly, from 0.005 to 2.0 parts by weight per 100 parts by weight of the core particles.

In the present invention, furthermore, it is desired that a cationic polar group is introduced into the coating resin. That is, provision of the resin coating layer having a cationic polar group helps increase the positively charging property of the carrier whereby the negatively charging property of the toner is further enhanced. Such a cationic polar group can be represented by a basic nitrogen-containing group such as primary, secondary or tertiary amino group, quaternary ammonium group, amide group, imino group, imide group, hydrazino group, guanidino group or amidino group. Among them, amino group and quaternary ammonium group are particularly preferred.

To introduce the cationic polar group, the resin should be produced by using, for example, a monomer component having the cationic group. The cationic polar group can be also introduced by treating the surfaces of the resin using a silane coupling agent having a cationic group. Examples of the silane coupling agent may include  $N$ - $\beta$  (aminoethyl)  $\gamma$ -aminopropyltrimethoxysilane,  $N$ - $\beta$  (aminoethyl)  $\gamma$ -aminopropylmethyldimethoxysilane,  $\gamma$ -aminopropyltriethoxysilane,  $N$ -phenyl- $\gamma$ -aminopropyltrimethoxysilane, etc.

It is further possible to introduce the cationic polar group into the resin by synthesizing the coating resin relying upon the polymerization using a polymerization initiator having a cationic polar group such as amidine-type azobis compound.

It is desired that the cationic polar group is introduced usually in an amount of from 0.1 to 2000 millimols and, particularly, from 0.5 to 1500 millimols per 100 g of the resin.

As desired, furthermore, the resin coating layer may be blended with a variety of known additives such as silica, alumina, carbon black, fatty acid metal salt, silane coupling agent, silicone oil, etc., as a matter of course.

The carrier particles serving as cores can be coated with a resin by a widely known method. For instance, the above-mentioned coating resin is dissolved in a suitable solvent. By using this resin solution, the resin is coated by immersion method, spray method, fluidized bed method, moving bed method or rolling bed method. In coating the thermosetting resin, furthermore, the resin may be cured by heating or the like means after the resin is coated by using a solution of uncured resin or oligomer.

According to the present invention, furthermore, it is allowable to use a binder-type carrier obtained by dispersing a magnetic powder in a binder resin.

As such a magnetic powder, there can be preferably used the aforementioned magnetic powder and, particularly, the magnetite having a particle diameter of not larger than  $2.0\ \mu\text{m}$  and, particularly, from  $0.05$  to  $1.0\ \mu\text{m}$ . The magnetic powder may be used in an amount of from 150 to 900 parts by weight and, particularly, from 250 to 600 parts by weight per 100 parts by weight of the binder resin.

Examples of the binder resin include thermoplastic resin, thermosetting resin which is uncured or in the form of an initial condensate, such as aromatic vinyl resin like polystyrene, as well as acrylic resin, polyvinyl acetal resin, polyester resin, epoxy resin, phenol resin, petroleum resin and polyolefin resin. Among them, styrene resin, acrylic resin and styrene-acrylic copolymer resin are preferred.

The binder-type carrier may be blended with a known assistant such as carbon black for adjusting electric resistance, dispersing agent, dispersion assistant, low molecular or high molecular charge control agent. In the same manner as described above, furthermore, the cationic polar group may be introduced to enhance the positively charging property of the carrier in order to enhance the negatively charging property of the toner.

Even in such a binder-type carrier, it is desired that the average particle diameter lies in the same range as that of the aforementioned carrier. (Two-Component Magnetic Developing Agent)

The toner of the present invention is mixed together with the above-mentioned various magnetic carriers and is used as a magnetic developing agent. Generally, it is desired that these carriers and the toner are mixed together at a ratio of from 98:2 to 90:10 and, particularly, from 97:3 to 94:6 on the weight basis.

In the electrophotographic copying method using the two-component magnetic developing agent, the electrostatic latent image can be formed by any known system. For instance, the photoconducting layer on the conducting substrate is uniformly charged and is exposed to light to form an electrostatic latent image.

The electrostatic image is easily developed by bringing a magnetic brush of the two-component magnetic developing agent into contact with the substrate. The toner image formed by developing is transferred onto a copying paper and is fixed upon contact with a heating roll.

The invention will now be described by way of the following Examples.

#### (Example 1)

##### A. Preparation of a fixing resin.

3 Parts of methacrylic acid, 17 parts by weight of butyl acrylate, 80 parts by weight of styrene and a polymerization initiator were mixed and stirred in a solvent to prepare a mixture solution thereof. The mixture solution was introduced into a reaction oven and was polymerized at  $160^\circ\text{C}$  for 6 hours with sufficient stirring using stirrer vanes. Then, the reaction solution was deaerated and dried to obtain a low molecular polymer having an acid value of 5.

Fig. 11 shows a curve of GPC molecular weight of the low molecular polymer, from which it will be obvious that the low molecular polymer has a peak molecular weight in a region of from 4,000 to 30,000.

Next, 10 parts by weight of methacrylic acid, 20 parts by weight of butyl acrylate, 70 parts by weight of styrene, a polymerization initiator and 100 parts by weight of the low molecular polymer obtained above were mixed and stirred in a solvent to prepare a mixture solution thereof. The mixture solution was introduced into a reaction oven and was polymerized at  $90^\circ\text{C}$  for 17 hours with sufficient stirring using stirrer vanes. Then, the reaction solution was deaerated and dried to obtain a desired resin for fixing having an acid value of 10.

Fig. 12 shows a curve of GPC molecular weight of the resin for fixing, from which it will be obvious that the resin for fixing exhibits nearly the same peak molecular weight as that of the above-mentioned low molecular polymer and further exhibits molecular weight distribution on the side of high molecular weight. The resin for fixing possessed a weight average molecular weight of 100,000.

##### B. Preparation of a toner.

The following components:

fixing resin for obtained above, 100 parts by weight,

carbon black (pH: 3.5, (7-pH)/specific surface area: 0.025, treated with nitric acid), 9 parts by weight, and

magnetite (magnetic powder), 2 parts by weight, were melt-kneaded using a biaxial extruder. The kneaded product was then pulverized using a jet mill and was classified by a wind classifier to obtain particles of a diameter of 10.0  $\mu\text{m}$ .

To 100 parts by weight of the particles were externally added 0.3 parts by weight of fine hydrophobic silica particles having an average particle diameter of 0.015  $\mu\text{m}$  as a fluidity improving agent and 0.6 parts by weight of alumina particles having an average particle diameter of 0.3  $\mu\text{m}$  as spacer particles. The mixture was then mixed together by the Henschel's mixer to obtain a toner.

#### C. Preparation of a developing agent.

The toner obtained above and an uncoated ferrite carrier having an average particle diameter of 100  $\mu\text{m}$  were mixed together to obtain a two-component developing agent having a toner concentration of 3.5%.

#### (Example 2)

1000 Parts by weight of spherical ferrite particles having an average particle diameter of 100  $\mu\text{m}$  were added to a coating solution obtained by dissolving 3.5 parts by weight of styrene-acrylic resin and 1.5 parts by weight of methylated melamine resin in 200 parts by weight of toluene, and were heated and stirred. Then, the solvent (toluene) was removed by drying from the mixture obtained above and was heat-treated at 200°C for one hour to obtain resin-coated carrier particles.

A two-component developing agent having a toner concentration of 3.5% by weight was obtained quite in the same manner as in Example 1 with the exception of using the above carrier particles as the magnetic carrier.

#### (Example 3)

The following components:

amino group-containing styrene-acrylic resin, 100 parts by weight,

magnetite (magnetic powder), 400 parts by weight, and

carbon black (pH = 9), 5 parts by weight, were melt-kneaded using a biaxial extruder. The kneaded product was

then pulverized using a jet mill and was classified by a wind classifier to obtain carrier particles of a diameter of 80  $\mu\text{m}$ .

A two-component developing agent having a toner concentration of 5.0% by weight was obtained in the same manner as in Example 1 by using magnetic carrier particles that were obtained by dispersing the magnetic powder in the resin.

#### (Comparative Example 1)

A toner and a developing agent were prepared in the same manner as in Example 1 but using the carbon black having a pH of 9 and a ratio (7-pH)/specific surface area of -0.013 (without treated with acid).

#### (Comparative Example 2)

A toner and a developing agent were prepared in the same manner as in Example 1 but using the carbon black having a pH of 3 and a ratio (7-pH)/specific surface area of -0.122 (treated with nitric acid).

#### (Evaluation of toner)

Copies were taken by using the developing agents obtained in the Examples and Comparative Examples and by using a copying machine manufactured by Mita Kogyo Co. (modified machine of a trade name of DC-4086). Measurements were taken concerning the following items to evaluate the toners. The results were as shown in Table 1.

##### (a) Transfer efficiency.

The amount of toner in a toner hopper prior to starting the copying operation and the amount of toner in the toner hopper after a predetermined number of copies were taken, were measured, and the amount of toner that was consumed was calculated from a difference therebetween. Furthermore, the amount of toner recovered in a step of cleaning was measured while the predetermined number of copies were being taken to find the amount of toner that was recovered. Based upon these values, the toner transfer efficiency was calculated in compliance with the following formula. Here, the document being copied was a character document having a black area of 8%.

$$\text{Transfer efficiency (\%)} = [(A - B)/A] \times 100$$

wherein A represents the amount of toner consumed, and B represents the amount of toner recovered.

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

By using a character document having a black area of 8%, copies were taken until the transfer efficiency became smaller than 70%. The density of a solid black portion in a sampling image was measured every after 5000 copies by using a reflection densitometer (Model TC-6D, manufactured by Tokyo Denshoku Co.). The document used for obtaining a sample every after 5000 copies possessed a black area inclusive of solid black portion of 15%.

(c) Fogging density (F.D.)

By using a character document having a black area of 8%, copies were taken until the transfer efficiency became smaller than 70%. The density of a solid black portion in a sampling image was measured every after 5000 copies by using the same reflection densitometer as the one mentioned above. A difference was calculated between this measured value and a value found by measuring a base paper of before being copied using the reflection densitometer, and a maximum value was regarded to be a fogging density (F.D.). The document used for obtaining a sample every after 5000 copies possessed a black area inclusive of solid black portion of 15%.

(d) Resolution.

After 50,000 pieces of copies were taken (or when the transfer efficiency became smaller than 70% even before 50,000 pieces of copies were taken) by using a character document having a black area of 8%, a copy was taken by using a predetermined chart document (document on which a predetermined number of parallel lines have been drawn within a width of 1 mm) and a copied image was evaluated by eyes.

(e) Amount of electric charge.

By using a character document having a black area of 8%, copies were taken until the transfer efficiency became smaller than 70%. Every after 5,000 pieces of copies were taken, the amount of electric charge of 200 mg of the developing agent was measured by using a device for measuring the amount of electric charge of blow-off powder (manufactured by Toshiba Chemical Co.) and was expressed in terms of an average amount of electric charge per gram of the toner.

(f) Spent amount.

After 50,000 pieces of copies were taken (or when the transfer efficiency became smaller than 70% even before 50,000 pieces of copies were taken) by using a character document having a black area of 8%, the developing agent was sampled. The developing agent was placed on a sieve of 400 mesh and was sucked by a blower from the lower side to separate it into the toner and the carrier. 5 Grams of the carrier remaining on the sieve was introduced into a beaker, and toluene was further added thereto in order to dissolve the toner that adhered onto the carrier surfaces as spent toner. Then, the toluene solution was discarded in a state where the carrier was attracted by a magnet from the lower side of the beaker. This was repeated several times until toluene became colorless and, then, toluene was dried in an oven to measure the weight. A difference between the weight in the beaker and the weight after drying was a spent amount. The spent amount was expressed in terms of milligrams of the spent toner adhered per gram of the carrier.

(g) Scattering of toner.

After 50,000 pieces of copies were taken (or when the transfer efficiency became smaller than 70% even before 50,000 pieces of copies were taken) by using a character document having a black area of 8%, scattering state of toner in the copying machine was observed by eyes and was evaluated on the following basis.

- : toner is not scattering  
X : toner is scattering

## (h) Durability.

Every after 10,000 pieces of copies were taken by using a character document having a black area of 8%, the amount of toner consumed was measured and the amount of toner recovered was measured, and from which the toner transfer efficiency was calculated. The number of pieces of copies after which the transfer efficiency became smaller than 70% for the first time was relied upon to evaluate the durability.

## (i) High-temperature high-humidity properties.

5,000 Pieces of copies were taken in an environment of a temperature of 35°C and a humidity of 85%, and fogging and scattering of toner were measured to evaluate high-temperature and high-humidity properties.

Table 1

Fixing resin	Examples			Comparative Examples	
	1	2	3	1	2
Acid value of resin	10	10	10	10	10
Acid value of low molecular component	5	5	5	5	5
Carbon black					
pH	3.5	3.5	3.5	9	3
(7-pH)/specific surface area	0.025	0.025	0.025	-0.013	0.120
<u>Carrier</u>	uncoated ferrite	resin-coated ferrite	binder-type carrier	uncoated ferrite	uncoated ferrite
Evaluated results					
ID	1.432	1.418	1.422	1.450	1.432
FD	0.003	0.002	0.002	0.008	0.003
Resolution	5	5	5	4	5
Amount of charge ( $\mu\text{C/g}$ )	-18.9	-21.9	-20.5	-14.8	-18.9
Spent amount (mg)	0.60	0.46	0.49	0.69	0.60
Toner scattering	○	○	○	X	○
Durability	60000 pieces	100000 pieces	90000 pieces	20000 pieces	60000 pieces
High-temp. high-humidity characteristics					
FD	0.003	0.003	0.003	-	0.009
Toner scattering	○	○	○	---	X

## (Consideration of the results of evaluation)

As will be understood from the results of Table 1, the toners of Examples 1 to 3 were very stable in regard to image density, fogging and resolution, and did not scatter. Good high-temperature and high-humidity properties were exhibited, too.

In Comparative Example 1, on the other hand, the toner scattered to a conspicuous degree at normal temperature. Under high-temperature and high-humidity conditions, furthermore, the toner developed fogging and scattered to a conspicuous degree.

According to the present invention which is not blended with a negative charge control agent, the toner maintains the electric charge in an amount large enough for effecting the developing, no charge control agent migrates onto the carrier surfaces, and the charging property is not deteriorated by the spent toner but is stably maintained for extended periods of time, enabling the life of the toner and the carrier to be lengthened.

By setting the acid value of the low molecular components contained in the fixing resin medium to be lower than the acid value of the whole resin, furthermore, the charging property of the toner is more reliably prevented from being impaired by the spent toner, and scattering of toner and fogging can be effectively avoided.

#### (Example 4)

As a fixing resin, use was made of a copolymerized resin containing units inherent in styrene, stearyl methacrylate, acrylic acid and butyl methacrylate at weight ratios of 74:4:5:16, having an acid value of 10, peak molecular weight of a low molecular polymer component of 10,000, and a weight average molecular weight of 100,000.

The following components:

fixing resin obtained above, 100 parts by weight,

polypropylene wax (average molecular weight: 4000), 3 parts by weight,

carbon black (pH: 3.5, (7-pH)/specific surface area ( $\text{m}^2/\text{g}$ ): 0.025, treated with nitric acid),

10 parts by weight, and

magnetite (magnetic powder), 2 parts by weight, were melt-kneaded using a biaxial extruder. The kneaded product was then pulverized using a jet mill and was classified by a wind classifier to obtain particles of a diameter of 10.0  $\mu\text{m}$ .

To 100 parts by weight of the particles were externally added 0.3 parts by weight of fine hydrophobic silica particles having an average particle diameter of 0.015  $\mu\text{m}$  as a fluidity improving agent and 0.6 parts by weight of alumina particles having an average particle diameter of 0.3  $\mu\text{m}$  as spacer particles, and were mixed together by the Henschel's mixer to obtain a toner.

The toner obtained above and a ferrite carrier having an average particle diameter of 100  $\mu\text{m}$  were mixed together to obtain a two-component developing agent having a toner concentration of 3.5% by weight.

#### (Example 5)

A fixing resin (containing no higher alkyl group) comprising a styrene-acrylic acid-butyl methacrylate copolymer was prepared in the same manner as in Example 1 but using styrene, acrylic acid and butyl methacrylate at weight ratios of 75:20:5. The resin possessed a peak molecular weight due to a low molecular polymer component of 10,000 and a weight average molecular weight of 100,000.

A toner and a developing agent were prepared in the same manner as in Example 4 but using the above resin for fixing.

#### (Example 6)

1000 Parts by weight of spherical ferrite particles having an average particle diameter of 100  $\mu\text{m}$  were added to a coating solution obtained by dissolving 3.5 parts by weight of styrene-acrylic resin and 1.5 parts by weight of methylated melamine resin in 200 parts by weight of toluene, and were heated and stirred. Then, the solvent (toluene) was removed by drying from the mixture obtained above and was heat-treated at 200°C for one hour to obtain resin-coated carrier particles.

A two-component developing agent having a toner concentration of 3.5% by weight was obtained quite in the same manner as in Example 4 but using the above carrier particles as the magnetic carrier.

#### (Example 7)

The following components:

amino group-containing styrene-acrylic resin, 100 parts by weight,

magnetite (magnetic powder), 400 parts by weight, and

carbon black (pH = 9), 5 parts by weight,

were melt-kneaded using a biaxial extruder. The kneaded product was then pulverized using a jet mill and was classified by a wind classifier to obtain carrier particles of a diameter of 80  $\mu\text{m}$ .



A two-component developing agent having a toner concentration of 5.0% by weight was obtained in the same manner as in Example 1 but using binder-type carrier particles that were obtained by dispersing the magnetic powder in the resin.

The developing agents prepared in Examples 4 to 7 above were tested in the same manner as in Examples 1 to 3, and were evaluated. The results were as shown in Table 2.

Table 2

Fixing resin	Ex.4	Ex.5	Ex.6	Ex.7
Higher alkyl group containing unit	stearyl methacrylate	none	stearyl methacrylate	stearyl methacrylate
Carbon black				
pH	3.5	3.5	3.5	3.5
7-pH/specific surface area	0.025	0.025	0.025	0.025
Carrier	uncoated ferrite	uncoated ferrite	resin-coated ferrite	binder-type carrier
Evaluated results				
ID	1.422	1.418	1.421	1.386
FD	0.003	0.005	0.003	0.002
Resolution	5	5	5	5
Amount of charge ( $\mu\text{C/g}$ )	-18.2	-17.2	-21.8	-23.9
Spent amount(mg)	0.62	0.87	0.40	0.38
Toner scattering	○	○	○	○
Durability	70000 pieces	50000 pieces	90000 pieces	90000 pieces

When the toner is blended with a parting agent (polypropylene) as will be obvious from Table 2, durability is not so high (50,000 pieces) in Example 5 which uses the fixing resin medium without higher alkyl group-containing polymer component. In Examples 4, 6 and 7 using a higher alkyl group-containing fixing resin medium, however, the durability is improved to a considerable degree.

(Example 8)

(Preparation of a fixing resin medium)

The following components:

a mixture of styrene, butyl methacrylate and acrylic acid at a weight ratio of 80:15:5, 100 parts by weight, and a polypropylene wax (average molecular weight: 4,000), 0.6 parts by weight, a polymerization initiator

were mixed, stirred and dissolved in a solvent. The obtained mixture solution was introduced into a reaction oven and was polymerized at 150°C for 5 hours with sufficient stirring using a stirrer vane. Thereafter, the reaction solution was deaerated and dried to obtain a low molecular polymer containing a component to which the polypropylene wax is graft-fixed.

The following components:

low molecular polymer obtained above, 100 parts by weight, a mixture of styrene, butyl methacrylate and acrylic acid at a weight ratio of 70:25:5, 100 parts by weight, the same polypropylene wax as the above one, 5.4 parts by weight, and a polymerization initiator,

were mixed and stirred in a solvent to prepare a mixture solution. The mixture solution was introduced into a reaction oven and was polymerized at 80°C for 15 hours with sufficient stirring using stirrer vanes. The reaction solution was then deaerated and dried to obtain a desired fixing resin having an acid value of 10.

The fixing resin possessed a peak molecular weight of 10,000, a molecular weight distribution on the side of high molecular weights, and a weight average molecular weight of 100,000.

The following components:

fixing resin obtained above, 103 parts by weight (containing 3 parts by weight of wax), carbon black (pH: 3.5, (7-  
5 pH)/specific surface area ( $\text{m}^2/\text{g}$ ): 0.025, treated with nitric acid), 10 parts by weight, and

magnetite (magnetic powder), 2 parts by weight,  
were melt-kneaded using a biaxial extruder. The kneaded product was then pulverized using a jet mill and was classified by a wind classifier to obtain particles of a diameter of  $10.0\ \mu\text{m}$ .

To 100 parts by weight of the particles were externally added 0.3 parts by weight of fine hydrophobic silica particles  
10 having an average particle diameter of  $0.015\ \mu\text{m}$  as a fluidity improving agent and 0.6 parts by weight of alumina particles having an average particle diameter of  $0.3\ \mu\text{m}$  as spacer particles, and were mixed together by the Henschel's mixer to obtain a toner.

The toner obtained above and a ferrite carrier having an average particle diameter of  $100\ \mu\text{m}$  were mixed together to obtain a two-component developing agent having a toner concentration of 3.5% by weight.

15 (Example 9)

A resin for fixing was prepared in the same manner as in Example 8 but without using polypropylene wax.

A toner was prepared quite in the same manner as in Example 8 but using 100 parts by weight of the above resin  
20 for fixing and 3 parts by weight of the polypropylene wax used in Example 8. Then, a two-component developing agent was prepared.

(Example 10)

25 1000 Parts by weight of spherical ferrite particles having an average particle diameter of  $100\ \mu\text{m}$  were added to a coating solution obtained by dissolving 3.5 parts by weight of styrene-acrylic resin and 1.5 parts by weight of methylated melamine resin in 200 parts by weight of toluene, and were heated and stirred. Then, the solvent (toluene) was removed by drying from the mixture obtained above and was heat-treated at  $200^\circ\text{C}$  for one hour to obtain resin-coated carrier particles.

30 A two-component developing agent having a toner concentration of 3.5% by weight was obtained quite in the same manner as in Example 8 but using the above resin-coated carrier particles.

(Example 11)

35 The following components:

amino group-containing styrene-acrylic resin,

100 parts by weight,

magnetite (magnetic powder), 400 parts by weight, and

carbon black (pH = 9), 5 parts by weight,

40 were melt-kneaded using a biaxial extruder. The kneaded product was then pulverized using a jet mill and was classified by a wind classifier to obtain binder-type carrier particles of a diameter of  $80\ \mu\text{m}$ .

A two-component developing agent having a toner concentration of 5.0% by weight was obtained in the same manner as in Example 8 but using binder-type carrier particles that were obtained by dispersing the magnetic powder in the resin.

45 The developing agents prepared in Examples 8 to 11 above were tested in the same manner as in Examples 1 to 3, and were evaluated. The results were as shown in Table 3.

Table 3

	Ex.8	Ex.9	Ex.10	Ex.11
<u>Fixing resin</u>	3% of wax is graft-fixed	no wax is graft graft-fixed	3% of wax is graft-fixed	3% of wax is graft-fied
Carbon black				
pH	3.5	3.5	3.5	3.5
7-pH/specific surface area	0.025	0.025	0.025	0.025
<u>Carrier</u>	uncoated ferrite	uncoated ferrite	resin-coated ferrite	binder-type carrier
Evaluated results				
ID	1.425	1.433	1.408	1.352
FD	0.003	0.005	0.002	0.002
Resolution	5	4	5	5
Amount of charge ( $\mu\text{C/g}$ )	-18.8	-15.9	-22.1	-24.0
Spent amount(mg)	0.60	0.80	0.42	0.40
Toner scattering	○	○	○	○
Durability	70000 pieces	50000 pieces	90000 pieces	90000 pieces

As will be obvious from Table 3, when the resin for fixing is simply blended with wax (Example 9), the durability is deteriorated to some extent. When the wax is graft-fixed to the resin for fixing as in Examples 8, 10 and 11, however, the durability is improved.

#### (Example 12)

The following components:

resin for fixing (styrene-acrylic copolymer having a carboxyl group, acid value of 8), 100 parts by weight, carbon black (pH: 3.5, (7-pH)/specific surface area ( $\text{m}^2/\text{g}$ ): 0.025, 7 parts by weight, magnetic powder (magnetite), 2 parts by weight, and polyethylene resin (molecular weight: 4000), 2 parts by weight,

were melt-kneaded using a biaxial extruder. The kneaded product was then pulverized using a jet mill and was classified by a wind classifier to obtain toner particles having an average particle diameter of 10.0  $\mu\text{m}$ .

To 100 parts by weight of the particles were externally added 0.3 parts by weight of fine hydrophobic silica particles having an average particle diameter of 0.015  $\mu\text{m}$  and 0.3 parts by weight of magnetite having an average particle diameter of 0.3  $\mu\text{m}$  as spacer particles, and were mixed together by the Henschel's mixer for two minutes to obtain a toner of the present invention.

The toner obtained above and a ferrite carrier having an average particle diameter of 100  $\mu\text{m}$  were mixed together to obtain a two-component developing agent having a toner concentration of 3.5% by weight.

#### (Example 13)

The toner particles were prepared quite in the same manner as in Example 12 but without being blended with polyethylene, and a developing agent was prepared.

By using the developing agents of Examples 12 and 13, images were formed in the same manner as in Examples 1 to 3, and fixing factors of the obtained images were found in accordance with a method described below.

A flat bottom of a weight of 400 g was wrapped with a uniformly stretched cotton cloth to rub a solid black portion of the image five round trips at a predetermined speed. The image density (ID) of before being rubbed and the image density (ID) of after rubbed were measured, and a peeling factor was regarded to be a fixing factor.

$$\text{Fixing factor (\%)} = \frac{\text{ID after rubbing}}{\text{ID before rubbing}} \times 100$$

5 In Example 13, the fixing factor was slightly smaller than 80% but in Example 12, the fixing factor was not smaller than 90%.

(Example 14)

10 Styrene, butyl methacrylate and acrylic acid were mixed together at weight ratios of 80:15:5, and were mixed and dissolved together with a polymerization initiator in a solvent with stirring. The reaction system was heated and polymerized. After polymerized, the reaction solution was deaerated and dried to prepare a resin for fixing comprising a styrene-butyl methacrylate-acrylic acid copolymerized resin. The resin for fixing possessed an acid value of 10.

The weight average molecular weight of the resin for fixing was 100,000.

15 The following components:

resin for fixing obtained above, 100 parts by weight,

carbon black (pH: 3.5, (7-pH)/specific surface area ( $\text{m}^2/\text{g}$ ): 0.025, treated with nitric acid), 7 parts by weight, and

magnetite (magnetic powder), 2 parts by weight,

20 were melt-kneaded using a biaxial extruder. The kneaded product was then pulverised using a jet mill and was classified by a wind classifier to obtain particles of a diameter of 10.0  $\mu\text{m}$ .

To 100 parts by weight of the particles were externally added 0.3 parts by weight of fine hydrophobic silica particles having an average particle diameter of 0.015  $\mu\text{m}$  as a fluidity improving agent and 0.5 parts by weight of magnetite particles ( $2 \times 10^3 \Omega \cdot \text{cm}$ ) having an average particle diameter of 0.3  $\mu\text{m}$  as spacer particles, and were mixed together by the Henschel's mixer to obtain a toner.

25 The surface-treated toner particles and a ferrite carrier having an average particle diameter of 100  $\mu\text{m}$  were mixed together to obtain a two-component developing agent having a toner concentration of 3.5% by weight.

Example 15

30 A toner and a developing agent were prepared quite in the same manner as in Example 14 but using, as spacer particles, 0.5 parts by weight of magnetite particles ( $2 \times 10^3 \Omega \cdot \text{cm}$ ) having an average particle diameter of 0.3  $\mu\text{m}$  and 0.5 parts by weight of alumina particles ( $10^{10} \Omega \cdot \text{cm}$ ) having an average particle diameter of 0.3  $\mu\text{m}$ .

(Example 16)

35 A toner and a developing agent were prepared quite in the same manner as in Example 14 but externally adding 0.2 parts by weight of zinc stearate.

(Example 17)

40 1000 Parts by weight of spherical ferrite particles having an average particle diameter of 100  $\mu\text{m}$  were added to a coating solution obtained by dissolving 3.5 parts by weight of styrene-acrylic resin and 1.5 parts by weight of methylated melamine resin in 200 parts by weight of toluene, and were heated and stirred. Then, the solvent (toluene) was removed by drying from the mixture obtained above and was heat-treated at 200°C for one hour to obtain resin-coated carrier particles.

45 A two-component developing agent having a toner concentration of 3.5% by weight was obtained quite in the same manner as in Example 14 but using the above carrier particles as a magnetic carrier.

(Example 18)

50 The following components:

amino group-containing styrene-acrylic resin, 100 parts by weight,

magnetite (magnetic powder), 400 parts by weight, and

carbon black (pH = 9), 5 parts by weight,

55 were melt-kneaded using a biaxial extruder. The kneaded product was then pulverized using a jet mill and was classified by a wind classifier to obtain binder-type carrier particles of a diameter of 80  $\mu\text{m}$ .

A two-component magnetic developing agent having a toner concentration of 5.0% by weight was obtained in quite the same manner as in Example 14 but using the binder-type carrier particles that were obtained by dispersing the magnetic powder in the resin.

(Comparative Example 3)

A toner and a developing agent were prepared quite in the same manner as in Example 14 but using the carbon black having pH of 9 and a ratio (7-pH)/specific surface area (m<sup>2</sup>/g) of -0.013, which has not been treated with acid.

(Example 19)

A toner and a developing agent were prepared in quite the same manner as in Example 14 but without using spacer particles.

The developing agents obtained in Examples 14 to 19 and Comparative Example 3 were tested in the same way as in Examples 1 to 3, and were further measured for their transfer efficiencies in accordance with a method described below. The results were as shown in Tables 4 and 5.

Transfer efficiency:

The amount of toner in a toner hopper prior to starting the copying operation and the amount of toner in the toner hopper after a predetermined number of copies were taken, were measured, and the amount of toner that was consumed was calculated from a difference therebetween. Furthermore, the amount of toner recovered in a step of cleaning was measured while the predetermined number of copies were being taken to find the amount of toner that was recovered. Based upon these values, the toner transfer efficiency was calculated in compliance with the following formula. Here, the document being copied was a character document having a black area of 8%.

$$\text{Transfer efficiency (\%)} = [(A - B)/A] \times 100$$

wherein A represents the amount of toner consumed, and B represents the amount of toner recovered.

Table 4

	Ex.14	Ex.15	Ex.16
<u>Spacer particles</u>	magnetite	magnetite and alumina	treated with stearic acid
Carbon black			
pH	3.5	3.5	3.5
7-pH/specific surface area	0.025	0.025	0.025
<u>Carrier</u>	uncoated ferrite	uncoated ferrite	uncoated ferrite
Evaluated results			
ID	1.430	1.426	1.465
FD	0.003	0.003	0.003
Resolution	5	5	5
Amount of charge (μC/g)	-18.1	-18.3	-17.5
Spent amount(mg)	0.60	0.57	0.62
Toner scattering	○	○	○
Durability	80000 pieces	100000 pieces	80000 pieces
Transfer efficiency (%)	82	83	82

Table 5

	Ex.17	Ex.18	Co.Ex.3	Ex.19
<u>Spacer particles</u>	magnetite	magnetite	magnetite	none
Carbon black				
pH	3.5	3.5	9	3.5
7-pH/specific surface area	0.025	0.025	-0.013	0.025
<u>Carrier</u>	resin-coated ferrite	binder-type carrier	uncoated ferrite	uncoated ferrite
Evaluated results				
ID	1.425	1.372	1.453	1.423
FD	0.002	0.002	0.009	0.003
Resolution	5	5	4	5
Amount of charge ( $\mu\text{C/g}$ )	-20.3	-23.0	-13.8	-18.8
Spent amount(mg)	0.41	0.43	0.85	0.80
Toner scattering	○	○	X	○
Durability	100000 pieces	100000 pieces	30000 pieces	50000 pieces
Transfer efficiency (%)	83	83	73	78

As will be obvious from Tables 4 and 5, use of the spacer particles makes it possible to enhance durability and transfer efficiency of the toner.

Accordingly, the invention provides a negatively chargeable toner which maintains an electric charge in an amount sufficient for developing in the absence of a negative charge control agent. Hence migration of charge control agent to the surface of the magnetic carrier is prevented and the deterioration of charging properties by the occurrence of spent toner is reduced.

### Claims

1. A negatively chargeable toner for a two-component magnetic developing agent obtainable by dispersing carbon black in a fixing resin medium, wherein:  
the fixing resin medium is a copolymerized resin or a resin composition comprising free or neutralized anionic polar groups and having an acid value from 4 to 30 as measured in the form of a free acid; and  
the carbon black has a pH less than 7 and a ratio (7-pH)/specific surface area ( $\text{m}^2/\text{g}$ ) of from 0.010 to 0.050, and is present in an amount from 4 to 15% by weight with respect to the fixing resin medium.
2. A toner according to claim 1, wherein an extract of the toner with methanol exhibits absorbency which is substantially zero over a region of wavelength from 400 to 700 nm, and does not exhibit an absorption peak over a region from 280 to 350 nm.
3. A toner according to claim 1 or 2, wherein the fixing resin medium has a weight average molecular weight from 70,000 to 200,000.
4. A toner according to claim 3, wherein the fixing resin medium contains a low molecular weight component having peak molecular weight from 4,000 to 30,000 and a high molecular weight component having molecular weight distributed over a region of high molecular weight.
5. A toner according to claim 4, wherein the low molecular weight component has an acid value from 3 to 15 and which is smaller than the overall acid value of the fixing resin medium.
6. A toner according to any one of the preceding claims, wherein the toner comprises a parting agent, and the fixing resin medium comprises a polymer having a higher alkyl group of at least 12 carbon atoms on a side chain thereof.

7. A toner according to claim 6, wherein the higher alkyl group-containing polymer is a copolymer obtainable by copolymerization of a monomer comprising a free or neutralized anionic polar group and a monomer comprising an alkyl group of at least 12 carbon atoms.
- 5 8. A toner according to any one of the preceding claims, wherein the fixing resin medium comprises a polymer to which a wax is graft-fixed.
9. A toner according to claim 8, wherein the wax is present in an amount from 0.01 to 10 parts by weight per 100 parts by weight of the fixing resin medium.
- 10 10. A toner according to claim 8 or 9, wherein the wax is graft-fixed to a polymer component which comprises an anionic polar group.
11. A toner according to claim 10, wherein the polymer component to which the wax is grafted-fixed is present in a  
15 copolymerized resin comprising anionic polar groups.
12. A toner according to any one of the preceding claims, wherein polyethylene having a number average molecular weight from 1000 to 7000 is present in an amount from 0.5 to 5 parts by weight per 100 parts by weight of the fixing  
20 resin medium.
13. A toner according to any one of the preceding claims, wherein the toner comprises particles having a volume-based average particle diameter from 5 to 15  $\mu\text{m}$ , and comprises spacer particles additional to the surface of the toner particles having a volume-based average particle diameter of from 0.05 to 1.0  $\mu\text{m}$ .
- 25 14. A toner according to any one of the preceding claims, wherein a magnetic powder is dispersed in the fixing resin medium in an amount from 0.1 to 5 parts by weight per 100 parts by weight of the resin medium.
15. A two-component magnetic developing agent comprising a toner as claimed in any one of claims 1 to 14 and a resin-coated magnetic carrier.
- 30 16. A two-component magnetic developing agent comprising a toner as claimed in any one of claims 1 to 14 and a magnetic carrier obtainable by dispersing a magnetic powder in a resin.
17. Use of a toner according to any one of claims 1 to 14 in electrophotographic printing or electrophotographic repro-  
35 duction of an image.

FIG. 1

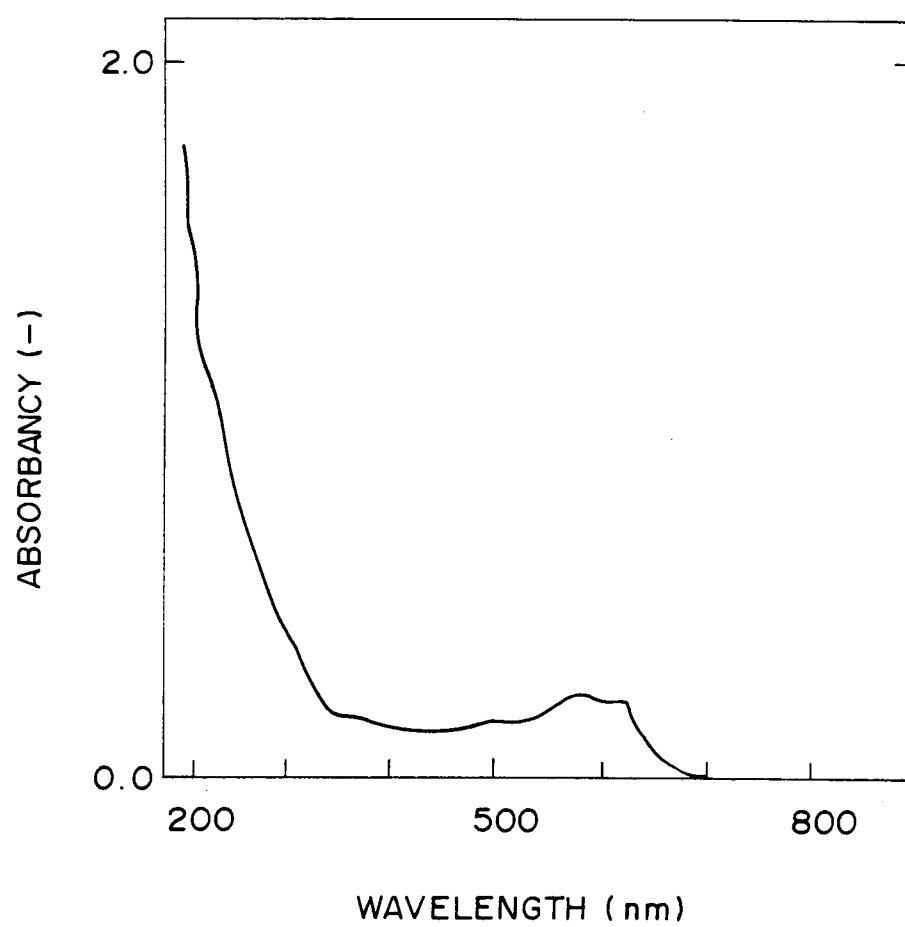




FIG. 2

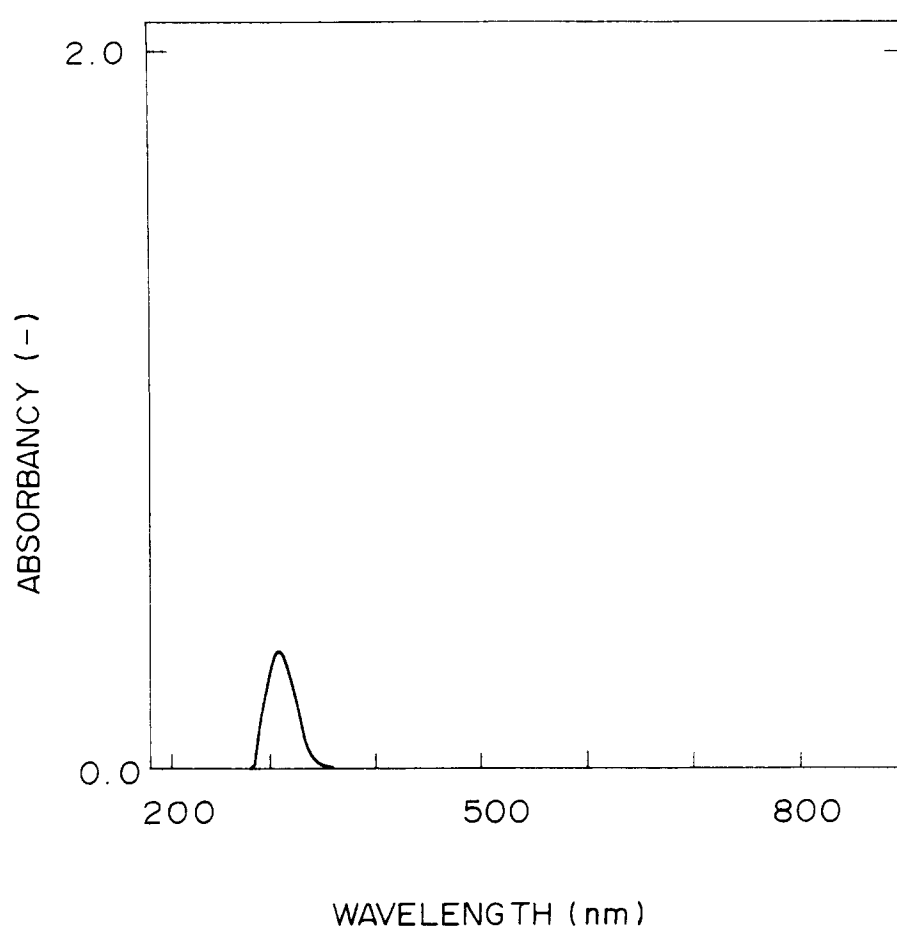


FIG. 3

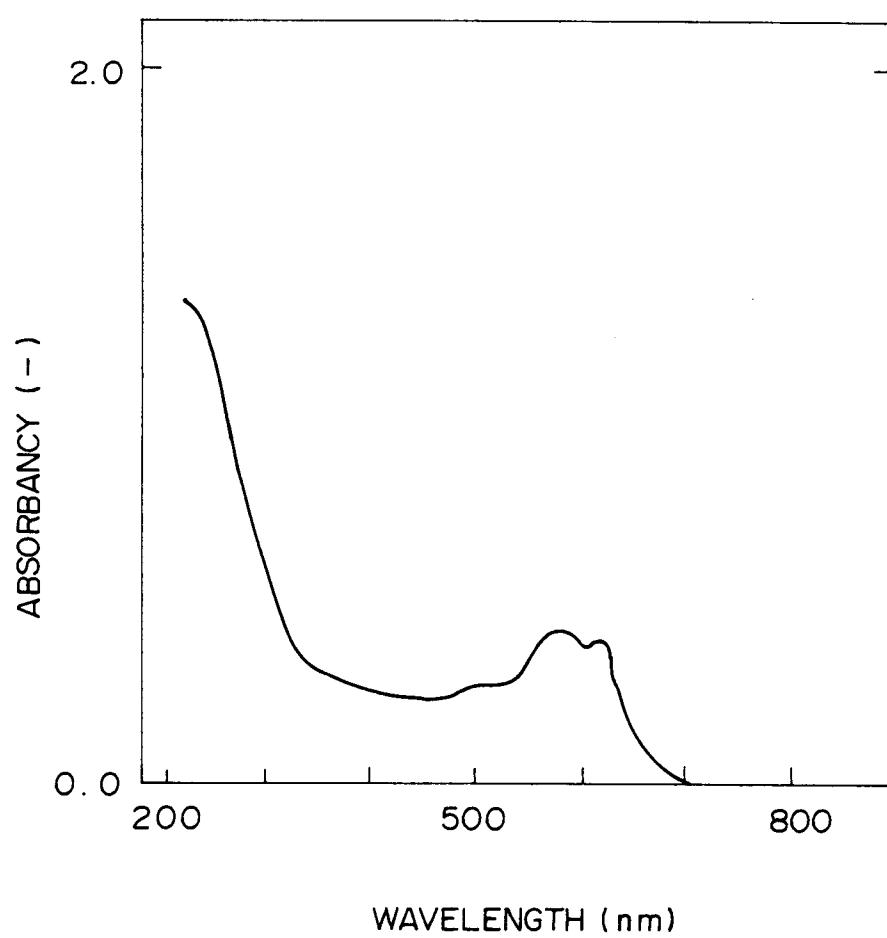


FIG. 4

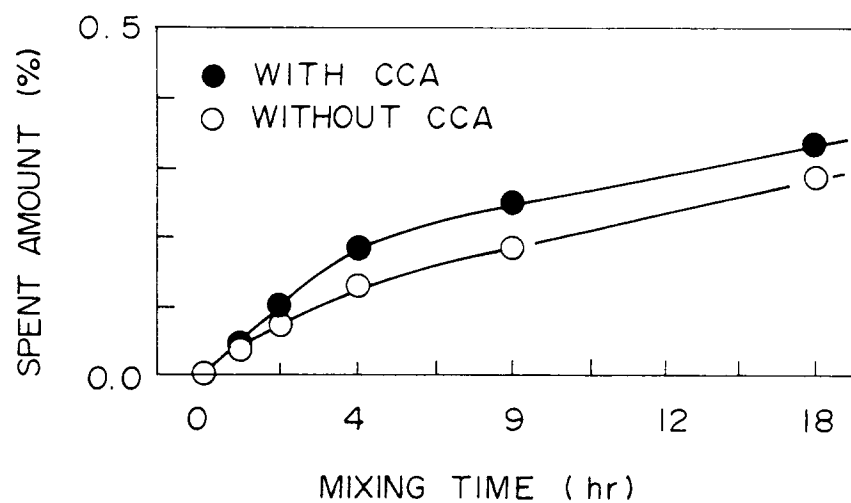


FIG. 5

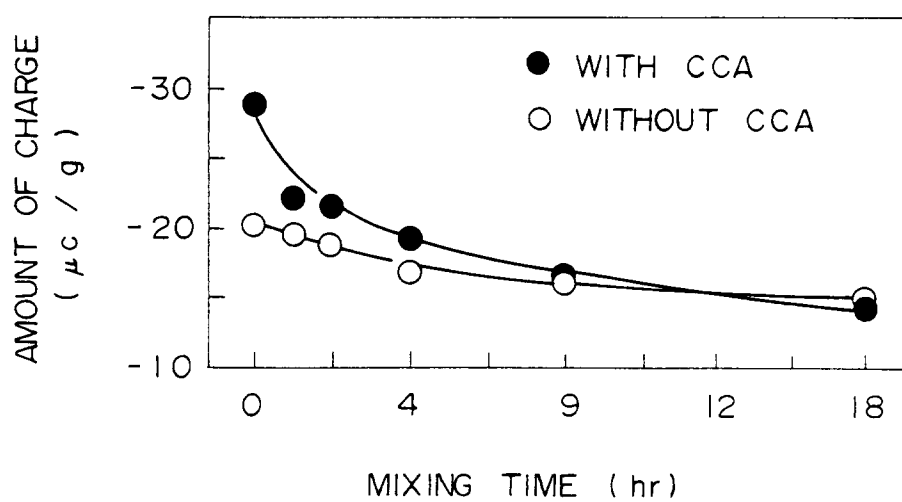


FIG. 6

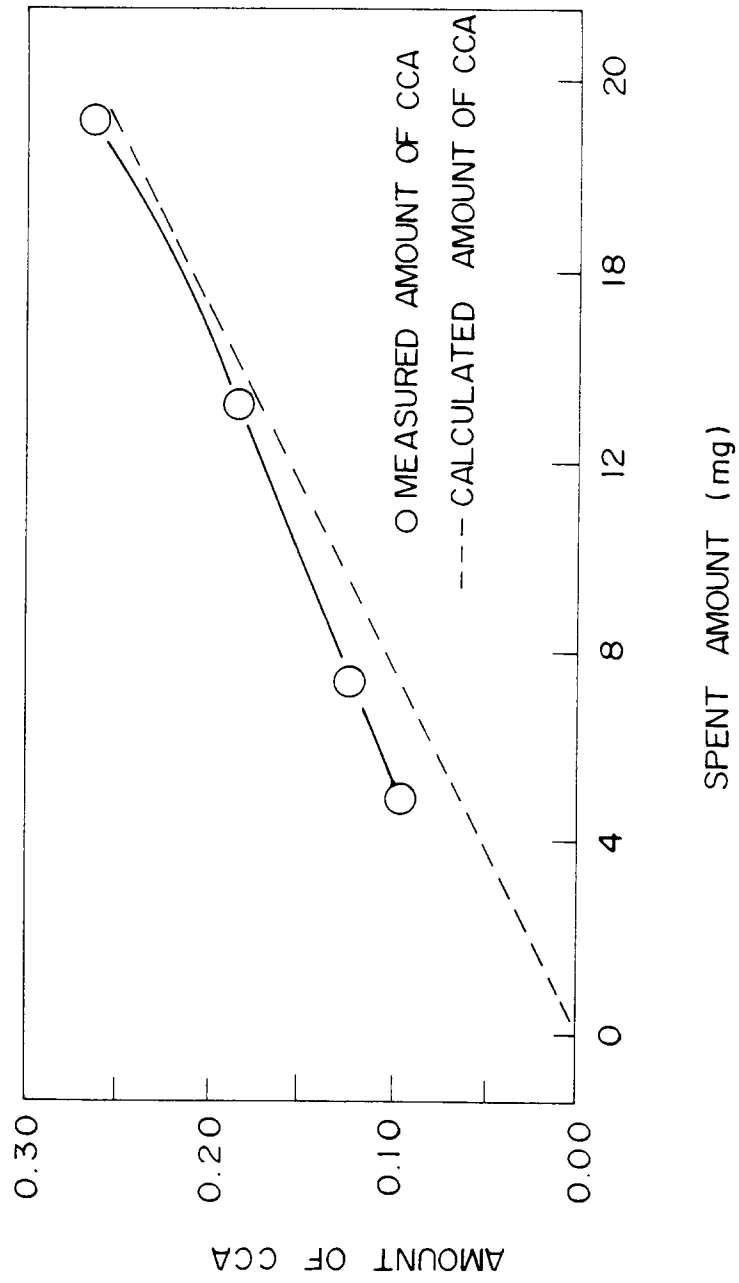


FIG. 7

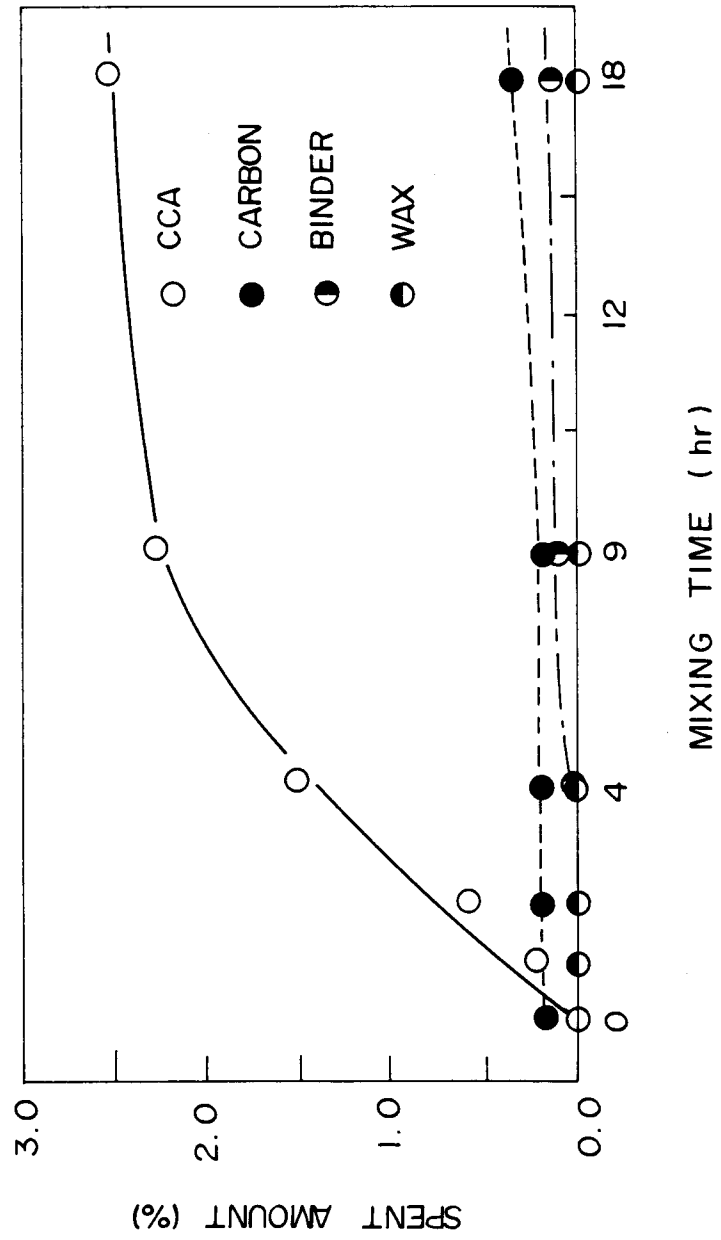


FIG. 8

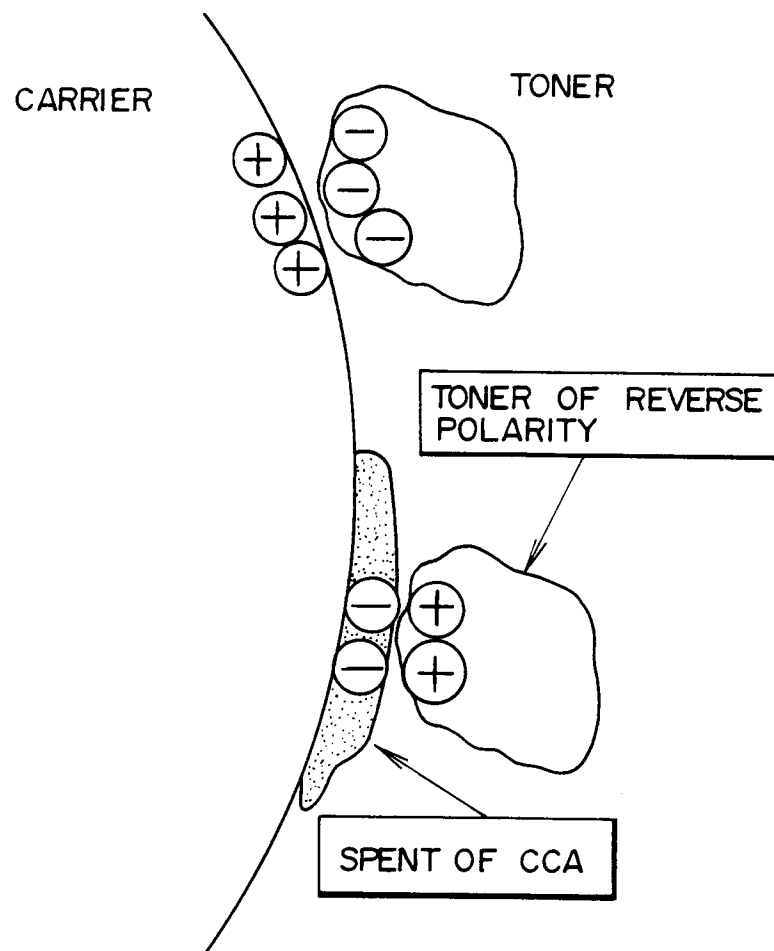


FIG. 9

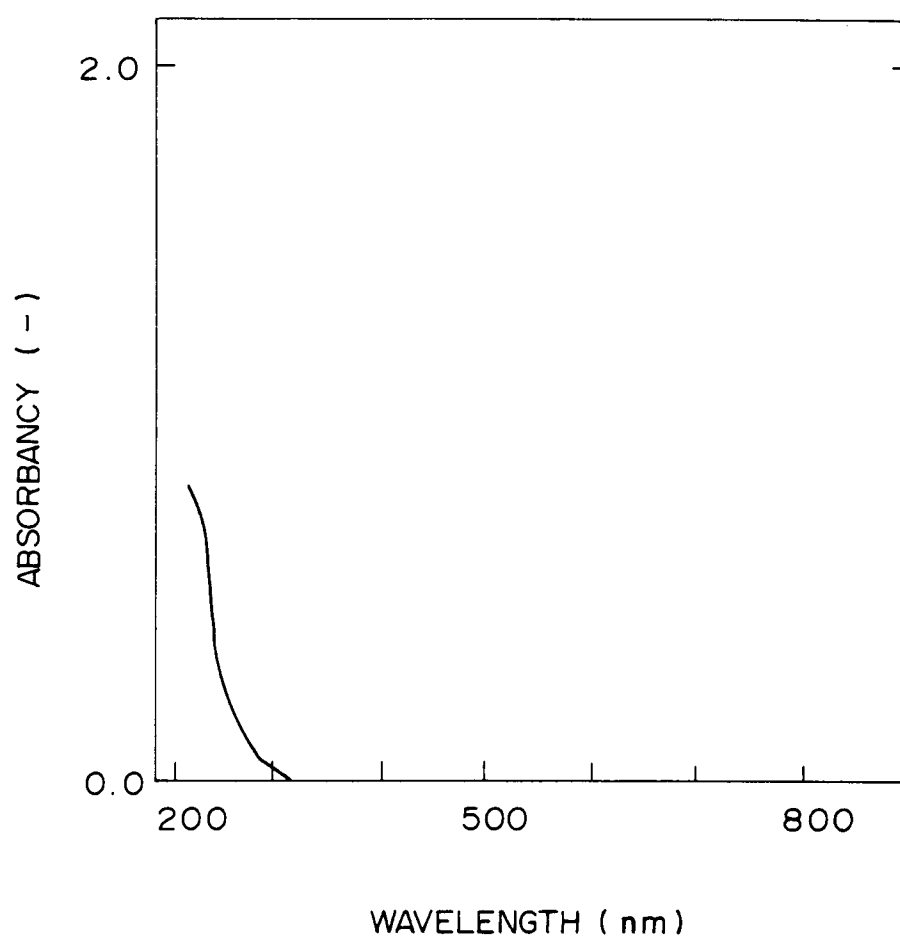


FIG. 10

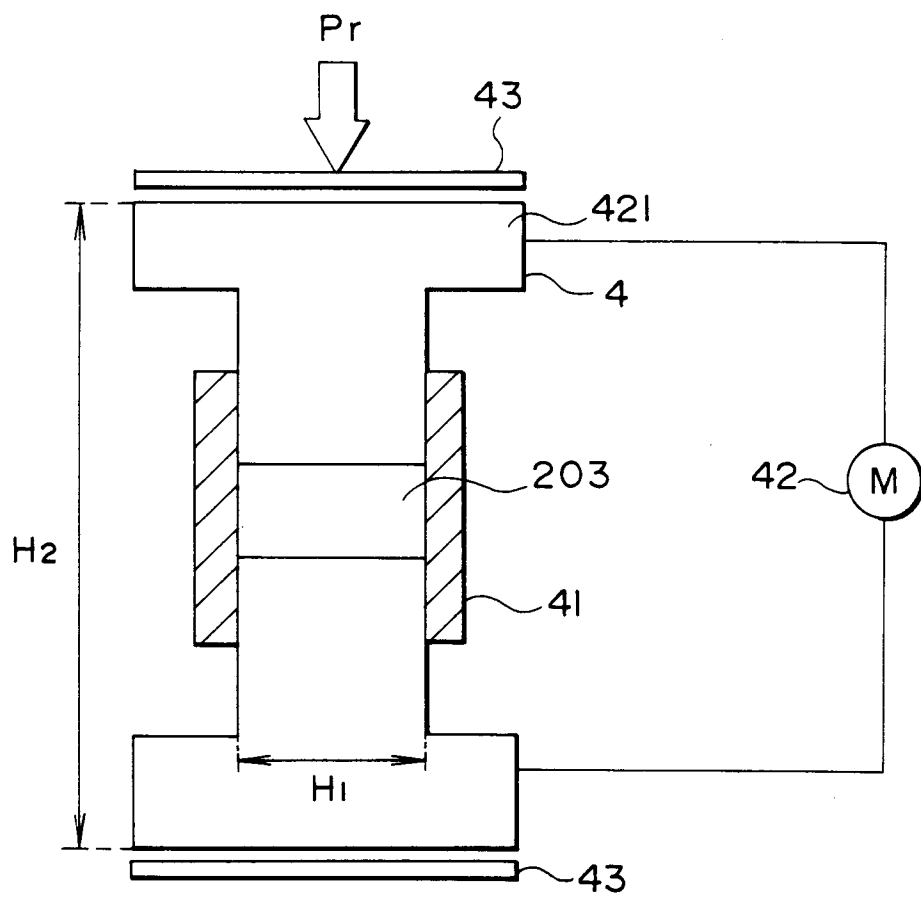




FIG. 11

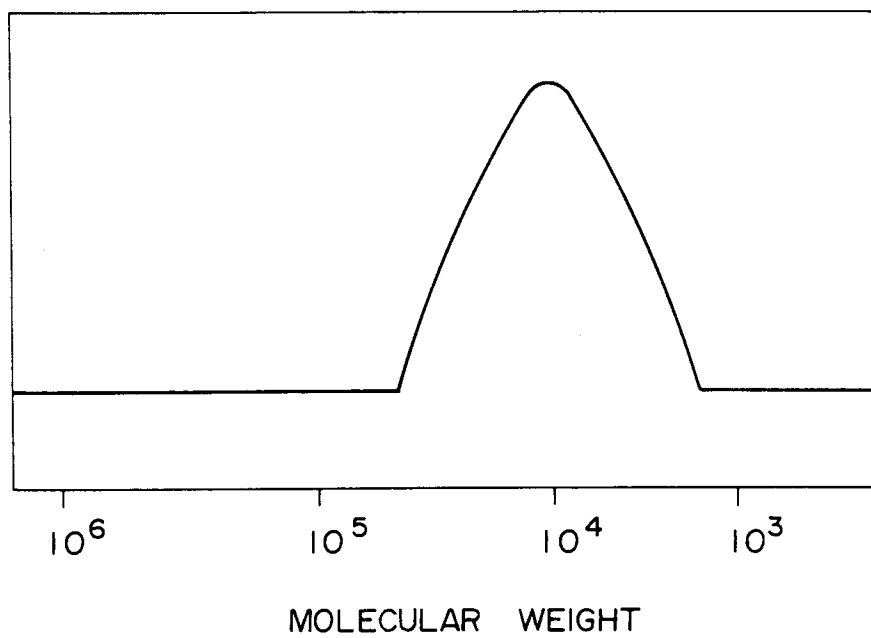


FIG. 12

