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(54) Developing agent and method of manufacturing the same

(57) An electrophotographic developing agent excellent in off-set resistance, shelf life, fluidity and fixing properties is provided by adding a first wax having a low viscosity in the first step of preparing a binder resin mixture by polymerization and by adding a second wax having a viscosity higher than that of the first wax in the second step of melting and kneading the wax-added binder resin so as to permit these waxes to be dispersed sufficiently in the resultant toner.

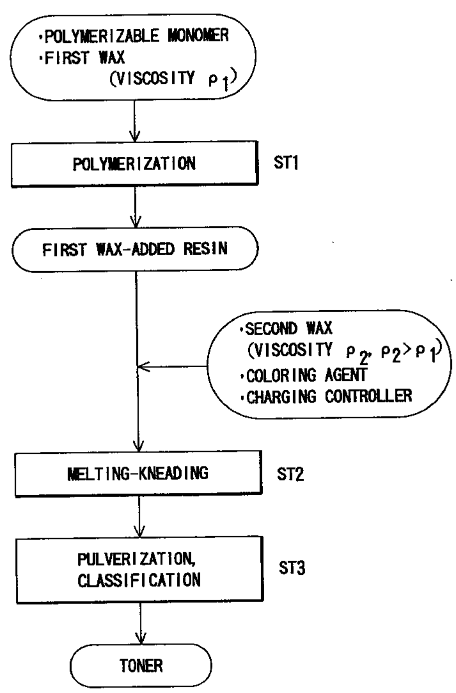

FIG. 1

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Description

The present invention relates to an electrophotographic developing agent, particularly, an electrophotographic developing agent used in a thermal fixing method.

A developing agent is required to meet various requirements. For example, the developing agent is required (i) to exhibit a high fix retention rate, (ii) to be satisfactory in smear characteristics, and (iii) not to bring about off-set phenomenon. The term "fix retention rate" denotes a fixing strength of the developing agent fixed to a recording medium. A high fix retention rate indicates that the developing agent is sufficiently fixed to the recording medium. The term "smear" denotes a phenomenon that a mechanical friction causes the developing agent after the fixing step to be peeled off the recorded paper sheet so as to bring about smear of the images recorded on another recording paper sheet. The smear often takes place in the case where, for example, a recorded paper sheet is transferred as an original through an automatic original transfer apparatus. Further, the term "off-set phenomenon" represents a difficulty that the developing agent, which is melted by heating in the fixing step, is attached to the fixing device so as to stain the images recorded on the recording medium. Particularly, where a pair of fixing rollers are used for the fixing under heat and pressure, a so-called back stain is brought about. Specifically, the molten toner is attached to the pressurizing roller so as to stain the back surface of the recording paper sheet.

Japanese Patent Disclosure (Kokai) No. 4-358159 discloses a measure for overcoming the above-noted problems. Specifically, this prior art proposes the idea of allowing a toner to contain two kinds of waxes having different softening points. However, it is difficult to disperse uniformly a plurality of different kinds of waxes in the binder resin constituting a main component of the developing agent.

In conclusion, it is desirable to allow the developing agent to contain a plurality of different kinds of waxes in order to meet the various properties required for the electrophotographic developing agent. However, it is difficult to disperse a plurality of different kinds of waxes uniformly in the binder resin, resulting in failure to obtain a satisfactory developing agent.

An object of the present invention is to provide an electrophotographic developing agent excellent in off-set resistance, shelf stability, fluidity and fixing capability.

According to a first aspect of the present invention, there is provided a method of manufacturing a developing agent, comprising:

a first step of preparing a wax-added binder resin by polymerizing a solution containing a polymerizable monomer and a first wax dispersed in the monomer and having a first viscosity;
a second step of melting and kneading a mixture comprising the wax-added binder resin prepared in the first step, a coloring agent, and a second wax having a second viscosity higher than the first viscosity; and
a third step of purverizing and classifying a kneeded mass prepared in the second step.

According to a second aspect of the present invention, there is provided a method of manufacturing a developing agent, comprising:

a first step of preparing a wax-added binder resin by polymerizing a solution containing a polymerizable monomer and a first wax dispersed in the polymerizable monomer and having a number average molecular weight of 1500 to 4000;
a second step of melting and kneading a mixture comprising the wax-added binder resin prepared in the first step, a coloring agent, and a second wax having a number average molecular weight of 8000 to 11000; and
a third step of purverizing/classifying for purverizing and classifying a kneeded mass prepared in the second step.

According to a third aspect of the present invention, there is provided a method of manufacturing a developing agent, comprising:

a first step of preparing a wax-added binder resin by polymerizing a solution containing a polymerizable monomer, having a number average molecular weight of 1500 to 4000, and having a first viscosity;
a second step of melting and kneading a mixture consisting of the wax-added binder resin prepared in the first step, a coloring agent, and a second wax having a number average molecular weight of 8000 to 11000, and a second viscosity higher than the first viscosity; and
a third step of purverizing and classifying a kneeded mass prepared in the second step.

According to a fourth aspect of the present invention, there is provided a developing agent, obtained by purverizing and classifying a kneaded mass prepared by melting and kneading a mixture consisting of a wax-added binder resin prepared by polymerizing a solution containing a polymerizable monomer and a first wax dispersed in the polymerizable monomer and having a first viscosity, a coloring agent, and a second wax having a viscosity higher than that of the first wax.

Further, according to a fifth aspect of the present invention, there is provided a developing agent obtained by pulverizing and classifying a kneaded mass prepared by melting and kneading a mixture consisting of a wax-added binder resin prepared by polymerizing a solution containing a polymerizable monomer and a first wax dispersed in the polymerizable monomer and having a number average molecular weight of 1500 to 4000, a coloring agent, and a second wax having a number average molecular weight of 8000 to 11000.

In the present invention, a first wax having a low viscosity is added in the first step of preparing a wax-added binder resin. Also, a second wax having a viscosity higher than that of the first wax is added in the second step of melting and kneading a mixture containing the wax-added binder resin prepared in the first step. Alternatively, a first wax having a low number average molecular weight is added in the first step of preparing a wax-added binder resin, and a second wax having a number average molecular weight higher than that of the first wax is added in the second step of melting and kneading a mixture containing the binder resin mixture prepared in the first step. The particular technique of the present invention permits markedly improving the dispersion capability of the waxes in the kneaded mass. Further, the developing agent obtained from the kneaded mass is excellent in its fixing properties such as the fix retention rate and smear properties, off-set resistance, shelf stability, and fluidity.

This invention can be more fully understood from the following detailed description when taken in conjunction with the accompanying drawings, in which:

FIG. 1 is a flow chart schematically showing a method of the present invention for manufacturing a developing agent;

FIG. 2 is a cross sectional view schematically showing an image forming apparatus in which the developing agent of the present invention is used;

FIG. 3 is a graph showing the relationship between the viscosity and temperature of the first wax; and

FIG. 4 is a graph showing the relationship between the viscosity and temperature of the second wax.

The method of manufacturing a developing agent according to a first aspect of the present invention comprises a first step of preparing a wax-added binder resin by polymerizing a solution containing a polymerizable monomer and a first wax dispersed in the polymerizable monomer and having a first viscosity, and a second step of melting and kneading a mixture consisting of the wax-added binder resin prepared in the first step, a coloring agent, and a second wax having a viscosity higher than that of the first wax.

Additives such as a electrostatic charge control agent can be added when kneading.

The kneaded mass is further subjected, as required, to a drying step, a pulverizing step, and a classifying step so as to prepare desired toner particles used for obtaining the developing agent of the present invention.

In the first step of preparing the wax-added binder resin, the particular solution is subjected to polymerization, preferably with stirring.

As described above, in the first aspect of the present invention, a first wax having a low viscosity is added in the first step of preparing a wax-added binder resin. Further, a second wax having a viscosity higher than that of the first wax is added in the second step of melting and kneading a mixture containing the binder resin mixture prepared in the first step so as to obtain a kneaded mass. The particular technique of the first aspect of the present invention permits improving the dispersion capability of the waxes in the resultant toner particles. Further, the developing agent obtained by using these toner particles exhibits excellent off-set resistance, shelf life, fluidity and fixing capability.

Where both first and second waxes are added together in the first step of preparing the wax-added binder resin, bleeding takes place in the resin mixture obtained after the second step of melting and kneading a mixture containing the binder resin mixture prepared in the first step. It should be noted that the developing agent prepared by using a resin mixture accompanied by the bleeding problem is attached to a drum, giving rise to a filming problem. If such a developing agent is used for an image formation, the formed image is rendered poor in image quality.

Where both first and second waxes are added together in the second step of melting-kneading a mixture containing the binder resin mixture prepared in the first step, the resultant developing agent is rendered markedly poor in both fluidity and shelf life. If such a developing agent is used for an image formation, fogging takes place in the formed image. Also, charging properties of the developing agent are made unsatisfactory.

Under the circumstances, the first and second waxes are added in different steps in the present invention. To reiterate, a first wax having a low viscosity and a second wax having a high viscosity are added in the first step of preparing a wax-added binder resin and the second step of melting and kneading a mixture containing the binder resin mixture prepared in the first step, respectively.

The flow chart in FIG. 1 schematically shows a method of manufacturing a developing agent according to the first aspect of the present invention. As seen from the flow chart, a first wax and a polymerizable monomer are dispersed in a solvent. The resultant dispersion is subjected to polymerization, which is performed while stirring the dispersion, in the first step (ST 1) so as to prepare a wax-added binder resin.

Then, a mixture prepared adding a second wax having a viscosity higher than that of the first wax, a coloring agent, etc. to the binder resin mixture prepared in the first step is melted and kneaded in the second step (ST 2). Further, the kneaded mass prepared in the second step is pulverized and classified in the third step (ST 3) so as to obtain toner particles of a desired particle size.

In the present invention, the viscosity of the wax is determined by a Brookfield viscometer. Originally, viscosity represents an inner friction of a liquid, which can be detected by measuring the time required for a predetermined amount of liquid to flow through a capillary tube. It should be noted that the viscosity of wax depends on the composition thereof. Specifically, the wax viscosity is increased with increase in the molecular weight of the main component of the wax. Where the wax contains an ester as a main component, the wax viscosity is lowered with increase in the degree of unsaturation of the ester, if the ester has the same number of carbon atoms. Viscosity can be roughly classified into an absolute viscosity, a kinetic viscosity and an industrial viscosity.

The absolute viscosity, which is precisely defined physically, is indicated by a unit poise (P), which is g/cm.s. In general, the absolute viscosity is indicated by centipoise (cP), i.e., 1/100 P. The kinetic viscosity is obtained by dividing an absolute viscosity of a liquid at a certain temperature by the density of the liquid at the same temperature, and is indicated by a unit stoke (St). In general, the kinetic viscosity is indicated by centistoke (cSt), i.e., 1/100 St. Further, the industrial viscosity is measured by a method defined individually by using a special measuring instrument such as a Redwood viscometer or a Saybolt viscometer.

As described previously, the wax viscosity defined in the present invention denotes a Brookfield viscosity measured by using a Brookfield viscometer. The Brookfield viscometer is a kind of an inner cylinder rotating type rotational viscometer. An outer cylinder is not used in the Brookfield viscometer, and an inner cylinder is allowed to hang directly a sample. The inner cylinder is rotated at a predetermined rotating speed. The Brookfield viscometer can be used conveniently because the viscosity of a sample in a liquid tank can be measured directly during operation of the factory including the liquid tank. The Brookfield viscometer can also be called a B-type viscometer.

In the first preferred embodiment of the method according to of the present invention, each of the first and second waxes is defined in terms of a preferred range of the viscosity. A first preferred embodiment relating to the first aspect of the present invention provides a method of manufacturing a developing agent, comprising:

a first step of preparing a wax-added binder resin by polymerizing a solution containing a polymerizable monomer and a first wax having a viscosity ρ_1 of 100 to 1000 cP at 100°C and dispersed in the monomer; and
a second step of melting and kneading a mixture containing the binder resin mixture prepared in the first step, a coloring agent, and a second wax having a viscosity of 10000 to 100000 cP at 100°C.

If the viscosity of the first wax at 100°C is less than 100 cP, the wax is not compatible with the resin and tends to fail to be dispersed sufficiently in the resultant toner. If the viscosity exceeds 1000 cP, however, the wax is too viscous to be dispersed sufficiently even if the wax is added in the first step of preparing the binder resin mixture.

If the viscosity of the second wax at 100°C is less than 10000 cP, a difference in viscosity between the wax and the binder resin is so large that the wax is not compatible with the resin and tends to fail to be dispersed sufficiently in the melting-kneading step. If the viscosity exceeds 100000 cP, however, fluidity of the wax itself tends to be impaired, leading to a poor dispersion.

In a preferred second embodiment relating to the first aspect of the present invention, the first and second waxes are further defined in terms of a further preferred range of viscosity. Specifically, the preferred second embodiment provides a method of manufacturing a developing agent, comprising:

a first step of preparing a wax-added binder resin by polymerizing a solution containing a polymerizable monomer and a first wax having a viscosity ρ_1 having a temperature characteristic represented by formula (1) given below and dispersed in the polymerizable monomer:

$$\rho_1 = \alpha_1 \times T_1 + C_1 \tag{1}$$

where $-9.78 \leq \alpha_1 < 0$, C_1 is a viscosity at 0°C, and where T_1 = 100°C, $100 < \rho_1 \leq 1000$, and
a second step of melting and kneading a mixture consisting of the wax-added binder resin prepared in the first step, a coloring agent, and a second wax having a viscosity ρ_2 having a temperature characteristic represented by formula (2) given below:

$$\rho_2 = \alpha_2 \times T_2 + C_2 \tag{2}$$

where $-950 \leq \alpha_2 < 0$, C_2 is a viscosity at 0°C, and where T_2 = 100°C, $10000 < \rho_2 \leq 100000$.

In a preferred third embodiment of the first aspect, the first and second waxes are defined in terms of the mixing amounts. Specifically, the third embodiment of the first aspect provides a method of manufacturing a developing agent, comprising:

a first step of preparing a wax-added binder resin by polymerizing a solution containing a polymerizable monomer and a first wax having a first viscosity; and

a second step of melting and kneading a mixture containing the wax-added binder resin prepared in the first step, a coloring agent, and a second wax having a second viscosity higher than that of the first viscosity;

characterized in that the first wax is added in an amount of 1 to 7 parts by weight relative to 100 parts by weight of the kneaded mass prepared in the second step, and the second wax is added in an amount of 0.1 to 3 parts by weight relative to 100 parts by weight of the kneaded mass prepared in the second step.

If the amount of the first wax is less than 1% by weight, the wax fails to act sufficiently as a repellent agent when the prepared developing agent is used in an image forming operation. As a result, the off-set resistance of the developing agent tends to be impaired. If the first wax is added in an amount exceeding 7% by weight, however, the wax particles once dispersed in the toner are fused again together, resulting in failure for the first wax to be dispersed sufficiently in the toner. On the other hand, if the amount of the second toner is less than 0.1% by weight, the prepared developing agent tends to be poor in its resistance to smear. If the amount exceeds 3% by weight, however, the second wax fails to be dispersed sufficiently in the toner.

In a preferred fourth embodiment of the first aspect, specified in combination are the preferred viscosities of the first and second waxes specified in the first embodiment and the preferred amounts of the first and second waxes specified in the third embodiment. Specifically, the fourth embodiment is directed to a method of manufacturing a developing agent, comprising:

a first step of preparing a wax-added binder resin by polymerizing a solution containing a polymerizable monomer and a first wax dispersed in the polymerizable monomer, said first wax having a viscosity ρ_1 at 100°C of 100 to 1000 cP; and

a second step of melting and kneading a mixture consisting of the wax-added binder resin prepared in the first step, a coloring agent and a second wax having a viscosity ρ_2 at 100°C of 10000 to 100000 cP,

characterized in that the first wax is added in an amount of 1 to 7 parts by weight relative to 100 parts by weight of the kneaded mass prepared in the second step, and the second wax is added in an amount of 0.1 to 3 parts by weight relative to 100 parts by weight of the kneaded mass prepared in the second step.

Since the features of the first and third preferred embodiments are included in combination, the method according to the fourth preferred embodiment of the first aspect permits producing the merits of both the first and third preferred embodiments.

The method according to the second aspect of the present invention is substantially equal to the method of the first aspect, except that a first wax having a number average molecular weight of 1500 to 4000 is used in the method of the second aspect in place of the first wax having a first viscosity, which is used in the method of the first aspect, and that a second wax having a number average molecular weight of 8000 to 11000 is used in the method of the second aspect in place of the second wax having a second viscosity, which is used in the method of the first aspect. The method of the second aspect is also substantially equal in function and produced effect to the method of the first aspect.

To reiterate, the second aspect of the present invention is directed to a method of manufacturing a developing agent, comprising:

a first step of preparing a wax-added binder resin by polymerizing a solution containing a polymerizable monomer and a first wax dispersed in said polymerizable monomer and having a number average molecular weight of 1500 to 4000; and

a second step of melting and kneading a mixture consisting of the wax-added binder resin prepared in the first step, a coloring agent, and a second wax having a number average molecular weight of 8000 to 11000.

It is important to note that, in the second aspect of the present invention, the first wax having a number average molecular weight of 1500 to 4000 is added in the first step of preparing the wax-added binder resin. Also, the second wax having a number average molecular weight of 8000 to 11000 is added in the second step of melting and kneading a mixture containing the binder resin prepared in the first step. The particular technique permits improving the dispersion capability of the waxes in the toner particles. Also, a developing agent prepared by using these toner particles is excellent in off-set resistance, shelf life, fluidity and fixing properties.

If the number average molecular weight of the first wax is less than 1500, an off-set phenomenon tends to take place under high temperatures. If the number average molecular weight of the first wax exceeds 4000, however, an off-set phenomenon tends to take place under low temperatures.

If the number average molecular weight of the second wax is less than 8000, a smear resistance tends to be impaired. If the number average molecular weight of the second wax exceeds 11000, however, the wax fails to be dispersed sufficiently in the toner, giving rise to a filming problem.

As described above, the method according to the second aspect of the present invention is defined in terms of the number average molecular weights of the first and second waxes. In the present invention, the limitation in terms of the number average molecular weight of the wax can be employed as a preferred embodiment of the invention relating to the first aspect of the present invention. Of course, the particular combination is expected to produce more excellent effects.

The present invention according to third aspect provides a method of manufacturing a developing agent, comprising:

a first step of preparing a wax-added binder resin by polymerizing a solution containing a polymerizable monomer and a first wax dispersed in said polymerizable monomer, having a number average molecular weight of 1500 to 4000, and having a first viscosity; and
a second step of melting and kneading a mixture consisting of the wax-added binder resin prepared in the first step, a coloring agent, and a second wax having a number average molecular weight of 8000 to 11000, and a second viscosity higher than the first viscosity.

A fifth preferred embodiment of the present invention is directed to a method of manufacturing a developing agent, comprising:

a first step of preparing a wax-added binder resin by polymerizing a solution containing a polymerizable monomer and a first wax dispersed in said polymerizable monomer, having a number average molecular weight of 1500 to 4000, and having a first viscosity ρ_1 at 100°C of 100 to 1000 cP; and
a second step of melting and kneading a mixture consisting of the wax-added binder resin prepared in the first step, a coloring agent, and a second wax having a number average molecular weight of 8000 to 11000, and a second viscosity ρ_2 at 100°C of 10000 to 100000 cP.

A sixth preferred embodiment of the present invention is directed to a method of manufacturing a developing agent, comprising:

a first step of preparing a wax-added binder resin by polymerizing a solution containing a polymerizable monomer and a first wax dispersed in said polymerizable monomer, having a number average molecular weight of 1500 to 4000, and having a first viscosity; and
a second step of melting and kneading a mixture consisting of the wax-added binder resin prepared in the first step, a coloring agent, and a second wax having a number average molecular weight of 8000 to 11000, and a second viscosity higher than the first viscosity;
wherein the first wax is added in an amount of 1 to 7 parts by weight relative to 100 parts by weight of the kneaded mass prepared in the second step, and the second wax is added in an amount of 0.1 to 3 parts by weight relative to 100 parts by weight of the kneaded mass prepared in the second step.

An seventh preferred embodiment of the present invention is directed to a method of manufacturing a developing agent, comprising:

a first step of preparing a wax-added binder resin by polymerizing a solution containing a polymerizable monomer and a first wax dispersed in said polymerizable monomer, having a number average molecular weight of 1500 to 4000, and having a first viscosity ρ_1 at 100°C of 100 to 1000 cP; and
a second step of melting and kneading a mixture consisting of the wax-added binder resin prepared in the first step, a coloring agent, and a second wax having a number average molecular weight of 8000 to 11000, and a second viscosity ρ_2 at 100°C of 10000 to 100000 cP;
wherein the first wax is added in an amount of 1 to 7 parts by weight relative to 100 parts by weight of the kneaded mass prepared in the second step, and the second wax is added in an amount of 0.1 to 3 parts by weight relative to 100 parts by weight of the kneaded mass prepared in the second step.

In the third, fourth, seventh, and eighth preferred embodiment, it is important to add the first wax in an amount of 1 to 7 parts by weight relative to 100 parts by weight of the kneaded mass prepared in the second step. Also, it is important to add the second wax in an amount of 0.1 to 3 parts by weight relative to 100 parts by weight of the kneaded mass prepared in the second step. It is desirable for the sum of the first and second waxes used in the manufacture of the developing agent to be at most 10% by weight. It is also desirable for the ratio by weight of the first wax to the second wax to fall within a range of between 1:3 and 70:1.

The components of the binder resin prepared in the first step included in the method of manufacturing the developing agent of the present invention can include, for example, a binder resin monomer, a solvent, a polymerization initiator, and a molecular weight controlling agent.

The resins used as a binder in the developing agent of the present invention include, for example, styrene-based copolymers such as polystyrene, styrene-butadiene copolymer, and styrene-acrylonitrile copolymer; ethylene-based copolymers such as polyethylene, ethylene-vinyl acetate copolymer, ethylene-vinyl alcohol copolymer; so-called petroleum resins such as phenolic resins, polyamide resins, polyester resins, maleic acid-based resins, polymethyl methacrylate, polyacrylic acid, polyvinyl butyral, aliphatic hydrocarbon resins, alicyclic hydrocarbon resins, and aromatic hydrocarbon resins; chlorinated paraffins; and mixtures thereof.

It is possible to use known coloring agents in the developing agent of the present invention including, for example, carbon black, fast yellow G, benzidine yellow, pigment yellow, indofast orange, irugagine red, carmine FB, permanent bordeaux FRR, pigment orange R, lithole red 2G, chelate red C, rhodamine FB, rhodamine B chelate, phthalocyanine blue, pigment blue, brilliant green B, phthalocyanine green, and quinacridone.

In order to control the amount of the electric charge imparted to the carrier particles, it is possible to add an antistatic agent such as a metal dye, a ligrocine based antistatic agent and a polyamine based antistatic agent to the developing agent of the present invention. These antistatic agents can be used in the form of a mixture with, for example, a nuclear toner and/or a surface treating agent. Further, in order to improve the fluidity of the colored particles and to improve the resistance to agglomeration of the developing agent, it is possible to add, as required, hydrophobic colloidal particles having a polarity equal to that of colored particles such as colloidal silica particles.

In order to improve the fluidity of the colored particles and to stabilize the charging amount, materials other than the colloidal silica particles can also be added to the developing agent of the present invention. For example, it is possible to add to the developing agent of the present invention materials such as inorganic oxides such as aluminum oxide, titanium oxide, silicon oxide, zinc oxide, magnesium oxide, calcium oxide, tin oxide, silicon, indium oxide, cerium oxide, and molybdenum trioxide; and inorganic oxide particles having the surfaces treated with coupling agents such as a silane coupling agent, titanium coupling agent, and a silicone oil. It is also possible to use as such additives fine powders of resins such as styrene-based copolymers including, for example, polystyrene, styrene-butadiene copolymer, and styrene-acrylic acid copolymer; aliphatic copolymers such as polyethylene and ethylene-based copolymer, and polymethyl methacrylate; alicyclic copolymers, silicone resins, and tefrons. Further, it is possible to use fine resin powders having the surfaces treated with a coupling agent, a silicone oil, etc. Still further, magnetic powders such as a magnetite powder and a ferrite powder can be added to the developing agent of the present invention.

The developing agents according to the fourth and fifth aspects of the present invention include the developing agents manufactured by the methods according to the first and second aspects of the present invention as well as those manufactured by the first to eighth preferred embodiments of the present invention.

Let us describe briefly the developing agents according to the fourth and fifth embodiments of the present invention. It should be noted that the function and produced effects of the developing agents manufactured by the methods according to the first and second aspects and by the first to seventh preferred embodiments of the present invention have already been described in conjunction with the description of these first and second aspects and first to seventh preferred embodiments. Therefore, let us omit the description of the particular function and produced effects of the developing agents according to the fourth and fifth aspects of the present invention.

The present invention according to the fourth aspect provides a developing agent obtained essentially from a kneaded mass prepared by melting and kneading a mixture consisting of a wax-added binder resin prepared by polymerizing a solution containing a polymerizable monomer and a first wax dispersed in the polymerizable monomer and having a first viscosity, a coloring agent, and a second wax having a viscosity higher than that of the first wax.

In a preferred first embodiment of the developing agent of the present invention, the first and second waxes contained therein are defined in terms of a preferred range of the viscosity of each of these waxes. Specifically, the preferred first embodiment noted above is directed to a developing agent obtained essentially by melting and kneading a mixture consisting of a wax-added binder resin prepared by polymerizing a solution containing a polymerizable monomer and a first wax dispersed in the polymerizable monomer and having a viscosity ρ_1 at 100°C of 100 to 1000 cP, a coloring agent, and a second wax having a viscosity at 100°C of 10000 to 100000.

In a preferred second embodiment of the developing agent of the present invention, the first and second waxes are defined in terms of ranges of the viscosities. Specifically, the preferred second embodiment noted above is directed to a developing agent obtained essentially by melting and kneading a mixture consisting of a wax-added binder resin prepared by polymerizing a solution containing a polymerizable monomer and a first wax dispersed in said polymerizable monomer and having a temperature characteristic denoted by formula (1) given below, a coloring agent, and a second wax having a temperature characteristic represented by formula (2) given below:

$$\rho_1 = \alpha_1 \times T_1 + C_1 \qquad (1)$$

where $-9.78 \leq \alpha_1 < 0$, C_1 is a viscosity at 0°C, and $100 \leq \rho_1 \leq 1000$ when T_1 is 100°C (T_1 = 100°C);

$$\rho_2 = \alpha_2 \times T_2 + C_2 \quad (2)$$

where $-950 \leq \alpha_2 < 0$, C_2 is a viscosity at 0°C, and $10000 \leq \rho_2 \leq 100000$ when T_2 is 100°C (T_1 = 100°C).

In a preferred third embodiment directed to the developing agent of the present invention, the first and second waxes are defined in terms of the contents thereof in the developing agent. Specifically, the third preferred embodiment noted above is directed to a developing agent obtained essentially by melting and kneading a mixture consisting of a wax-added binder resin prepared by polymerizing a solution containing a polymerizable monomer and a first wax dispersed in the polymerizable monomer and having a first viscosity, a coloring agent, and a second wax having a second viscosity higher than the first viscosity noted above, wherein the first wax is added in an amount of 1 to 7 parts by weight relative to 100 parts by weight of the kneaded mass, and the second wax is added in an amount of 0.1 to 3 parts by weight relative to 100 parts by weight of the kneaded mass.

Further, a preferred fourth embodiment directed to the developing agent of the present invention is intended to provide a developing agent obtained essentially by melting and kneading a mixture consisting of a wax-added binder resin prepared by polymerizing a solution containing a polymerizable monomer and a first wax dispersed in the polymerizable monomer and having a viscosity ρ_1 at 100°C of 100 to 1000 cP, a coloring agent, and a second wax having a viscosity at 100°C of 10000 to 100000 cP, wherein the first wax is added in an amount of 1 to 7 parts by weight relative to 100 parts by weight of the kneaded mass, and the second wax is added in an amount of 0.1 to 3 parts by weight relative to 100 parts by weight of the kneaded mass.

The present invention according to the fifth aspect is directed to a developing agent obtained essentially by melting and kneading a mixture consisting of a wax-added binder resin prepared by polymerizing a solution containing a polymerizable monomer and a first wax dispersed in the polymerizable monomer, and having a number average molecular weight of 1500 to 4000, a coloring agent, and a second wax having a number average molecular weight of 8000 to 11000.

The present invention according to a preferred fifth embodiment directed to the developing agent of the present invention provides a developing agent obtained essentially by melting and kneading a mixture consisting of a wax-added binder resin prepared by polymerizing a solution containing a polymerizable monomer and a first wax dispersed in the polymerizable monomer, having a first viscosity, and also having a number average molecular weight of 1500 to 4000, a coloring agent, and a second wax having a second viscosity higher than the first viscosity noted above, and also having a number average molecular weight of 8000 to 11000.

The present invention according to a preferred sixth embodiment directed to the developing agent of the present invention provides a developing agent obtained essentially by melting and kneading a mixture consisting of a wax-added binder resin prepared by polymerizing a solution containing a polymerizable monomer and a first wax dispersed in the polymerizable monomer, having a viscosity at 100°C of 100 to 1000 cP, and also having a number average molecular weight of 1500 to 4000, a coloring agent, and a second wax having a viscosity at 100°C of 10000 to 100000, and also having a number average molecular weight of 8000 to 11000.

The present invention according to a preferred seventh embodiment directed to the developing agent of the present invention provides a developing agent obtained essentially by melting and kneading a mixture consisting of a wax-added binder resin prepared by polymerizing a solution containing a polymerizable monomer and a first wax dispersed in the polymerizable monomer and also having a number average molecular weight of 1500 to 4000, a coloring agent, and a second wax having a number average molecular weight of 8000 to 11000, wherein the first wax is added in an amount of 1 to 7 parts by weight relative to 100 parts by weight of the kneaded mass, and the second wax is added in an amount of 0.1 to 3 parts by weight relative to 100 parts by weight of the kneaded mass.

Further, the present invention according to a preferred eighth embodiment directed to the developing agent of the present invention provides a developing agent obtained essentially by melting and kneading a mixture consisting of a wax-added binder resin prepared by polymerizing a solution containing a polymerizable monomer and a first wax dispersed in the polymerizable monomer, having a number average molecular weight of 1500 to 4000 and also having a viscosity at 100°C of 100 to 1000 cP, a coloring agent, and a second wax having a number average molecular weight of 8000 to 11000 and also having a viscosity at 100°C of 10000 to 100000, wherein the first wax is added in an amount of 1 to 7 parts by weight relative to 100 parts by weight of the kneaded mass, and the second wax is added in an amount of 0.1 to 3 parts by weight relative to 100 parts by weight of the kneaded mass.

FIG. 2 schematically shows the construction of an image forming apparatus in which the developing agent of the present invention can be used. As shown in the drawing, the apparatus comprises a photosensitive drum 3, which acts as an image carrier and can be rotated in a direction denoted by an arrow. A charger 5 for uniformly charging the photosensitive drum 3 is arranged to face the drum 3. Arranged above the photosensitive drum 3 are a glass plate 7 for supporting an original, an automatic original feeder (ADF) 8 for feeding the original onto the glass plate 7, and an exposure section 9 for exposing the charged photosensitive drum 3 with light in accordance with the images of the original so as to form electrostatic latent images. The detailed construction of the ADF 8 will be described herein later.

The exposure section 9 comprises a light-exposing lamp 11 which acts as a light source, reflecting mirrors 13a, 13b, 13c, 13d, 13e, and 13f for guiding the light emitted from the lamp 11 onto the photosensitive drum 3, a slit glass

13g, and a lens unit 14 for forming images from the light reflected by the reflecting mirrors 13a to 13f.

A developing apparatus 15 housing a toner T and a carrier (not shown) is arranged downstream of the photosensitive drum 3. The electrostatic latent images formed in the exposure section 9 are developed with the toner T in the developer 15. Further, a transfer charger 17 is arranged downstream of the developer 15. The toner images formed in the developer 15 are transferred onto a paper sheet P acting as an image forming medium in the transfer charger 17.

It should be noted that the electrostatic charger 5, the exposure section 9 and the developer 15 collectively constitute a means for forming images of the developing agent.

A peeling charger 19 for peeling the paper sheet P which has been electrostatically attached to the photosensitive drum 3 in the transfer step is arranged adjacent to the transfer charger 17. A cleaning device 21 for removing the residual toner T on the photosensitive drum 3 after the transfer step is arranged downstream of the peeling charger 19. The cleaning device 21 is provided with a cleaning blade 23. Further, a static eliminator 25 for removing the electric charge of the photosensitive drum 3 is arranged downstream of the cleaning device 19.

FIG. 2 shows that a paper feeding cassette 27 housing the paper sheets P is detachably mounted to main body of the image forming apparatus. The cassette 27 is positioned on the right hand side of the photosensitive drum 3. A pick up roller 29 for picking up the paper sheets P one by one is arranged near the paper feeding cassette 27. Also, a pair of paper feeding rollers 31 for feeding the paper sheets P one by one are arranged in the vicinity of the pick up roller 29.

A pair of aligning rollers 32 for feeding the paper sheet P toward the photosensitive drum 3 at a predetermined timing are arranged upstream of the transfer charger 17 in the transfer direction of the paper sheet P. It should be noted that the paper sheet P is held between the aligning rollers 32 so as to be fed into a clearance between the photosensitive drum 3 and the transfer charger 17.

Arranged downstream of the transfer charger 17 in the transfer direction of the paper sheet P are the peeling charger 19, a transfer belt 33 for transferring the paper sheet P into a fixer 35 acting as a fixing means for fixing the toner images on the paper sheet P.

The transfer belt 33, which is made of an insulating material, electrostatically holds the paper sheet P charged by the transfer charger 17 so as to transfer the charged paper sheet P toward the fixer 35.

The fixer 35 comprises a pair of rollers, i.e., a heating roller 37 and a pressing roller 39. These heating roller 37 and the pressing roller 39 are rotated in directions denoted by arrows c and d, respectively, so as to melt and fix the toner images on the paper sheet P.

Arranged downstream of the fixer 35 in the transfer direction of the paper sheet P are a pair of paper discharge rollers 43 for discharging the paper sheet P after the fixing step to the outside of the image forming apparatus and a paper discharge tray 45 for receiving the paper sheet P discharged from within the image forming apparatus.

On the other hand, the ADF 8 comprises an original table 47 on which the original is placed, and a pick up roller 49 for taking up the original placed on the original table 47. The original is placed on the original table 47 such that the images formed on the original are allowed to face upward. A separating belt 51 and a paper feeding roller 53 are arranged to face each other in the vicinity of the pick up roller 49 so as to permit the originals to be separated and fed one by one onto the glass plate 7 for supporting the original. Further, an aligning roller 55 is arranged on the glass plate 7 such that the roller 55 is positioned in the vicinity of the separating belt 51 and the paper feeding roller 53.

An original transfer belt 57 for transferring the original along the upper surface of the glass plate 7 is arranged to run along the original-supporting glass plate 7. Further, arranged downstream of the original transfer belt 57 in the transfer direction of the original are an inverting roller 59 for turning the original upside down and a discharge roller 61 for discharging the original to the outside of the ADF 8.

The image forming apparatus of the construction described above is operated as follows. In the first step, an instruction to start the image forming operation is given to the apparatus via an operating panel (not shown). As a result, the photosensitive drum 3 begins to rotate in the direction denoted by the arrow a so as to cause the static charger 5 to charge uniformly the surface of the photosensitive drum 3.

Then, the ADF 8 permits the original to be fed one by one onto the glass plate 7 for supporting the original. The original supported by the glass plate 7 is irradiated with light emitted from the exposing lamp 11, with the result that an electrostatic latent image is formed by the light exposing section 9 on the charged surface of the photosensitive drum 3 in accordance with the picture image formed on the original.

In the developer 15, the charged toner T is attached to the electrostatic latent image so as to form a toner image.

The paper sheets P are taken up one by one from the paper feeding cassette 27 in accordance with rotation of the pick up roller 29 and the paired paper feeding rollers 31 and, then, fed into the clearance between the photosensitive drum 3 and the transfer charger 17 by the paired aligning rollers 32. In this step, the transfer charger 17 serves to impart an electric charge of a polarity opposite to that of the charged toner T to the back surface of the paper sheet P so as to permit the toner image to be transferred onto the paper sheet P.

The peeling charger 19 performs an AC corona discharge so as to peel the paper sheet P, which has been electrostatically attached to the photosensitive drum 3 in the transfer step of the toner image, from the photosensitive drum 3. Further, the paper sheet P peeled from the drum 3 is transferred by the transfer belt 33 toward the fixer 35.

The toner image formed on the paper sheet P is melted by the heating within the fixer 35, with the result that the toner image is fixed to the paper sheet P. Then, the paper sheet P is discharged onto the discharge tray 45 in accordance with rotation of the paired paper discharge rollers 43.

On the other hand, the toner T remaining on the photosensitive drum 3 after the toner image transfer step is removed by the cleaning device 21, followed by removing the charge on the surface of the photosensitive drum 3 by the operation of the static eliminator 25 so as to finish one cycle of the image forming process. Naturally, the photosensitive drum 3 is charged again by the electrostatic charger 5 when starting the next image forming process. On the other hand, the original is transferred by the original transfer belt 57 so as to be discharged out of the ADF 8.

Image forming processes were actually performed by using the image forming apparatus of the construction described above. The developing agents in Examples 1 to 9 reported below were used in these processes:

Examples 1 to 9 and Comparative Examples 1 to 3:

A binder resin mixture having a first wax of a low viscosity included therein was prepared as follows. In the first step, predetermined amounts of xylene as a solvent and polypropylene wax were put in a reaction vessel, followed by putting styrene, n-butyl acrylate and di-t-butyl peroxide in the reaction vessel and subsequently substituting a nitrogen gas for the air atmosphere within the reaction vessel. Under this condition, the reaction system was heated to a boiling point of xylene (135 to 145°C). While stirring the reaction system under reflux of xylene, a mixed solution consisting of styrene, n-butyl acrylate and benzoyl peroxide (polymerization initiator) was dripped into the reaction system over 2 hours so as to carry out a solution polymerization. After completion of the dripping, the reaction mixture was subjected to aging over one hour while stirring the reaction mixture under xylene reflux, followed by slowly elevating the temperature within the reaction vessel to 180°C so as to remove the solvent xylene under a reduced pressure and, thus, to obtain a binder resin containing a polypropylene wax having a low viscosity.

In the next step, a toner was prepared as follows by using a styrene-acrylate copolymer resin having the polypropylene was of a low viscosity added thereto. Specifically, a toner material mixture was prepared by adding 5 parts by weight of carbon black, 2 parts by weight of a metal complex salt of a monoazo dye, 0. 1 part by weight of hydrophobic silica, and a polyethylene-based wax of a high viscosity to 100 parts by weight of the styrene-acrylate copolymer resin having the polypropylene-based wax of a low viscosity added thereto in the polymerizing step. Table 1 shows the toner material mixtures for Examples 1 to 9 obtained by changing the amounts of the polyethylene-based high viscosity wax and the polypropylene-based low viscosity wax and also changing the mixing ratio of these waxes. Of course, the viscosities of these waxes fall within the scopes defined in the present invention. On the other hand, Table 2 shows the toner material mixtures for Comparative Examples 1 to 3, in which the polyethylene-based high viscosity wax and the polypropylene-based low viscosity wax were mixed in amounts and mixing ratio failing to fall within the scopes defined in the present invention.

Table 1

Examples	Viscosity	A / B	Dispersibility	Fix Retention Rate	Smear Characteristics	Offset Resistance	Shelf Life	Overall Evaluation
1	ρ_1=100 ρ_2=10000	5%/1%	○	○	○	○	○	○
2	ρ_1=100 ρ_2=10000	1%/3%	○	○	○	○	○	○
3		7%/0.1%	○	○	○	○	○	○
4	ρ_1=100 ρ_2=100000	1%/3%	○	○	○	○	○	○
5		7%/0.1%	○	○	○	○	○	○
6	ρ_1=100 ρ_2=10000	1%/3%	○	○	○	○	○	○
7		7%/0.1%	○	○	○	○	○	○
8	ρ_1=100 ρ_2=100000	1%/3%	○	○	○	○	○	○
9		7%/0.1%	○	○	○	○	○	○

Notes

A: First wax having a low viscosity (polypropylene wax);

B: Second wax having a high viscosity (polyethylene wax);

ρ_1, ρ_2: Viscosity (Cp) at 100°C.

Table 2

Comparative Examples	Viscosity	A	B	Dispersibility	Fix Retention Rate	Smear Characteristics	Off-set Resistance	Shelf Life	Qverall Evaluation
		Addition in First Step;	Addition in Second Step;						
1	ρ_1=100	7%	0%	○	△	X	○	○	△
2	ρ_2=10000	0%	3%	○	△	△	X	○	△
		Addition in second step;	Addition in First Step;						
3	ρ_1=100 ρ_2=10000	5%	1%	X	○	△	△	X	△

Notes
A: First wax having a low viscosity (polypropylene wax);
B: Second wax having a high viscosity (polyethylene wax);
ρ_1, ρ_2: Viscosity (Cp) at 100°C.

Each of the toner material mixtures shown in Tables 1 and 2 was kneaded at about 170°C for 30 minutes in a pressure kneader, followed by pulverizing the kneaded mass to obtain a powdery material. Further, the powdery material was finely pulverized by an I-type jet mill (DS classifier), followed by an air classification so as to obtain a toner having a 50% volume average particle diameter of 11.0 µm.

The toner thus obtained was subjected to various tests as reported below, with the results as shown in Tables 1 and 2:

1) Test for Fix Retention Rate

A half tone picture image (ID 0.6 to 0.8) was fixed at a fixing temperature of 200°C under a low temperature (10°C) and a low humidity (20%). The fixed image was subjected to a rubbing test with a friction fastness tester, and the image densities before and after the rubbing test were measured so as to evaluate the fix retention rate.

Used in the test was "Leo Dry 6550", which is a trade name of a friction fastness tester manufactured by Toshiba Corporation, Japan. An image density retention rate of 75% or more after the rubbing test, compared with the image density before the test, is denoted by a mark "o" in each of Tables 1 and 2. On the other hand, the rate falling within a range of between 70 and 74%, and the rate not higher than 69% are denoted by marks "△" and "x", respectively, in each of Tables 1 and 2.

2) Test for Smear Characteristics

Fifty sheets of "TOSHIBA TEST CHART-61" prepared by Toshiba Corporation, Japan, were printed with a hammer mill letter size and, then, fed into the ADF included in the image forming apparatus shown in FIG. 2 so as to evaluate the smear of the picture image caused by the pressure, friction, etc. of the separating belt roller, etc.

The "Leo Dry 6550" by Toshiba Corporation, which was referred to previously, was used for the test. Also used was an ADF, which was exclusively for use in the Leo Dry 6550. The fixing temperature was 200°C. The smear characteristics, which are ranked as levels 0 to 10 according to the degree of the smearing, were evaluated in this test in terms of "o" which denotes level 5 or less, "△" which denotes levels 6 to 7, and "x" which denotes level 8 or more.

3) Off-set Resistance Test

Ten sheets of a chart for the off-set resistance test were printed with a hammer mill letter size by using the image forming apparatus shown in FIG. 2. Before performing the test, all the cleaning members of the fixer were removed so as to wipe off cleanly the oil attached to the heat roller and the press roller.

The "Leo Dry 6550" by Toshiba Corporation, Japan, which was referred to previously, was used for the test. The off-set resistance, which is ranked as levels 0 to 5, was evaluated in this test in terms of "o" which denotes level 2 or less, "△" which denotes level 3, and "x" which denotes level 4 or more.

4) Shelf Life Test

Twenty grams of the toner was put in a polyvinyl chloride bottle having an inner volume of 100 ml and left to stand in a water bath of 55°C for 8 hours, followed by evaluating the fluidity of the toner by using a powder tester manufactured by Hosokawa Micron Ltd., Japan. In this test, the toner put on a sieve of 200 meshes was kept vibrated for 10 seconds.

The test result was evaluated in terms of the amount of the toner left on the sieve after the vibration of the sieve such that "o" denotes 5g or less, "△" denotes 5.1g to 10g, and "x" denotes 10.1g or more.

As apparent from Table 1, the toner according to any of Examples 1 to 9 of the present invention was found to be satisfactory in any of the dispersion capability, fix retention rate, smear characteristics, off-set resistance and shelf life. However, where the toner contained only one kind of wax, i.e., polypropylene wax having a low viscosity, was found to be poor in smear characteristics even if the wax was added in the step of polymerization for preparing the binder resin, as apparent from Comparative Example 1 shown in Table 2. On the other hand, where the toner contained only the polyethylene wax having a high viscosity, the resultant toner was found to be poor in the off-set resistance, even if the wax was added in the step of melting and kneading the binder resin, as apparent from Comparative Example 2. Certainly, two kinds of waxes differing from each other in viscosity were used in Comparative Example 3. In this case, however, the polyethylene wax having a high viscosity was added in the step of preparing the wax-added binder resin, with the polypropylene wax having a low viscosity added in the step of melting and kneading the wax-added binder resin. As a result, the toner in Comparative Example 3 was found to be poor in, particularly, the dispersion capability and the shelf life.

<u>Examples 10 to 17:</u>

A toner material mixture was prepared by adding 5 parts by weight of carbon black, 2 parts by weight of a metal complex salt of monoazo dye, 0.1 part by weight of hydrophobic silica, and 1 part by weight of a polyethylene-based high viscosity wax having a viscosity of 10000 cP at 100°C, to 100 parts by weight of a styrene-acrylate copolymer resin containing 3 parts by weight of a polypropylene-based low viscosity wax having a viscosity of 100 cP at 100°C which had been added in the step of polymerization for preparing the copolymer resin. The toner material mixtures for Examples 10 to 17 were prepared by changing in a various fashion the number average molecular weight of the polyethylene-based high viscosity wax and the number average molecular weight of the polypropylene-based low viscosity wax.

Toner was prepared as in Examples 1 to 9 by using the toner material mixtures thus prepared. Various properties of the resultant toner were tested and evaluated, with the results as shown in Table 3.

Table 3

Examples	Mn_1/Mn_2	Dispersibility	Fix Retention Rate	Smear Characteristics	Off-set Resistance	Shelf Life	Over-all Evaluation
10	1500/8000	○	○	○	○	○	○
11	1500/11000	○	○	○	○	○	○
12	4000/8000	○	○	○	○	○	○
13	4000/11000	○	○	○	○	○	○
14	1000/8000	○	○	○	△	△	△
15	5000/8000	△	△	○	○	○	△
16	3000/7000	○	○	○	△	△	△
17	3000/12000	△	○	○	○	○	△

Notes
Mn_1 : Number average molecular weight of polypropylene-based low viscosity wax.
Mn_2 : Number average molecular weight of polyethlene-based high viscosity wax.

As apparent from Table 3, the toner material mixture in any of Examples 10 to 13 contains a polypropylene-based low viscosity wax, which is added in the first step of preparing the wax-added binder resin and has a number average molecular weight falling within the range of between 1500 and 4000 specified in the present invention. The toner material mixture also contains a polyethylene-based high viscosity wax, which is added in the second step of melting and kneading the binder resin prepared in the first step and has a number average molecular weight falling within the range of between 8000 and 11000 specified in the present invention. As a result, the toner obtained in any of Examples 10 to 13 was found to be satisfactory in any of the dispersion capability, fix retention rate, smear characteristics and shelf life. On the other hand, at least one of the polypropylene-based low viscosity wax, which is added in the first step specified in the present invention, and the polyethylene-based high viscosity was, which is added in the second step specified in the present invention, failed to meet the preferred range of the number average molecular weight specified in the present invention in any of the toner material mixture used in Examples 14 to 17. In this case, the resultant toner was found to be somewhat inferior to the toner obtained in each of Examples 10 to 13 in any of the dispersion capability, fix retention rate, smear characteristics, off-set resistance and shelf life.

Test to see Stains of Paper Back Surface and Members of Image Forming Apparatus

The off-set phenomenon causes the toner remaining on the heat roller to be transferred onto the press roller so as to stain the back surface of the recording paper sheet and the cleaning members of the fixer. The toner obtained in each of the Examples 1 to 17 and Comparative Examples 1 to 3 was tested to see these stains.

The "Leo Dry 6550" by Toshiba Corporation, Japan, which was referred to previously, was used for the test. Level 3 or less of the stain was evaluated as satisfactory.

The toner for each of Examples 1 to 17 was found to be satisfactory. The toner for Comparative Example 1 was also found to be satisfactory. However, the toner for each of Comparative Examples 2 and 3 was also found to be unsatisfactory.

In the present invention, the low viscosity wax is defined to have a viscosity at 100°C of 100 to 1000 cP. Also, the high viscosity wax is defined to have a viscosity at 100°C of 10000 to 100000 cP. In addition, it is desirable for the wax having a low viscosity ρ_1 to have temperature characteristics meeting equation (1) given below:

$$\rho_1 = \alpha_1 \times T_1 + C_1 \qquad (1)$$

where $-9.78 \le \alpha_1 \le 0$, C_1 denotes a viscosity at 0°C, and when T_1 is 100°C (T_1 = 100°C), $100 \le \rho_1 \le 1000$.

It is also desirable for the wax having a high viscosity to have temperature characteristics meeting equation (2) given below:

$$\rho_2 = \alpha_2 \times T_2 + C_2 \qquad (2)$$

where $-950 \leq \alpha_2 \leq 0$, C_2 denotes a viscosity at 0°C, and when T_2 is 100°C (T_2 = 100°C), $10000 \leq \rho_1 \leq 100000$.

The viscosity of the wax is changed with temperature. The present inventors have used various waxes as a wax having a low viscosity and a wax having a high viscosity in an attempt to find waxes most suitable for use in the present invention. It has been found that, as far as equation (1) or (2) given above is satisfied, the wax exhibits a suitable viscosity under the temperature at which the toner is used. Naturally, the toner containing the waxes meeting the equations (1) and (2) respectively exhibits excellent smear characteristics and fix retention rate.

FIG. 3 shows experimental data on the relationship between the viscosity and temperature in respect of some waxes which can be used as the first wax in the present invention. On the other hand, FIG. 4 shows experimental data on the relationship between the viscosity and temperature in respect of some waxes which can be used as the second wax in the present invention. Further, Table 4 shows the data on some points marked in each of FIGS. 3 and 4. It should be noted that graphs 101 to 104 shown in FIG. 3 represent the temperature characteristics of low viscosity waxes A to D shown in Table 4. On the other hand, graphs 105 shown in FIG. 4 represent the temperature characteristics of high viscosity waxes E to G shown in Table 4.

Table 4

Wax		Temperature (°C)	Viscosity (cp)
Low Viscosity Wax;	Wax A	100	1000
		200	22
	Wax B	100	950
		200	900
	Wax C	140	750
		180	620
	Wax D	100	200
		140	70
		180	80
		200	50
High Viscosity Wax;	Wax E	100	100000
		200	5000
	Wax F	140	90000
		180	95000
		200	90000
	Wax G	100	10000
		140	8000
		180	8500
		200	5000

Claims

1. A method of manufacturing a developing agent, comprising:

a first step of preparing a wax-added binder resin by polymerizing a solution containing a polymerizable monomer and a first wax dispersed in said monomer;
a second step of melting and kneading a mixture comprising the wax-added binder resin prepared in the first step, a colorant, and a second wax; and
a third step of purverizing/classifying for purverizing and classifying a kneeded mass prepared in the step;
characterized in that said first wax has a first viscosity, and said second wax has a viscosity higher than the first viscosity.

2. The method of manufacturing a developing agent according to claim 1, characterized in that said first wax has a viscosity ρ_1 at 100°C of 100 to 10000 cP, and said second wax has a viscosity ρ_2 at 100°C of 10000 to 100000 cP.

3. The method of manufacturing a developing agent according to claim 2, characterized in that said first wax has a viscosity ρ_1 having a temperature characteristic represented by formula (1) given below:

$$\rho_1 = \alpha_1 \times T_1 + C_1 \quad (1)$$

where $-9.78 \leq \alpha_1 < 0$, C_1 is a viscosity at 0°C, and where T_1 = 100°C, $100 \leq \rho_1 \leq 1000$, and said second wax has a viscosity ρ_2 having a temperature characteristic represented by formula (2) given below:

$$\rho_2 = \alpha_2 \times T_2 + C_2 \quad (2)$$

where $-950 \leq \alpha_2 < 0$, C_2 is a viscosity at 0°C, and where T_2 = 100°C, $10000 \leq \rho_2 \leq 100000$.

4. The method of manufacturing a developing agent according to claim 1, characterized in that said first wax is added in an amount of 1 to 7 parts by weight relative to 100 parts by weight of the kneaded mass prepared in the second step, and said second wax is added in an amount of 0.1 to 3 parts by weight relative to 100 parts by weight of the kneaded mass prepared in the second step.

5. A method of manufacturing a developing agent, comprising:

a first step of preparing a wax-added binder resin by polymerizing a solution containing a polymerizable monomer and a first wax dispersed in said monomer;
a second step of melting and kneading a mixture comprising the wax-added binder resin prepared in the first step, a coloring agent, and a second wax;
a third step of purverizing/classifying for purverizing and classifying a kneeded mass prepared in the second step;
characterized in that said first wax has a number average molecular weight of 1500 to 4000, and said second wax has a number average molecular weight of 8000 to 11000.

6. A method of manufacturing a developing agent, comprising:

a first step of preparing a wax-added binder resin by polymerizing a solution containing a polymerizable monomer and a first wax dispersed in said monomer;
a second step of melting and kneading a mixture comprising the wax-added binder resin prepared in the first step, a colorant, and a second wax;
characterized in that said first wax has a first viscosity and a number average molecular weight of 1500 to 4000, and said second wax has a second viscosity higher than the first viscosity and a number average molecular weight of 8000 to 11000.

7. The method of manufacturing a developing agent according to claim 6, characterized in that said first wax has a viscosity ρ_1 at 100°C of 100 to 10000 cP, and said second wax has a viscosity ρ_2 at 100°C of 10000 to 100000 cP.

8. The method of manufacturing a developing agent according to claim 7, characterized in that said first wax has a viscosity ρ_1 having a temperature characteristic represented by formula (1) given below:

$$\rho_1 = \alpha_1 \times T_1 + C_1 \quad (1)$$

where $-9.78 \leq \alpha_1 < 0$, C_1 is a viscosity at 0°C, and where T_1 = 100°C, $100 \leq \rho_1 \leq 1000$, and said second wax has a viscosity ρ_2 having a temperature characteristic represented by formula (2) given below:

$$\rho_2 = \alpha_2 \times T_2 + C_2 \quad (2)$$

where $-950 \leq \alpha_2 < 0$, C_2 is a viscosity at 0°C, and where T_2 = 100°C, $10000 < \rho_2 \leq 100000$.

9. The method of manufacturing a developing agent according to claim 6, characterized in that said first wax is added in an amount of 1 to 7 parts by weight relative to 100 parts by weight of the kneaded mass prepared in the second step, and said second wax is added in an amount of 0.1 to 3 parts by weight relative to 100 parts by weight of the

kneaded mass prepared in the second step.

10. A developing agent obtained by purverizing/classifying a kneaded mass prepared by melting and kneading a mixture comprising a wax-added binder resin prepared by polymerizing a solution containing a polymerizable monomer and a first wax dispersed in said polymerizable monomer, a colorant, and a second wax, characterized in that said first wax has a first viscosity, and said second was has a second viscosity higher than that of said first wax.

11. The developing agent according to claim 10, characterized in that said first wax has a viscosity ρ_1 at 100°C of 100 to 1000, and said second wax has a viscosity ρ_2 at 100°C of 10000 to 100000.

12. The developing agent according to claim 11, characterized in that said first wax has a viscosity ρ_1 having a temperature characteristic represented by formula (1) given below:

$$\rho_1 = \alpha_1 \times T_1 + C_1 \qquad (1)$$

where $-9.78 \leq \alpha_1 < 0$, C_1 is a viscosity at 0°C, and where T_1 = 100°C, $100 \leq \rho_1 \leq 1000$, and said second wax has a viscosity ρ_2 having a temperature characteristic represented by formula (2) given below:

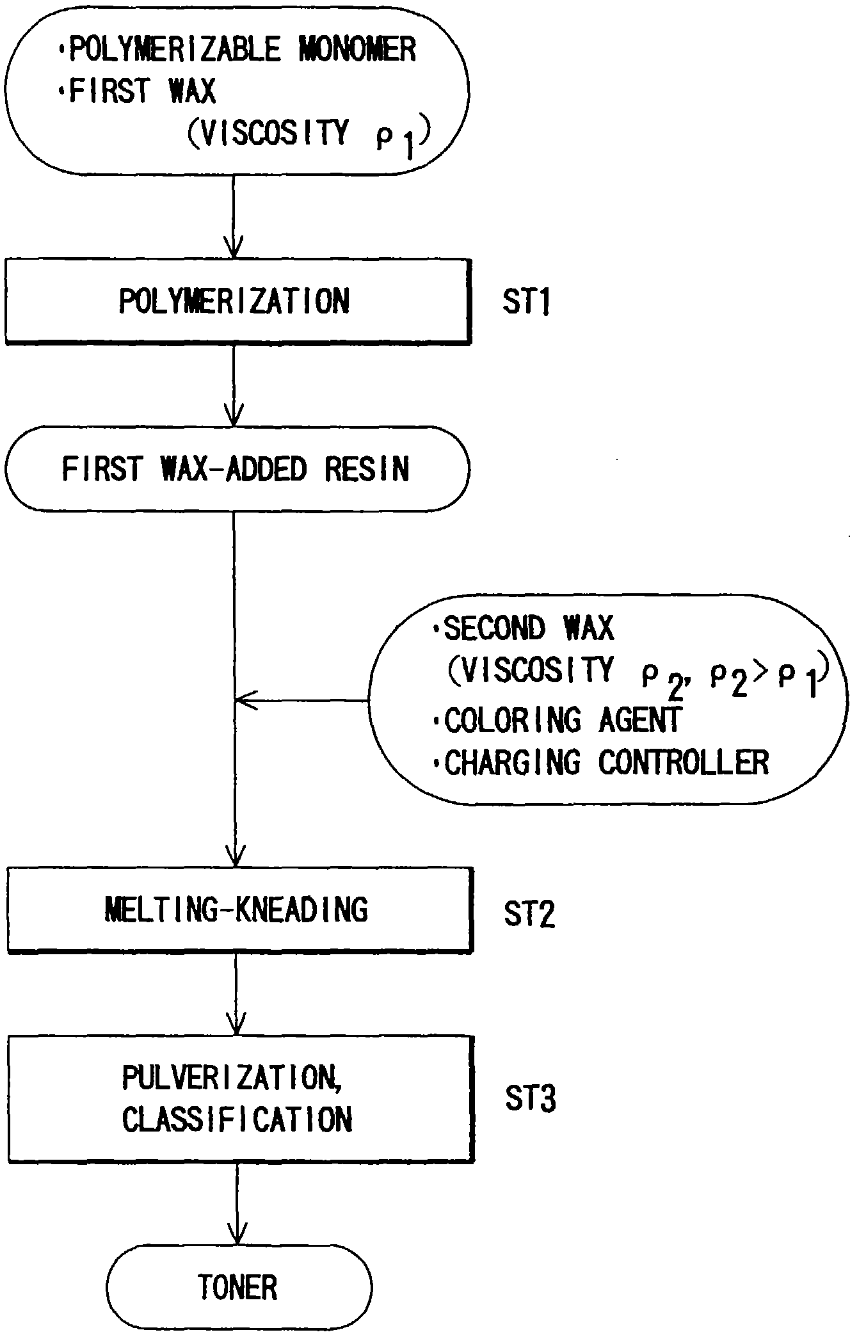
$$\rho_2 = \alpha_2 \times T_2 + C_2 \qquad (2)$$

where $-950 \leq \alpha_2 < 0$, C_2 is a viscosity at 0°C, and where T_2 = 100°C, $10000 \leq \rho_2 \leq 100000$.

13. The developing agent according to claim 10, characterized in that said first wax is added in an amount of 1 to 7 parts by weight relative to 100 parts by weight of the kneaded mass prepared in the second step, and said second wax is added in an amount of 0.1 to 3 parts by weight relative to 100 parts by weight of the kneaded mass prepared in the second step.

14. The developing agent according to claim 10, characterized in that said first wax has a number average molecular weight of 1500 to 4000, and said second wax has a number average molecular weight of 8000 to 11000.

15. A developing agent obtained by purverizing/classifying a kneaded mass prepared by melting and kneading a mixture consisting of a wax-added binder resin prepared by polymerizing a solution containing a polymerizable monomer, characterized in that said first wax has a number average molecular weight of 1500 to 4000, and said second wax has a number average molecular weight of 8000 to 11000.


·POLYMERIZABLE MONOMER
·FIRST WAX
(VISCOSITY ρ1)
POLYMERIZATION
ST1
FIRST WAX-ADDED RESIN
·SECOND WAX
(VISCOSITY ρ2, ρ2>ρ1)
·COLORING AGENT
·CHARGING CONTROLLER
MELTING-KNEADING
ST2
PULVERIZATION,
CLASSIFICATION
ST3
TONER

F I G. 1

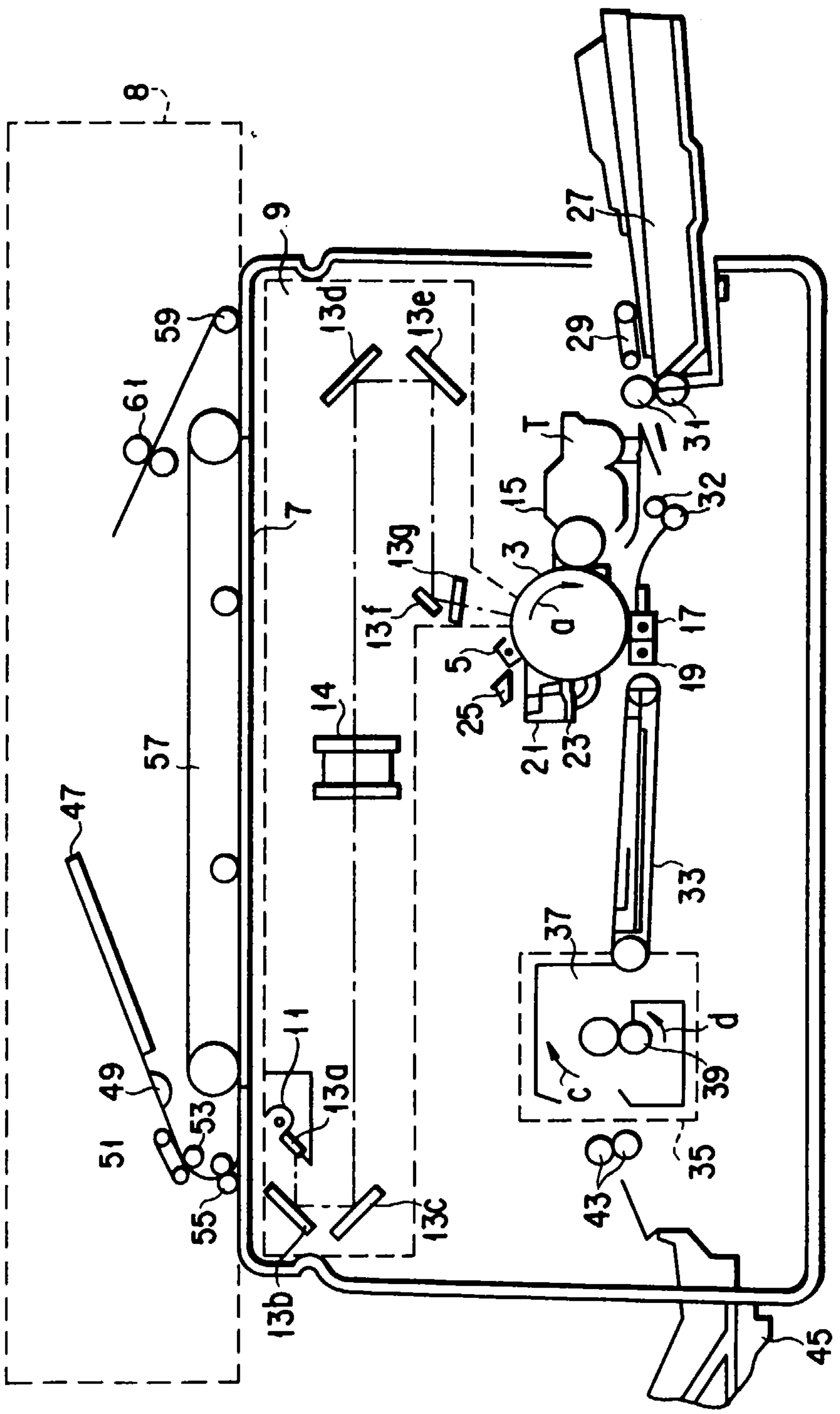

1
8
9
7
57
59
61
47
49
51
53
55
11
13a
13b
13c
13d
13e
13f
13g
14
3
a
5
25
21
23
15
T
17
19
27
29
31
32
33
35
37
39
c
d
43
45

FIG. 2

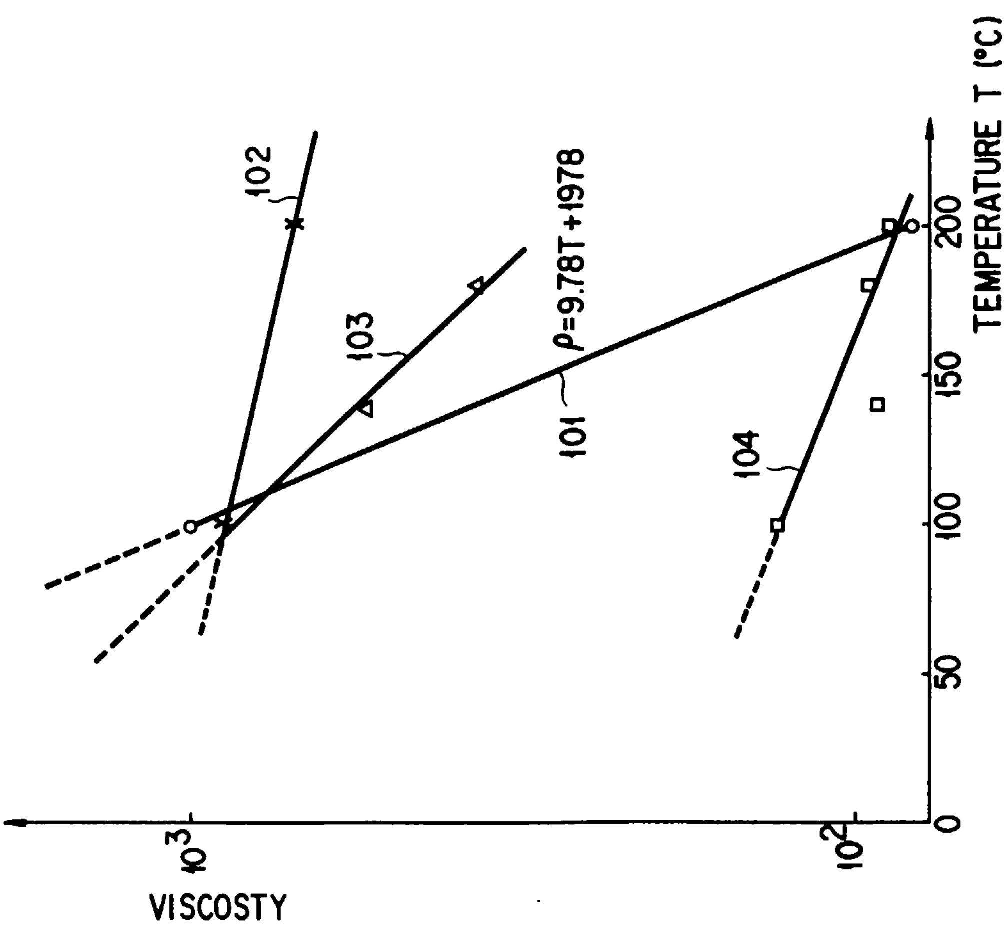

VISCOSTY
10^3
10^2
0
50
100
150
200
TEMPERATURE T (°C)
102
103
101
104
ρ=9.78T+1978

FIG. 3

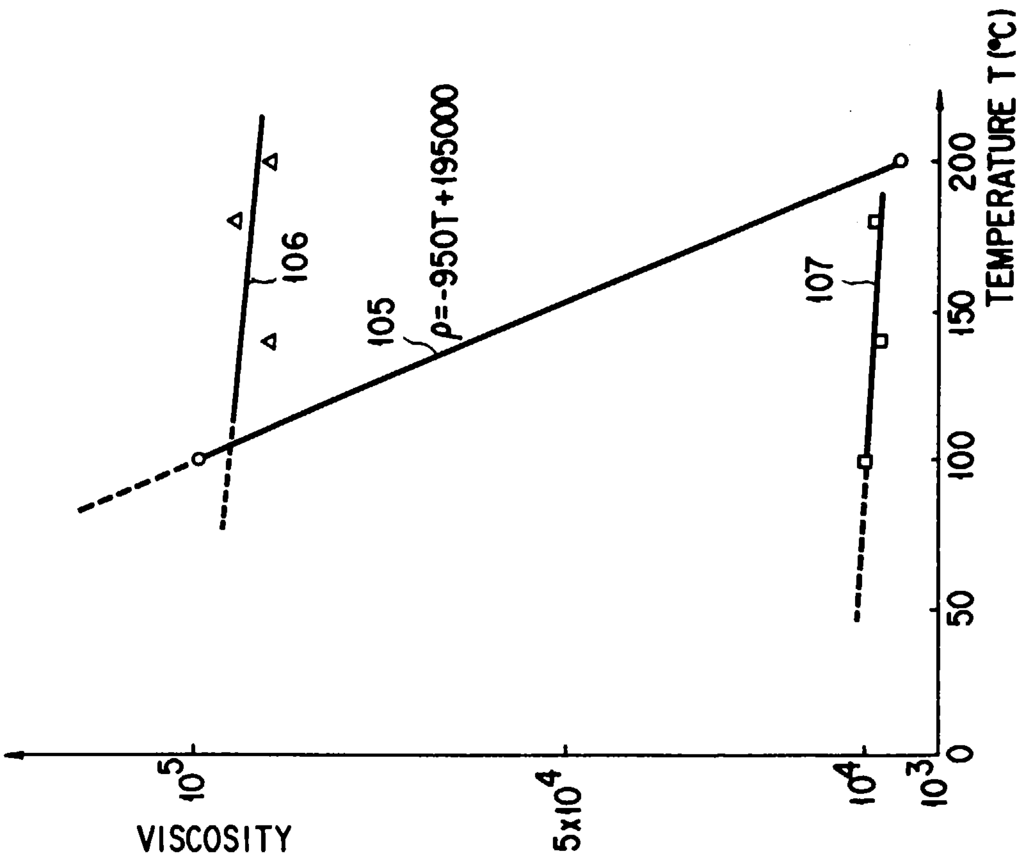

VISCOSITY
10^5
5x10^4
10^4
10^3
0
50
100
150
200
TEMPERATURE T (°C)
105
106
107
ρ=-950T+195000

FIG. 4

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 97 10 7882

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
D,X	PATENT ABSTRACTS OF JAPAN vol. 017, no. 228 (P-1531), 11 May 1993 & JP 04 358159 A (TOSHIBA CORP;OTHERS: 01), 11 December 1992,	1,10	G03G9/08 G03G9/087
A	* abstract *	2-9, 11-15	
X	& US 5 292 609 A (YOSHIKAWA YUZABURO ET AL) 8 March 1994	1,10	
A	* column 7 - column 8; examples 1-3 * ---	2-9, 11-15	
X	US 5 344 737 A (BERKES JOHN S ET AL) 6 September 1994	15	
A	* claims 1,3,6,8 * ---	1-14	
X	PATENT ABSTRACTS OF JAPAN vol. 007, no. 101 (P-194), 28 April 1983 & JP 58 025642 A (CANON KK), 15 February 1983, * abstract * ---	15	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
A	PATENT ABSTRACTS OF JAPAN vol. 096, no. 008, 30 August 1996 & JP 08 106173 A (TOSHIBA CORP), 23 April 1996, * abstract * ---	1-15	G03G
A	EP 0 703 505 A (MITA INDUSTRIAL CO LTD) 27 March 1996 * page 17; example 3.1 * * page 14; example 1 * ---	1-15	
A	PATENT ABSTRACTS OF JAPAN vol. 006, no. 133 (P-129), 20 July 1982 & JP 57 056851 A (CANON INC), 5 April 1982, * abstract * -----	1-15	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	17 September 1997	Vogt, C

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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