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(71) Applicant: **Ricoh Company, Ltd.**
Tokyo 143-8555 (JP)

(72) Inventors:
- **Takahashi, Hiroshi**
  Tokyo 143-8555 (JP)
- **Kuroda, Noboru**
  Tokyo 143-8555 (JP)
- **Kadota, Takahiro**
  Tokyo 143-8555 (JP)
- **Nishizaki, Toshinobu**
  Tokyo 143-8555 (JP)
- **Kohzu, Osamu**
  Tokyo 143-8555 (JP)

(74) Representative: **Barz, Peter**
Patentanwalt
Kaiserplatz 2
80803 München (DE)

(54) Toner manufacturing method, image forming method, image forming apparatus, and process cartridge

(57) A method of manufacturing a toner including forming an emulsion by mixing and stirring an aqueous phase and an oil phase in an emulsification mechanism by a stirring blade. The oil phase contains a dissolved material or a dispersed material which contains an organic phase formed of at least one of a resin, a resin precursor, and a monomer.

The emulsification mechanism includes an emulsification circulation route formed of pipes having a main portion, and an emulsification device located in the middle of the emulsification circulation route.

A stirring blade is provided in the emulsification device. In addition, the stirring Reynolds number (Stirring Re) during the stirring is from 3,000 to 15,000 when calculated based on the following relationship (1): Stirring Reynolds number (stirring Re) = $\rho n d^2/\mu$ (1). In the relationship (1), ρ represents the density of the emulsion (kg/m^3), n represents the rotation number (rps) of the stirring blade, d represents the blade diameter (m) of the stirring blade, and μ represents the viscosity (Pa s) of the emulsion.

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Description

BACKGROUND OF THE INVENTION

Field of the Invention

[0001] The present invention relates to a method of manufacturing toner for use in electrophotography, electrostatic recording, electrostatic printing, etc., and more particularly to an image forming method, an image forming apparatus using the toner, and a process cartridge using the toner.

Discussion of the Background

[0002] Developers for use in electrophotography, electrostatic recording, electrostatic printing, etc., for example, are attached in a development process to an image bearing member such as a photoreceptor on which an electrostatic image is formed. Subsequent to a transfer process in which the developed image is transferred from the image bearing member to a transfer material such as a transfer paper, the transferred image is fixed to the transfer material in a fixing process.

[0003] As a developer to develop an electrostatic image formed on the surface of the image bearing member (photoreceptor) carrying a latent image, a two-component developer containing a carrier and a toner and a single-component developer formed of a magnetic toner or a non-magnetic toner which does not use a carrier are used. These are referred to as a dry toner. Dry toners which are manufactured by melting and kneading a toner binder made of a styrene-based resin or a polyester-based resin together with a colorant, etc., and finely-pulverizing the resultant are typically used as the dry toner for use in electrophotography, electrostatic recording, electrostatic printing, etc.

[0004] Methods in which the particle diameter of toner is reduced in size are typically adopted and have been attempted to improve image quality and grade. However, when a manufacturing method using a typical kneading and pulverizing method is used, the toner obtained thereby has an irregular form. Therefore, when a two-component developer containing the toner is used, the developer receives a stress while stirred with a carrier in a development portion. When it is the case with a single-component developer, the developer receives stress when contacting with a developing roller, a toner supply roller, a layer regulating blade, a contact-charging blade, etc. Thereby, the toner is further pulverized to produce super-fine particles and a fluidizer attached thereto is sunk in the surface of the toner particle, which leads to deterioration of image quality.

[0005] In addition, toner particles having an irregular form have a poor fluidity as powder, which makes it necessary to increase its fluidity. Further, such toner particles have a low filling rate in a toner bottle and thus become an obstructive factor to reduce the size of a device. Therefore, the merit obtained by the size reduction of toner particles is not fully achieved in the current status. With regard to the toner particles manufactured by the pulverization method, there is a limit to the size reduction thereof so that it is not possible to deal with further size reduction.

[0006] To compensate such demerits brought about by toner particles having an irregular form, various kinds of methods of manufacturing a toner having a spherical form have been devised. For example, polymer suspension methods and emulsion methods are typically used. In such manufacturing methods, a process of emulsifying an oil phase in an aqueous phase by a mechanical emulsification device to obtain liquid droplets having a toner size is included. In the oil phase, a toner composition including a resin, a colorant such as a dye, and wax is dissolved or dispersed in an organic solvent.

[0007] When a toner is manufactured by a suspension method or an emulsion method, liquid droplets are formed in a process of forming liquid droplets having a toner size, i.e., in an emulsion staying area in an emulsification mechanism provided to a toner manufacturing device. In the process, equilibrium reactions in the emulsion in which formation of fine particles by shearing and coalescence of the fine particles are repeated. When the formation of fine particles by shearing and the coalescence are balanced, the particle size and the particle size distribution are temporarily determined.

[0008] There are major factors by which the particle size and the particle size distribution of a toner are determined. These are considered to be an energy provided to the raw material by an emulsification device during shearing, and all shearing energy (herein referred to as unit total energy) per raw material feed unit flow amount provided during the equilibrium reactions in which the emulsion is sheared to obtain fine particles and the coalescence of the fine particles occurs.

[0009] However, the reaction rates of formation of fine particles by shearing and coalescence of the fine particles depend on a prescription of a toner composition. Therefore, it is impossible to control to make the reaction condition suitable, which leads to creation of a problem in the emulsion process in that a variance among particle diameters (volume average particle diameter) is created and particle size distribution is not sharp. To deal with this problem, a post-emulsion process such as eliminating fine particles and coarse particles has been introduced to adjust the volume average particle diameter and the particle size distribution of the toner. Thereby, the toner particles having target values can be obtained. However, this creates problems such that the manufacturing processes are complicated and take an extra time and the toner yield deteriorates.

[0010] The following method is proposed to improve the granularity and particle size distribution of toner particles.

[0011] For example, unexamined published Japanese Patent Application No. (hereinafter referred to as JOP) 2000-321821 describes a method of manufacturing a toner in which a stirring chamber equipped with stirring blades adjacent to each other in the top and bottom direction is used to obtain toners having a sharp particle size distribution and a performance capability having no variance among the toner particles. The top stirring blade is provided against the bottom stirring blade with a cross angle less than 90 degrees front in the rotation direction.

[0012] In addition, JOP 2001-125309 describes a polymerization method of manufacturing a toner having a sharp particle size distribution after polymerization, which can be obtained by controlling the tip speed of a blade in the polymerization reaction, the depth of the stirring blade provided at the top from the water surface, and the stirring power required during polymerization.

[0013] JOP 2002-91071 describes a method of efficiently manufacturing a toner having a sharp particle size distribution, which can be obtained by satisfying the following relationship: $15 < P/V < 100$, wherein V (m^3) represents the volume occupied by a matter having a liquid form in a granulating container in a toner granulating process, and P (kW) represents the power of a stirring device.

[0014] However, in each manufacturing method mentioned above, toner particles are prepared to achieve target values by controlling the form, the position and/or the power supply of a stirring blade. Therefore, it is difficult to say that a toner granulated by these methods is prepared considering the behavior of coalescence of toner particles, which is dealt with by the present invention described later as a major factor in the granulating mechanism. That is, these controls are not performed in consideration of the reactions mentioned above, which are formation of fine particles by shearing and coalescence of the fine particles. As a result, these methods are not sufficient to obtain a toner having a more stable particle diameter and a more sharp particle size distribution.

SUMMARY OF THE INVENTION

[0015] Because of these reasons, the present inventors recognize that a need exists for a toner manufacturing method to obtain a stable particle diameter (volume average particle diameter) and a sharp particle size distribution, a toner obtained by the methods, and an image forming method using the toner.

[0016] Accordingly, an object of the present invention is to provide a toner manufacturing method by which a toner having a stable particle diameter (volume average particle diameter) can be obtained. Another object of the present invention is to provide a toner obtained by the method which can truly reproduce a latent image to obtain a quality full color image. Further, another object of the present invention is to provide an image forming method, a process cartridge, and an image forming device using the toner.

[0017] Briefly these objects and other objects of the present invention as hereinafter will become more readily apparent and can be attained by a method of manufacturing a toner including forming an emulsion by mixing and stirring an aqueous phase and an oil phase in an emulsification mechanism by a stirring blade. The oil phase contains a dissolved material or a dispersed material which contains an organic phase formed of at least one of a resin, a resin precursor, and a monomer. The emulsification mechanism includes an emulsification circulation route formed of pipes having a main portion, and an emulsification device located in the middle of the emulsification circulation route. The stirring blade is provided in the emulsification device. In addition, the stirring Reynolds number (Stirring Re) during the stirring is from 3, 000 to 15, 000 when calculated based on the following relationship (1) : Stirring Reynolds number (stirring Re) = $\rho nd^2/\mu$ (1). In the relationship (1), ρ represents the density of the emulsion (kg/m^3) , n represents the rotation number (rps) of the stirring blade, d represents the blade diameter (m) of the stirring blade, and μ represents the viscosity (Pa s) of the emulsion.

[0018] It is preferred that, in the method of manufacturing a toner mentioned above, the pipes have a straight portion.

[0019] It is still further preferred that, in the method of manufacturing a toner mentioned above, the emulsion circulation route has one to four right angle elbows.

[0020] It is still further preferred that, in the method of manufacturing a toner mentioned above, the ratio ((S)/(D)) of the length (S) of the straight portion between the right angle elbows to the inner diameter (D) of the emulsion circulation route satisfies the following relationship:$(S)/(D) > 10$.

[0021] It is still further preferred that, in the method of manufacturing a toner mentioned above, the emulsion is discharged from the emulsion circulation route without passing through any one of the right angle elbows.

[0022] It is still further preferred that, in the method of manufacturing a toner mentioned above, the pipes have the same diameter.

[0023] It is still further preferred that, in the method of manufacturing a toner mentioned above, one of the resin and the resin precursor contains at least two polymers having a different molecular weight.

[0024] It is still further preferred that, in the method of manufacturing a toner mentioned above, the two polymers having a different molecular weight are a modified polyester resin modified by a urea linkage, and an unmodified polyester resin.

[0025] It is still further preferred that, in the method of manufacturing a toner mentioned above, the aqueous phase is an aqueous medium containing a solid particulate dispersant.

[0026] It is still further preferred that, in the method of manufacturing a toner mentioned above, the shearing energy (E) generated by rotation of the stirring blade is from 400 to 2, 000 based on the following relationship (2) : $E = (n \times 60)^3 \times d^5/Q$ (2). In the relationship (2), n represents the rotation number (rps) of the stirring blade, d represents the blade diameter (m) of the stirring blade, and Q represents the flow amount (L/min) in the emulsion circulation route.

[0027] It is still further preferred that, in the method of manufacturing a toner mentioned above, the total energy of the emulsion received from the emulsification device based on unit total energy (e) per material feed unit flow amount while the emulsion is circulated and stayed in the emulsion circulation route is from 1×10^6 to 5×10^6 based on the following relationship (3) : $e = [(n \times 60) \times d^5 \times Q] / F^2$ (3), In the relationship (3), n represents the rotation number (rps) of the stirring blade, d represents the blade diameter (m) of the stirring blade, Q represents a flow amount (L/min) in the emulsion circulation route, and F represents a material feed amount (kg/min).

[0028] It is still further preferred that, in the method of manufacturing a toner mentioned above, the flow speed (v) of the emulsion in the emulsion circulation route is from 0.5 to 3 m/sec.

[0029] It is still further preferred that, in the method of manufacturing a toner mentioned above, the pipes forming the emulsion circulation route have an inner diameter (D) of from 0.02 to 0.10 m.

[0030] It is still further preferred that, in the method of manufacturing a toner mentioned above, the emulsion has a flow Reynolds number (flow Re) of from 500 to 4,000 at the straight portion of the pipes forming the emulsion circulation route based on the following relationship (4): Flow Reynolds number $= \rho v D/\mu$ (4). In the relationship (4), ρ represents the density of the emulsion (kg/m^3), v represents the flow speed (m/s) of the emulsion, D represents the inner diameter (m) of the pipe, and μ represents the viscosity (Pa s) of the emulsion.

[0031] It is still further preferred that, in the method of manufacturing a toner mentioned above, the surface roughness (Ra) of the inner side of the pipes forming the emulsion circulation route is less than 0.8.

[0032] It is still further preferred that, in the method of manufacturing a toner mentioned above, the variation ratio of the inner diameter of the pipes is from 0.8 to 1.2 when the inner diameter of the main portion of the pipes is set to 1.

[0033] It is still further preferred that, in the method of manufacturing a toner mentioned above, in the variation ratio of an inner diameter of the pipes, the flow energy loss (E loss) of the emulsion generated is from 20 to 100 J/kg.

[0034] As another aspect of the present invention, a toner is provided which contains toner particles having a volume average particle diameter (Dv) of from 3 to 10 μm. In addition, the toner particles are prepared by the method of manufacturing a toner mentioned above.

[0035] It is preferred that, in the toner mentioned above, the value obtained by dividing the volume average particle diameter (Dv) of the toner with the number average particle diameter (Dn) thereof is 1.05 to 1.25.

[0036] As another aspect of the present invention, an image forming method is provided which includes developing a latent electrostatic image formed on an image bearing member with the toner mentioned above, transferring the toner-developed image on a recording medium, and fixing the transferred image on the recording medium.

[0037] As another aspect of the present invention, a process cartridge is provided which includes an image bearing member, a developing device holding a developer containing the toner mentioned above, and optionally at least one of a charging device and a cleaning device. In addition, the process cartridge is integrally and detachably attached to a main body of an image forming apparatus.

[0038] As another aspect of the present invention, an image forming apparatus includes an image bearing member, a charging device configured to charge the image bearing member, an irradiator configured to irradiate the image bearing member to form a latent electrostatic image on the image bearing member, a developing device configured to develop the latent electrostatic image on the image bearing member with the toner mentioned above, a cleaning member configured to remove residual toner on the image bearing member, a transferring device configured to transfer the developed image on a recording medium, and a fixing device configured to fix the developed image onto the recording medium. In addition, the image bearing member, the developing device, and optionally at least one of the charging device and the cleaning device are provided as the process cartridge mentioned above.

[0039] These and other objects, features and advantages of the present invention will become apparent upon consideration of the following description of the preferred embodiments of the present invention taken in conjunction with the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWING

[0040] Various other objects, features and attendant advantages of the present invention will be more fully appreciated as the same becomes better understood from the detailed description when considered in connection with the accompanying drawing in which like reference characters designate like corresponding parts throughout and wherein:

Figure is a schematic diagram illustrating an example of the granulation device for use in the emulsification process in toner manufacturing of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

[0041] As mentioned above, the present inventors have focused attention on the process in which liquid droplets are formed while equilibrium reactions of the formation of fine particles by imparting shearing force and the coalescence of the fine particles are repeated in the emulsifying process in which an aqueous phase and an oil phase containing a toner composition are mixed and stirred. By suitably controlling the combination of the shearing condition and the coalescence condition, a toner having a stable volume average particle diameter and a sharp particle size distribution can be manufactured in an easy and efficient manner.

[0042] The present invention will be described below in detail with reference to several embodiments and the accompanying drawing.

[0043] Figure is a schematic diagram illustrating an example of a granulation device 1 for use in an emulsion process of the toner manufacturing method of the present invention. In Figure, an emulsification mechanism 4 includes an emulsification device (PLHM) 2, and an emulsion circulation route 3 including pipes having a main portion which has the standard inner diameter thereof. In the emulsification mechanism 4, an oil phase and an aqueous phase supplied from each supplier tank 17 to 19 are mixed and liquid droplets having a toner particle size are formed while equilibrium reactions of the formation of fine particles by imparting shearing force (hereinafter referred to as fine particle formation by shearing) and the coalescence of the fine particles are repeated. The oil phase is a dissolved matter and/or a dispersed matter containing an organic phase containing at least one of a resin, a resin precursor, and a monomer. An example there of is a dissolved matter and/or a dispersed matter in which a resin, a colorant, and a release agent is dissolved or dispersed in an organic solvent. The aqueous phase is an aqueous medium containing a solid particulate dispersant. For convenience of description, the structure illustrated in Figure includes a right angle elbow 11 in the emulsion circulation route 3.

[0044] The oil phase of the present invention may include a resin, a resin precursor and a monomer. To impart good balance to properties of a toner, for example, it is suitable to use two or more kinds of polymers having a different molecular weight as the resin or the resin precursor.

[0045] Especially preferred specific examples of such polymers include a polyester resin because the polyester resin can show good reproducibility for a full color image. Among such polyester resins, it is preferred to use a composition containing at least a modified polyester resin modified by a urea linkage, and an unmodified polyester which is not modified by a urea linkage (hereinafter referred to as an unmodified polyester resin). Further, such a modified polyester resin and an unmodified polyester resin preferably have a different molecular weight in terms of a combination of low temperature fixing property, high temperature preservability, and anti-hot offset property. The resins are detailed later. Resins, such as styrene acrylic resins and polyol resins, which can be used for a typical toner can be used as the toner composition of the present invention.

[0046] Below are descriptions of cases in which a modified polyester resin and an unmodified resin are used as the toner composition for use in the manufacturing method of the present invention.

[0047] In the embodiment illustrated in Figure, the resin material for use in a toner composition is separately supplied from an A oil phase 7 contained in an A oil phase supplying tank 17 and a B oil phase 8 contained in a B oil phase supplying tank 18. The oil phase 7 is a mixture of an elongation agent and a dissolved matter or a dispersed liquid in which a resin such as an unmodified polyester resin, a colorant, and a release agent are dissolved or dispersed in an organic solvent. Specific example of such an elongation agent includes an active hydrogen compound which performs addition reaction with a prepolymer in the B oil phase 8. The B oil phase 8 is a solution in which a prepolymer having one or more isocyanate linkages is dissolved in an organic solvent. An aqueous phase 9 contained in an aqueous phase supplying tank 19 is an aqueous medium containing a solid particulate dispersant such as a solid resin particulate dispersant. Each oil phase component and the aqueous phase are detailed later.

[0048] The A oil phase 7 and the B oil phase 8 are pre-stirred in a static mixer (STM) 10 before being mixed with the aqueous phase 9. The liquid obtained after this pre-stirring is referred to as an oil phase.

[0049] The oil phase mixed in the static mixer 10 and the aqueous phase 9 are continuously transferred to the emulsification mechanism 4 with a pre-determined amount. Emulsification is performed receiving a shearing force while stirred by the emulsification device (PLHM) 2 provided in the middle of the emulsion circulation route 3. Characters PLHM is an abbreviation of a pipeline homomixer. Liquid droplets having a suitable toner particle size are formed from the emulsion while the emulsion is circulated and stayed in the emulsion circulation route 3. The emulsion is discharged to a transfer pipe 5 and transferred to a storing tank 6.

[0050] As mentioned above, it is necessary to control the equilibrium reactions in which the emulsion is sheared to obtain fine particles and coalescence of the fine particles occurs to stably obtain a toner having a small particle diameter and a sharp particle size distribution.

[0051] That is, it is preferred to regulate both conditions of the formation of fine particles and the coalescence, which is described below in due order.

[0052] First, as factors having a great influence on formation of fine particles, stirring Reynolds number (stirring Re), shearing energy (E) and unit total energy (e) per raw material feed unit flow amount which the emulsion receives from the emulsification 2 can be mentioned. During emulsification, a polymerization reaction is also performed in which the modified polyester resin mentioned above (such as polyester prepolymer having one or more isocyanate groups) reacts with an elongation agent (such as an active hydrogen compound which performs addition reaction with a prepolymer). In addition, the number of the right angle elbows is taken into consideration when the pipe forming the emulsion circulation route 3 has right angle elbows.

[0053] Each regulation on the conditions and its grounds are described below.

[Formation of fine particle]

[0054] The stirring Reynolds number (stirring Re) by the stirring blade of an emulsification device is determined by the following relationship (1): Stirring Re = = $\rho n d^2/\mu$ (1), wherein ρ represents a density of an emulsion (kg/m^3), n represents the rotation number (rps) of a stirring blade, d represents the blade diameter (m) of the stirring blade, and μ represents the viscosity (Pa s) of the emulsion.

[0055] The stirring Re during stirring an emulsion is from 3,000 to 15,000, and preferably from 5, 000 to 15,000. When the stirring Re is in this range, the entire fluid is microscopically stirred, which leads to turbulent diffusion.

[0056] That is, when the stirring Re is not less than 3,000, and preferably not less than 5, 000, the molecules in the fluid are violently moved, resulting in increase in the number of impacts among the molecules. Therefore, shearing and coalescence reaction during stirring become active, which is advantageous to coalescence after shearing. In addition, in a turbulent diffusion state, high and uniform energy is transmitted and transitioned instantly, which is advantageous to controlling forming fine particles and particle size distribution. To the contrary, stirring Re is too small, turbulent diffusion is not created so that the number of impacts among the molecules decreases. Therefore, coalescence of the fine particles is not sufficient. This is disadvantageous to forming a sharp particle size distribution. To the contrary, when the stirring Reynolds is too large, it is likely that the emulsion system may be damaged.

[0057] In addition, when the shearing force is applied to the oil phase and the aqueous phase by the emulsification device, oil droplets are formed in the aqueous phase, which is referred to as O/W type emulsion state. In producing this O/W type emulsion state, oil droplets having a desired particle diameter is produced when the shearing energy (E) generated by the rotation of the stirring blade, which is determined by the relationship (2), is preferably from 400 to 2,000 and more preferably from 700 to 1,500:

$$E = (n \times 60)^3 \times d^5/Q \qquad (2),$$

wherein n represents a rotation number (rps) of the stirring blade, d represents a blade diameter (m) of the stirring blade, and Q represents a flow amount (L/min) in the emulsion circulation route.

[0058] When the shearing energy (E) is too small, poor emulsion state is created due to shortage of the shearing force. On the contrary, when the shearing energy (E) is too large, the obtained emulsion state is unstable due to excessive shearing, which achieves an emulsion corruption state. As a result, the particles become too large during the coalescence. That is, the shearing energy (E) has a large impact on particle design, i.e., particle control.

[0059] Further, while the emulsion stays and circulates in the emulsion circulation route 3, the unit total energy (e) per raw material feed unit flow amount provided to the emulsion by the emulsification device 2 is determined by the following relationship (3):

$$e = [(n \times 60)^3 \times d^5 \times Q]/F^2 \qquad (3),$$

wherein n represents a rotation number (rps) of the stirring blade, d represents a blade diameter (m) of the stirring blade, Q represents a flow amount (L/min) in the emulsion circulation route, and F represents a feed amount (kg/min) of the material feed. The unit total energy (e) per raw material feed unit flow amount is preferably from 1 x 10^6 to 5 x 10^6, and more preferably from 3 x 10^6 to 5 x 10^6.

[0060] Specifically, when the shearing energy provided from the emulsification device 2 is set to be P (= $(n \times 60)^3$ x d^5) , an energy of P/F is applied to the unit flow amount of a supplied raw material by one shearing of the emulsification device 2. The number of shearing applied to the emulsion while the emulsion stays and circulates until the emulsion is discharged from the emulsion circulation route 3 to the transfer pipe 5 is defined to be Q/F. Therefore, the unit total energy (e) received until the emulsion is discharged is the energy represented by the relationship (3) described above.

[0061] When the unit total energy (e) is regulated in the range mentioned above, a suitable equilibrium reaction of shearing and coalescence proceeds, which works to advantage in forming a sharp particle size distribution. Too small unit total energy (e) tends to work advantage to shearing. Too large unit total energy (e) tends to work advantage to coalescence. Therefore, in theses cases, it is difficult to form a sharp particle size distribution.

[0062] Next, the factors having a great impact on coalescence of fine particles in the equilibrium reaction are, for example, the flow speed (v) of the emulsion in the emulsion circulation route 3, the inner diameter (D) of the pipe forming the emulsion circulation route 3, the flow Reynolds number (Flow Re) of the emulsion in the straight portion of the pipe; the surface roughness (Ra) of the inner side of the pipe forming the emulsion circulation route 3, the number of the right angle elbows 11; the ratio (S) / (D) of the length (S) of the straight portion of the pipe between the right angle elbows 11 to the inner diameter (D) of the pipe, the variation ratio of the inner diameter, the fluxion energy loss (Eloss) of the emulsion, etc.

[0063] Each regulation condition is as follows. [Coalescence]

[0064] The flow speed (v) of the emulsion in the emulsion circulation route 3 is preferably from 0.5 to 3 m/sec, and more preferably from 1 to 2 m/sec.

[0065] The inner diameter (D) of the pipe forming the emulsion circulation route 3 is preferably from 0.02 to 0.10 m, and more preferably from 0.02 to 0.05 m.

[0066] The flow Reynonlds number (flow Re) of the emulsion in the straight portion forming the emulsion circulation route 3, which is determined by the following relationship (4) is preferably from 500 to 4,000, and more preferably from 1,000 to 2,500.

$$\text{Flow Reynolds number} = \rho vD/\mu \quad (4),$$

wherein ρ represents a density of the emulsion (kg/m^3), v represents the flow speed (m/s) of the emulsion, D represents the inner diameter (m) of the pipe, and μ represents the viscosity (Pa s) of the emulsion.

[0067] The surface roughness (Ra) of the inner side of the pipe forming the emulsion circulation route 3 is preferably less than 0.8, and more preferably from 0.5.

[0068] When the pipe forming the emulsion circulation route 3 has a right angle elbow, the number of the right angle elbows 11 is preferably 4 at a maximum, and more preferably 0.

[0069] In addition, when the pipe has 4 right angle elbows 11 at a maximum, the ratio (S) / (D) of the length (S) of the straight portion of the pipe between the right angle elbows 11 to the inner diameter (D) of the pipe is secured to be at least 10.

[0070] When the standard inner diameter of the pipe forming the emulsion circulation route 3 is set to be 1, the variation ratio of the inner diameter of the pipe is preferably 0.8 to 1.2.

[0071] The fluxion energy loss (Eloss) of the emulsion in the range of the variation ratio of the inner diameter of the pipe is preferably from 20 to 100 J/kg, and more preferably from 20 to 50 J/kg.

[0072] When each condition mentioned above is satisfied, the flow state is suitable for coalescence and woks to advantage to forming a sharp particle size distribution. The emulsion tends to be close to a static state when each value is below the ranges mentioned above. In this case, particles tend to agglomerate instead of coalescence, resulting in formation of particles having a large particle diameter. To the contrary, when each value is above the range mentioned above, coalescence is restrained so that the next shearing occurs while the existence ratio of fine particles is still high. Therefore, it is impossible to obtain particles having a target particle diameter.

[0073] Further, by regulating the emulsion circulation route 3 as mentioned above, local turbulence created when the emulsion stays and circulates, i.e., turbulent flow, can be restrained. Therefore, the equilibrium reaction is not prevented. In addition, the impact of load variation caused by changes in viscosity of the disposed liquid, restraint of cavitation and pressure variation during circulation is thought to be reduced. When each value is above the ranges mentioned above, the chance of particles meeting local turbulence after shearing increases so that the variance of frequency of impact increases, which makes it difficult to have a target particle size. In addition, the main pipe of the emulsion circulation route 3 is preferably formed having the same diameter. [Condition of discharging the emulsion from the emulsion circulation route]

[0074] Further, to obtain mother toner particles having a sharp and stable particle size distribution, it is preferred to regulate the condition of discharging the emulsion from the emulsion circulation route 3 to the next process, i.e., the process of discharging the emulsion to the transfer pipe 5. That is, the form of the circulation route 3 is such that the emulsion is discharged from the emulsion circulation route 3 to the transfer pipe 5 without passing through a right angle elbow, and in addition, the main pipe has a form by which the emulsion is discharged without passing through the portion having a different diameter.

[0075] When shearing and coalescence are balanced in the emulsion, the particle diameter is temporarily definite. By regulating the condition discharging from the emulsion circulation route 3 as mentioned above, the emulsion is transferred to the next process while the equilibrium state in which shearing and coalescence are balanced is maintained. Therefore, a toner having a target particle size and a target sharp particle size distribution can be obtained.

[Toner particle diameter]

[0076] When the polyester resin mentioned above is used as a toner component, the dry toner obtained has a good high temperature preservability, a good low temperature fixabiltiy, and a good anti-hot offset property by regulating the volume average particle diameter (Dv) in the range of from 3 to 10 μm, and the value (ratio (Dv/Dn)) obtained by dividing the volume average particle diameter (Dv) by the number average particle diameter (Dn) in the range of from 1.05 to 1.25. Especially when the toner is used in a full color photocopier, etc., obtained images have good gloss. In addition, when the toner is used in a two-component developer, the variance of the toner particle diameter in the developer is reduced even when the toner is repeatedly replenished over an extended period of time. Further, when the developer is stirred in a developing device over an extended period of time, good and stable developability can be obtained.

[0077] Further, when the toner is used as a single component developer and is replenished, the variance in the particle diameter of the toner is small and filming of the toner on a developing roller and fusion bonding of the toner onto a member such as a blade for regulating the thickness of the toner layer hardly occur. Therefore, images having good and stable developability are obtained even for an extended use of a developing unit in which the toner is stirred.

[0078] It is generally said that a toner having a small particle diameter is advantageous to obtain high definition and high quality images, but is disadvantageous in light of transferability and cleaning properties. In addition, when a toner having a volume average particle diameter below the range of the present invention is used in a two component developer, the toner tends to be fusion bonded to the surface of the carrier as stirring repeats for a long period of time and therefore charging ability of the carrier degrades. In the case of a single component developer having too small a volume average particle diameter, filming of the toner on a developing roller and fusion bonding of the toner onto a member such as a blade for regulating the thickness of the toner layer easily occur.

[0079] These problems can be solved by using a resin described later as a toner component of the present invention and adopting the manufacturing method mentioned above.

[0080] In addition, a toner having a smaller particle diameter is more advantageous in terms of the resistance property to the impact of load variation caused by changes in viscosity of the disposed liquid, and restraint of cavitation and pressure variation during circulation. To the contrary, when the particle diameter of a toner is too large, obtaining quality images having a high definition is difficult. Further, when such a toner in a developer is replenished, the variance of the particle diameter of the toner increases in most cases. In addition, it is found that, when Dv/Dn is too large, the same is true. When Dv/Dn is too small, it is found that, although there are merits such that the behavior of the toner is stabilized and the amount of charge thereof is uniform, the toner may not be sufficiently charged or the cleanability thereof may deteriorate.

(Particle size distribution measuring method)

[0081] The particle diameter (volume average particle diameter) and the particle size distribution of the toner mentioned above are measured as follows:

[0082] Coulter Multisizer III (manufactured by Beckman Coulter, Inc.) was used as a measuring device; a personal computer (manufactured by International Business Machine Corporation) was connected thereto; and data was analyzed using dedicated analysis software (manufactured by Beckman Coulter, Inc.). Kd value was set using a standard particle having a particle diameter of 10 μm. Aperture current was performed with automatic. As an electrolytic solution, 1 % NaCl aqueous solution prepared using primary sodium chloride was used. ISOTON-II (Coulter Scientific Japan Co., Ltd.) can be also used.

[0083] A specific measuring method is as follows: Add a surface active agent as a dispersant, preferably 0.1 to 5 ml of a salt of an alkyl benzene sulfide, to 100 to 150 ml of the electrolytic solution mentioned above; further add 2 to 20 mg of a sample material thereto; the electrolytic solution in which the sample material is suspended is subject to a dispersion treatment for about 1 to 3 minutes with a supersonic disperser; measure the volume and the number of the toner particle having a particle diameter not less than 2 μm for 50,000 counts using a 100 μm aperture tube to calculate the volume distribution and the number distribution; and obtain the volume average particle diameter (Dv) from the volume distribution and the number average particle diameter (Dn) from the number distribution. The closer Dv/Dn is to 1.0, the sharper the particle size distribution is.

[0084] Next, the toner composition contained in the oil phase (of the present invention), i.e., the organic phase, is now described.

[0085] In the organic phase, a resin, a resin precursor or monomer can be contained. As mentioned above, as a resin or a resin precursor, at least two kinds of polymers having a different molecular weight suitable to obtain good-balanced characteristics, especially polyester resins (a combination of an unmodified polyester resin and a modified polyester resin) suitable to reproduce full color images, are described as an example.

(Modified polyester resin)

[0086] The modified polyester resin is defined as follows:

[0087] A resin containing a function group or a linkage group in a polyester resin other than a functional group deriving from a monomer unit of an acid and an alcohol used as a material component and an ester linkage, or a resin containing resin components having a different structure linked with a covalent linkage, an ion linkage, etc., in a polyester resin.

[0088] As an example of such an unmodified polyester resin, a resin modified by a linkage other than ester linkage at the end of the polyester resin can be mentioned. Specifically, a resin can be mentioned which is formed by introducing a functional group, such as an isocyanate group, by reacting a compound such as an isocyanate compound reactive with an acid group or a hydroxyl group at the end of a polyester resin and further by reacting the function group with an active hydrogen compound to modify or elongate the end of the polyester resin. Such modified polyester resins include a urea-modified polyester resin and a urethane-modified polyester resin.

[0089] In addition, there can be included resins which are formed by introducing a reactive group such as a double linkage in the polyester main chain and thereafter introducing a graft component of a carbon-carbon linkage in a side chain thereof by generating a radical polymerization or linking double linkages with each other. Specific examples of such resins include a styrene-modified polyester resin and an acrylic-modified polyester resin.

[0090] Further, there can be included resins which are formed by copolymerizing a resin component having a different structure in the main chain of a polyester resin, or reacting a polyester resin with a compound having a carboxyl group and/or a hydroxyl group at its end, for example, copolymerizing with a silicone resin having a carboxyl group, a hydroxyl group, an epoxy group and a mecapto group (e.g., silicone modified polyester). Typical modified polyester resins are specifically described below.

(Urea modified polyester resin)

[0091] Specific examples of polyesters modified by a urea linkage (a urea modified polyester resin) (i) include a reactant product of a polyester prepolymer (A) having an isocyanate group with amine (B). Specific examples of the polyester prepolymer (A) having an isocyanate group include polyesters prepared by reacting an active hydrogen group of a polycondensation compound of a polyol (1) and a polycarboxylic acid (2) with a polyisocyanate (3).

[0092] Specific examples of the active hydrogen groups contained in the polyesters mentioned above include hydroxyl groups (alcohol hydroxyl groups and phenol hydroxyl groups), amino groups, carboxylic groups, and mercarpto groups. Among these, alcohol hydroxyl groups are preferred.

[0093] Specific examples of the polyols (1) are diols (1-1) and polyols (1-2) having at least 3 hydroxyl groups. The diol (1-1) alone or in combination with a small quantity of the polyols (1-2) are preferred as the polyol (1).

[0094] Specific preferred examples of the diols (1-1) are alkylene glycols (e.g., ethylene glycol, 1,2-propylene glycol, 1,3-propylene glycol, 1,4-butane diol and 1,6-hexan diol), alkylene ether glycol (e.g., diethylene glycol, triethylene glycol, dipropylene glycol, polyethylene glycol, polypropylene glycol, and polytetra methylene ether glycol), alicyclic diols (e.g., 1,4-cyclo hexane dimethanol, hydrogen added bisphenol A, and bisphenol groups (e.g., bisphenol A, bisphenol F and bisphenol S) , adducts of the alicyclic diols mentioned above with alkylene oxides (e.g., ethylene oxides, propylene oxides, butylene oxides), and the bisphenols mentioned above with alkylene oxides (e.g., ethylene oxides, propylene oxides and butylene oxides).

[0095] Among these, alkylene glycols having 2 to 12 carbon atoms and adducts of bisphenol groups with alkylene oxides are preferred, and adducts of bisphenol groups with alkylene oxides and combinations of adducts of one or more bisphenols with one or more alkylene oxides and alkylene glycols having 2 to 12 carbon atoms are especially preferred.

[0096] Specific examples of the polyols (1-2) having at least 3 hydroxyl groups include aliphatic alcohols having 3 or more hydroxyl groups (e.g., glycerine, trimethylol ethane, trimethylol propane, pentaerythritol and sorbitol), polyphenols having at least 3 hydroxyl groups (e.g., trisphenol PA, phenol novolak and cresol novolak) and adducts of polyphenols having at least 3 hydroxyl groups with the alkylene oxides mentioned above.

[0097] Specific examples of the polycarboxylic acids (2) are dicarboxylic acids (2-1) and polycarboxylic acids (2-2) having at least 3 hydroxyl groups, with a dicarboxylic acid (2-1) alone or in combination with a small quantity of one or more polycarboxylic acids (2-2) being preferred as the polycarboxylic acid (2).

[0098] Specific preferred examples of dicarboxylic acids (2-1) include alkylene dicarboxylic acid (e.g., succinic acid, adipic acid and sebacic acid), alkenylene dicarboxylic acid (e.g., maleic acid and fumaric acid), and aromatic dicarboxylic acids (e.g., phthalic acid, isophthalic acid, terephthalic acid and naphthalene dicarboxylic acid) . Among these, the alkenylene dicarboxylic acids having 4 to 20 carbon atoms and the aromatic dicarboxylic acids having 8 to 20 carbon atoms are preferred.

[0099] Specific preferred examples of polycarboxylic acids (2-2) having at least 3 carboxyl groups include aromatic polycarboxylic acid having 9 to 12 carbon atoms (e.g., trimellitic acid and pyromellitic acid). In addition, the polycarboxylic acids (2) can be obtained by reacting acid anhydrides of the above-mentioned or lower alkyl esters (e.g., methyl esters, ethyl esters and isopropyl esters) with the polyols (1).

[0100] The mixing ratio of the polyol (1) to the polydicarboxylic acid (2) , i.e., the equivalent ratio ([OH] /[COOH]) of a hydroxyl group [OH] to a carboxyl group [COOH], is normally from 2/1 to 1/1, preferably from 1.5/1 to 1/1, and more preferably from 1.3/1 to 1.02/1.

[0101] Specific preferred examples of the polyisocyanates (3) include aliphatic polyisocyanates (e.g., tetramethylene diisocyanate, hexamethylene diisocyanate and 2,6-diisocyanate methylcaproate); alicyclic polyisocyanates (e.g., isophorone diisocyanate and cyclohexyl methane diisocyanate); aromatic diisocyanates (e.g., tolylene diisocyanate and diphenylmethane diisocyanate); aromatic aliphatic diisocyanates (e.g., α, α, α', α'-tetramethyl xylylene diisocyanate) ; isocyanurates; and blocked polyisocyanates in which the polyisocyanates mentioned above are blocked with phenol derivatives, oximes or caprolactams. These compounds can be used alone or in combination.

[0102] The mixing ratio of the polyisocyanate (3) to the polyester, i.e. , the equivalent ratio ([NCO] /[OH]) of an isocyanate group [NCO] to a hydroxyl group [OH] of a polyester having hydroxyl groups, is normally from 5/1 to 1/1, preferably from 4/1 to 1.2/1, and more preferably from 2.5/1 to 1.5/1. When the [NCO] /[OH] ratio is too large, the low temperature fixability of the toner tends to deteriorate. When the equivalent ratio of [NCO] /[OH] is too small, the urea content in the resultant modified polyesters decreases and thereby the anti-hot offset property of the toner tends to deteriorate.

[0103] The content of the constitutional component, which is obtained from the polyisocyanate (3), in the prepolymer (A) having an isocyanate group at its end portion is from 0.5 to 40 % by weight, preferably from 1 to 30 % by weight and more preferably from 2 to 20 % by weight. When the content is too small, the hot offset resistance of the toner tends to deteriorate and in addition it is hard for the toner to have good heat resistance and low temperature fixability. In contrast, when the content is too large, the low temperature fixability of the toner tends to deteriorate.

[0104] The number of isocyanate groups included in the prepolymer (A) per molecule is normally not less than 1, preferably from 1.5 to 3, and more preferably from 1.8 to 2.5. When the number of isocyanate groups is too small, the molecular weight of the modified polyester tends to decrease and thereby the anti-hot offset property tends to deteriorate.

[0105] Specific preferred examples of the amine (B) include diamines (B1) , polyamines (B2) having three or more amino groups, amino alcohols (B3), amino mercaptans (B4), amino acids (B5) and blocked amines (B6) in which the amines (B1-B5) mentioned above are blocked.

[0106] Specific preferred examples of the diamines (B1) include aromatic diamines (e.g., phenylene diamine, diethyltoluene diamine and 4,4' -diaminodiphenyl,methane); alicyclic diamines (e.g., 4,4' -diamino-3,3'-dimethyldicyclohexyl methane, diaminocyclohexane and isophoron diamine); aliphatic diamines (e.g., ethylene diamine, tetramethylene diamine and hexamethylene diamine); etc.

[0107] Specific examples of the polyamines (B2) having three or more amino groups include diethylene triamine, and triethylene tetramine. Specific preferred examples of the amino alcohols (B3) include ethanol amines and hydroxyethyl anilines. Specific examples of the amino mercaptans (B4) include aminoethyl mercaptans and aminopropyl mercaptans. Specific preferred examples of the amino acids (B5) include amino propionic acids and amino caproic acids.

[0108] Specific examples of the blocked amines (B6) of B1 to B5 include ketimine compounds which are prepared by reacting one of the amines B1-B5 mentioned above with a ketone such as acetone, methyl ethyl ketone and methyl isobutyl ketone; oxazoline compounds, etc. Among these amines(B), B1 and a mixture of B1 and a small quantity of B2 are preferred.

[0109] Further, the molecular weight of the urea-modified polyester resins (i) can be controlled using a molecular-weight control agent, if desired.

[0110] Specific preferred examples of the molecular-weight control agent include monoamines (e.g., diethyle amine, dibutyl amine, butyl amine and lauryl amine), and blocked amines (e.g., ketimine compounds) prepared by blocking the monoamines mentioned above.

[0111] The mixing ratio of the amines (B) to the prepolymer (A) , i.e., the equivalent ratio ([NCO] /[NHx]) of the isocyanate group [NCO] contained in the prepolymer (A) to the amino group [NHx] contained in the amines (B), is normally from 1/2 to 2/1, preferably from 1.5/1 to 1/1.5 and more preferably from 1.2/1 to 1/1.2. In the amino group [NH_x] , X is 1 or 2, and mostly 2. When ([NCO] /[NH_x]) is too great or too small, the molecular weight of the resultant urea-modified polyester (i) tends to decrease, resulting in deterioration of the anti-hot offset property of the resultant toner.

[0112] In the present invention, polyesters modified by a urea linkage, i.e., the modified polyester (i) can include a urethane linkage as well as a urea linkage. The molar ratio of the content of the urea linkage to the content of the urethane linkage is normally from 100/0 to 10/90, preferably from 80/20 to 20/80 and more preferably from 60/40 to 30/70. When the molar ratio of the urea linkage is too small, the anti-hot offset property of the resultant toner deteriorates.

[0113] The urea-modified polyester (i) of the present invention can be prepared by a method such as one-shot methods or prepolymer methods. The weight average molecular weight of the urea-modified polyester (i) is not less than 10, 000, preferably from 20, 000 to 10, 000, 000 and more preferably from 30, 000 to 1, 000, 000. When the weight average molecular weight is too small, the hot offset resistance of the resultant toner tends to deteriorate. When an unmodified polyester (ii) described later is used in combination with the modified polyester (i) , the number average molecular weight of the modified polyester (i) is not particularly limited if the weight average molecular weight mentioned above is allowed. When the modified polyester (i) is used alone, the number average molecular weight is normally not less than 20,000, preferably from 1000 to 10, 000 and more preferably from 2, 000 to 8, 000. When the number average molecular weight is too large, low temperature fixability of the resultant toner tends to deteriorate and, in addition, the gloss properties thereof also tend to deteriorate when the toner is used in a full color device.

(Unmodified polyester)

[0114] In the present invention, not only can the urea-modified polyester resin (i) mentioned above be used alone as a toner binder constituent, but also the unmodified polyester (ii) can be contained as a binder resin in combination with the modified polyester (i) . The combinational use of (i) and (ii) can improve the low temperature fixability and gloss property when the toner is used in a full color device.

[0115] Specific preferred examples of the unmodified polyester resins (ii) include polycondensation products of polyol (1) and polycarboxylic acid (2) as mentioned above for use in the polyester constituents of the modified polyester (i) mentioned above. Specific preferred examples of the unmodified polyester resins (ii) are the same as those for the modified polyester resins (i). In addition, the unmodified polyester resins (ii) include not only unmodified polyesters but also polyester resins modified by a chemical linkage other than urea linkage, for example, urethane linkage. It is preferred that (i) and (ii) are at least partially mixed with each other in light of the low temperature fixability and anti-hot offset property.

[0116] Therefore, it is preferred, but not mandatory, that the unmodified polyester resins (ii) have a similar composition to that of the polyester component of the unmodified polyester resins (i) . The weight ratio of (i)/(ii) is normally from 5/95 to 80/20, preferably from 5/95 to 30/70, more preferably from 5/95 to 25/75 and even more preferably from 7/93 to 20/80 when (ii) is contained. When the weight ratio of the modified polyester (i) is too small, the anti-hot offset property of the toner tends to deteriorate and in addition it is difficult for the toner to have a good combination of a high temperature preservability and a low temperature fixability.

[0117] The peak weight average molecular weight of the unmodified polyester (ii) is normally from 1,000 to 30, 000, preferably from 1,500 to 10,000, and more preferably from 2,000 to 8,000. When the peak molecular weight is too small, the high temperature preservability tend to deteriorate. When the peak molecular weight is too large, the low temperature fixability tends to deteriorate. The hydroxyl group value of the unmodified polyester resin (ii) is preferably not less than 5 mgKOH/g, more preferably from 10 to 120 mgKOH/g and even more preferably 20 to 80 mgKOH/g. When the hydroxyl group value of the unmodified polyester (ii) is too small, it is disadvantageous in terms of the toner having a good combination of a high temperature preservability and a low temperature fixability. The acid value of the unmodified polyester resin (ii) is normally from 1 to 30 mgKOH/g, and preferably from 5 to 20 mgKOH/g. When the (ii) has such an acid value, the resultant toner tends to be negatively charged.

[0118] In the present invention, the resin as a toner binder preferably has a glass transition temperature (Tg) of from 50 to 70 °C, and more preferably from 55 to 65 °C. When the glass transition temperature is too low, the high temperature preservability of the toner tends to deteriorate. When the glass transition temperature is too high, the low temperature fixability tends to be insufficient. Since the unmodified polyester resin (ii) coexists with the urea-modified polyester resin (i), the dry toner of the present invention tends to have a good high temperature preservability even when the toner has a relatively low glass transition temperature compared with that of a known polyester-based toner.

[0119] The resin as the toner binder preferably has a storage modulus of elasticity of 10, 000 dyne/cm^2 (10^3 N/m^2) at a temperature (TG') not lower than 100 °C, and more preferably from 110 to 200 °C when measured at a frequency of 20 Hz. When the temperature TG' is too low, the toner tend to have a poor anti-hot offset property. In addition, the toner binder preferably has a viscosity of 1, 000 poise at a temperature (Tη) not higher than 180 °C, and more preferably from 90 to 160 °C. When the temperature Tη is too high, the low temperature fixability of the toner tends to deteriorate. Namely, to have a good combination of low temperature fixability and anti-hot offset property, the temperature TG' of the toner is preferably higher than the temperature Tη, i.e., the difference between TG' and Tη (TG' -Tη) is preferably not less than 0 °C. More preferably, the difference is not less than 10 °C, and even more preferably not less than 20 °C. There is no specific upper limit to the difference. However, in view of good combination of high temperature preservability and low temperature fixability, the difference (TG' - Tη) is preferably from 0 to 100 °C, more preferably from 10 to 90 °C, and even more preferably from 20 to 80 °C.

(Colorant)

[0120] Suitable colorants for use in the toner component of the present invention include any known dyes and pigments.

[0121] Specific examples of such colorants include carbon black, Nigrosine dyes, black iron oxide, Naphthol Yellow S, Hansa Yellow (10G, 5G and G), Cadmium Yellow, yellow iron oxide, loess, chrome yellow, Titan Yellow, polyazo yellow, Oil Yellow, Hansa Yellow (GR, A, RN and R), Pigment Yellow L, Benzidine Yellow (G and GR), Permanent Yellow (NCG) , Vulcan Fast Yellow (5G and R) , Tartrazine Lake, Quinoline Yellow Lake, Anthrazane Yellow BGL, isoindolinone yellow, red iron oxide, red lead, orange lead, cadmium red, cadmium mercury red, antimony orange, Permanent Red 4R, Para Red, Fire Red, p-chloro-o-nitroaniline red, Lithol Fast Scarlet G, Brilliant Fast Scarlet, Brilliant Carmine BS, Permanent Red (F2R, F4R, FRL, FRLL and F4RH), Fast Scarlet VD, Vulcan Fast Rubine B, Brilliant Scarlet G, Lithol Rubine GX, Permanent Red F5R, Brilliant Carmine 6B, Pigment Scarlet 3B, Bordeaux 5B, Toluidine Maroon, Permanent Bordeaux F2K, Helio Bordeaux BL, Bordeaux 10B, BON Maroon Light, BON Maroon Medium, Eosin Lake, Rhodamine Lake B, Rhodamine Lake Y, Alizarine Lake, Thioindigo Red B, Thioindigo Maroon, Oil Red, Quinacridone Red, Pyrazolone Red, polyazo red, Chrome Vermilion, Benzidine Orange, perynone orange, Oil Orange, cobalt blue, cerulean blue, Alkali Blue Lake, Peacock Blue Lake, Victoria Blue Lake, metal-free Phthalocyanine Blue, Phthalocyanine Blue, Fast Sky Blue, Indanthrene Blue (RS and BC), Indigo, ultramarine, Prussian blue, Anthraquinone Blue, Fast Violet B, Methyl Violet Lake, cobalt violet, manganese violet, dioxane violet, Anthraquinone Violet, Chrome Green, zinc green, chromium oxide, viridian, emerald green, Pigment Green B, Naphthol Green B, Green Gold, Acid Green Lake, Malachite Green Lake, Phthalocyanine Green, Anthraquinone Green, titanium oxide, zinc oxide, lithopone and the like. These materials can be used alone or in combination.

[0122] The content of the colorant is preferably from 1 to 15 % by weight, and more preferably from 3 to 10 % by weight, based on the total weight of the toner component.

[0123] Master batch pigments, which are prepared by combining a colorant with a resin, can be used as the colorant of the toner composition of the present invention. Specific examples of the resins for use in the master batch pigments or for use in combination with master batch pigments include the modified and unmodified polyester resins mentioned above; styrene polymers and substituted styrene polymers such as polystyrene, poly-p-chlorostyrene and polyvinyltoluene; styrene copolymers such as styrene-p-chlorostyrene copolymers, styrene-propylene copolymers, styrene-vinyltoluene copolymers, styrene-vinylnaphthalene copolymers, styrene-methyl acrylate copolymers, styrene-ethyl acrylate copolymers, styrene-butyl acrylate copolymers, styrene-octyl acrylate copolymers, styrene-methyl methacrylate copolymers, styrene-ethyl methacrylate copolymers, styrene-butyl methacrylate copolymers, styrene-methyl α -chloromethacrylate copolymers, styrene-acrylonitrile copolymers, styrene-vinyl methyl ketone copolymers, styrene-butadiene copolymers, styrene-isoprene copolymers, styrene-acrylonitrile-indene copolymers, styrene-maleic acid copolymers and styrene-maleic acid ester copolymers; and other resins such as polymethyl methacrylate, polybutyl methacrylate, polyvinyl chloride, polyvinyl acetate, polyethylene, polypropylene, polyesters, epoxy resins, epoxy polyol resins, polyurethane resins, polyamide resins, polyvinyl butyral resins, acrylic resins, rosin, modified rosins, terpene resins, aliphatic or alicyclic hydrocarbon resins, aromatic petroleum resins, chlorinated paraffin, paraffin waxes, etc. These resins can be used alone or in combination.

[0124] The master batch mentioned above is typically prepared by mixing and kneading a resin and a colorant upon application of high shear stress thereto. In this case, an organic solvent can be used to boost the interaction of the colorant with the resin. In addition, flushing methods in which an aqueous paste including a colorant is mixed with a resin solution of an organic solvent to transfer the colorant to the resin solution and then the aqueous liquid and organic solvent are separated to be removed can be preferably used because the resultant wet cake of the colorant can be used as it is. In this case, three-roll mills can be preferably used for kneading the mixture upon application of high shear stress thereto.

(Release agent)

[0125] A wax can be included as a release agent as part of the toner composition of the present invention.

[0126] Specific examples of the release agent include polyolefin waxes such as polyethylene waxes and polypropylene waxes; long chain hydrocarbons such as paraffin waxes and SAZOL waxes; waxes including a carbonyl group, etc. Among these waxes, the waxes including a carbonyl group are preferred. Specific examples of the waxes including a carbonyl group include polyalkane acid esters such as carnauba wax, montan waxes, trimethylolpropane tribehenate, pentaerythritol tetrabehenate, pentaerythritol diacetate dibehenate, glycerin tribehenate, and 1,18-octadecanediol distearate; polyalkanol esters such as trimellitic acid tristearyl, and distearyl maleate; polyalkylamide such as trimellitic acid tristearylamide; dialkyl ketone such as distearyl ketone, etc. Among these materials, polyalkane acid esters are preferred.

[0127] The waxes for use in the toner of the present invention preferably have a melting point of from 40 to 160 °C, more preferably from 50 to 120 °C, and even more preferably from 60 to 90 °C. When the melting point of the wax included in the toner is too low, the high temperature preservability of the toner tends to deteriorate. In contrast, when the melting point is too high, a cold offset tends to occur during fixing at a low temperature.

[0128] In addition, the wax used in the toner of the present invention preferably has a melt viscosity of from 5 to 1, 000 cps (5 to 1, 000 mPas) and more preferably from 10 to 100 cps (10 to 100 mPas) at a temperature 20 °C higher than the melting point of the wax. When the melt viscosity is too high, the effect of improving the ant-hot offset property and low temperature fixability is reduced. The content of the wax in the toner is from 0 to 40 % by weight and preferably from 3 to 30 % by weight based on the total weight of the toner.

(Charge controlling agent)

[0129] A charge controlling agent may be included as the toner component of the present invention.

[0130] Specific examples of the charge controlling agent include known charge controlling agents such as Nigrosine dyes, triphenylmethane dyes, metal complex dyes including chromium, chelate compounds of molybdic acid, Rhodamine dyes, alkoxyamines, quaternary ammonium salts (including fluorine-modified quaternary ammonium salts) , alkylamides, phosphor and compounds including phosphor, tungsten and compounds including tungsten, fluorine-containing activators, metal salts of salicylic acid, metal salts of salicylic acid derivatives, etc.

[0131] Specific examples of the marketed products of the charge controlling agents include BONTRON 03 (Nigrosine dyes), BONTRON P-51 (quaternary ammonium salt), BONTRON S-34 (metal-containing azo dye) , E-82 (metal complex of oxynaphthoic acid), E-84 (metal complex of salicylic acid), and E-89 (phenolic condensation product), which are manufactured by Orient Chemical Industries Co., Ltd. ; TP-302 and TP-415 (molybdenum complex of quaternary ammonium salt), which are manufactured by Hodogaya Chemical Co., Ltd.; COPY CHARGE PSY VP2038 (quaternary ammonium salt) , COPY BLUE (triphenyl methane derivative) , COPY CHARGE NEG VP2036 and NX VP434 (quaternary ammonium salt), which are manufactured by Hoechst AG; LRA-901, and LR-147 (boron complex), which are manufactured by Japan Carlit Co., Ltd.; copper phthalocyanine, perylene, quinacridone, azo pigments and polymers having a functional group such as a sulfonate group, a carboxyl group, a quaternary ammonium group, etc.

[0132] The content of the charge controlling agent is determined depending on the species of the binder resin used, whether or not an additive is added and toner manufacturing method (such as dispersion method) used, and is not particularly limited. However, the content of the charge controlling agent is from 0.1 to 10 parts by weight, and preferably from 0.2 to 5 parts by weight, per 100 parts by weight of the binder resin included in the toner. When the content is too high, the toner tends to have too large chargeability, and thereby the electrostatic force of a developing roller attracting the toner increases, resulting in deterioration of the fluidity of the toner and a decrease of the image density of toner images. The charge controlling agent can be dissolved or dispersed in an organic solvent after kneaded together with a master batch pigment and resin. In addition, the charge controlling agent can be directly dissolved or dispersed in an organic solvent when the toner constituents are dissolved or dispersed in the organic solvent.

(Formation of liquid droplets in an aqueous medium)

[0133] Formation of liquid droplets by emulsification in an aqueous medium is now described.

[0134] As mentioned above, in the emulsification process in the toner manufacturing method mentioned above of the present invention, an oil phase and an aqueous phase are continuously mixed and emulsified by an emulsification mechanism including an emulsification device having a stirring blade and an emulsion circulation route to form liquid droplets having a toner particle size for granulation. Subsequent to granulation, the emulsion is transferred to the next process. After the processes of solvent removal, filtration, washing, drying, etc., mother toner particles are formed.

[0135] Water can be used alone or in combination with a water soluble solvent as the aqueous medium for use in the present invention. Specific examples of such water soluble solvents include alcohols (such as methanol, isopropanol and ethylene glycol), dimethylformamide, tetrahydrofuran, cellosolves (such as methyl cellosolve) and lower ketones (such as acetone and methyl ethyl ketone).

[0136] The resins as toner binder for use in a toner composition are preferably polyester resins as mentioned above. Such toner binders can be manufactured, for example, by the following method:

(1) Heat the polyol (1) and the polycarbonic acid (2) to 150 to 280 °C in the presence of a known esterification catalyst such as tetra butoxy titanate and dibutyl tin oxide.
(2) Remove the generated water while decreasing the pressure if necessary to obtain a polyester having a hydroxyl group.
(3) React the polyester with the polyisocyanate (3) mentioned above at a temperature in the range of from 40 to 140 °C to obtain a prepolymer (A) having an isocyanate group.

[0137] In the method of manufacturing a toner of the present invention, as illustrated in Figure, an oil phase (A oil phase 7) in which a dissolved material or dispersed liquid in which an unmodified polyester resin, a colorant, and a release agent are dissolved or dispersed is mixed with an elongation agent, and an oil phase (B oil phase 8) in which a solution in which a prepolymer (A) having an isocyanate linkage is dissolved in an organic solvent is separately prepared are separately prepared. In the emulsification mechanism 4, emulsification is continuously performed while polymerization reaction proceeds.

By this polymerization reaction, a polyester (modified polyester resin) (i) modified by a urea linkage is obtained. A polyester (unmodified polyester resin) (ii) not modified by a urea linkage can be obtained in the same manner as in the polyester resin having a hydroxyl group. A solvent can be used to react (3), or (A) and (B).

[0138] Specific examples of usable solvents include compounds inactive to the isocyanates (3) such as aromatic solvents (e.g., toluene, xylene), ketones (e.g., acetone, methylethylketone, methylisobutylketone), esters (e.g., ethyl acetate), amides (e.g., dimethylformamide, dimethylacetamide) and ethers (e.g., tetrahydrofuran).

[0139] It is preferred to use a volatile organic solvent having a boiling point lower than 100 °C, which enables emulsification while lowering the viscosity of an oil phase containing a toner component and further which can dissolve, for example, the modified polyester resin (i) and the prepolymer (A) mentioned above.

[0140] Specific examples of such solvents include toluene, xylene, benzene, carbon tetrachloride, methylene chloride, 1,2-dichloroethane, 1,1,2-trichloroethane, trichloroethylene, chloroform, monochlorobenzene, dichloroethylidene, methyl acetate, ethyl acetate, methylethyl ketone, and methyl isobutyl ketone. These can be used alone or in combination. Especially, aromatic solvents, such as toluene and xylene, and halogenated hydrocarbons, such as methylene chloride, 1,2-dichloroethane, chloroform and carbon tetrachloride, are preferred. In addition, it is possible to further control the form of a toner by using a solvent soluble to an aqueous medium such as alcohol and water in combination. The content of such a solvent is preferably from 10 to 900 parts based on 100 parts of a toner component.

[0141] High speed shearing type dispersing devices are preferably used as the emulsification device equipped with a stirring blade provided to the emulsification mechanism mentioned above which disperses an oil phase in an aqueous medium for emulsification. Specific examples of such high speed shearing type dispersing devices include market products such as Ebara Milder (manufactured by Ebara Corporation) and TK pipeline homomixer (manufactured by Tokushukika Kogyo Co., Ltd.) .

[0142] When a high speed shearing type dispersing device is used, the number of rotation is controlled such that the stirring Reynolds number (stirring Re) during stirring the emulsion, shearing energy (E), etc., suitably satisfy the conditions mentioned above for formation of fine particles and coalescence of the fine particles.

[0143] The number of rotation is, for example, 1,000 to 30,000 rpm, and preferably from 5,000 to 20,000 rpm. The temperature during dispersion is from 0 to 150 °C (under pressure), and preferably from 10 to 98 °C. A high temperature is preferred because a dispersion body formed of a modified polyester resin (i) and a prepolymer (A) having an isocyanate group has a low viscosity so that dispersion is easy.

[0144] The content of the aqueous medium for use in emulsification in the emulsification mechanism is preferably from 50 to 2,000 parts by weight, and more preferably from 100 to 1, 000 parts by weight based on 100 parts of the toner component in an oil phase containing a urea-modified polyester resin (i) and a prepolymer (A). When the content of the aqueous medium is too small, the toner component is poorly dispersed so that liquid droplets having a target particle diameter are not obtained. Too large a content of the aqueous medium is not cost effective.

(Solid particulate dispersant)

[0145] The solid particulate dispersant dispersed in an aqueous medium in the present invention is present in a solid form hardly soluble to water in the aqueous medium and preferably has an average particle diameter of from 0.01 to 1 μm. Such solid particulate dispersants include inorganic solid particulate dispersants and organic solid particulate dispersants.

[0146] Specific preferred examples of such inorganic solid particulate dispersants include silica, alumina, titanium oxide, barium titanate, magnesium titanate, calcium titanate, strontium titanate, zinc oxide, tin oxide, quartz sand, clay, mica, sand-lime, diatom earth, chromium oxide, cerium oxide, red iron oxide, antimony trioxide, magnesium oxide, zirconium oxide, barium sulfate, barium carbonate, calcium carbonate, silicon carbide, and silicon nitride.

[0147] More preferred specific examples of the inorganic dispersants include tricalcium phosphate, calcium carbonate, colloidal titanium oxide, colloidal silica, and hydroxyapatite. Among them, hydroxyapatite which is synthesized by reacting natrium phosphate and calcium chlorinate in water under basic condition is especially preferred.

[0148] Specific preferred examples of such solid organic particulates include fine crystal of organic compounds having a low molecular weight, polymer particulates having a high molecular weight, such as polystyrene which is copolymerized with a monomer having a carboxyl group such as a methacrylic acid ester which can be prepared by a method such as soap free emulsion polymerization, suspension polymerization or dispersion polymerization, copolymers of a methacrylic acid ester or an acrylic acid ester, polycondensation resins such as silicone, benzoguanamine and nylon, and polymer particles of thermosetting resins.

[0149] As mentioned above, a solid particulate dispersant is dispersed in an aqueous medium in advance. To adjust the absorption property of the solid particulate dispersant to liquid droplets, other dispersants can be used in combination.

[0150] After the solid particulate dispersants are adjusted in water, an inorganic substance such as tricalcium phosphate soluble to an acid is made to be partially dissolved in advance by adding a suitable amount of an acid such as hydrochloric acid. The amount of the acid added is preferably from 0.01 to 10 %, and more preferably from 0.1 to 5 % based on the amount thereof by which the whole of the inorganic substance can be totally dissolved.

[0151] When a solid particulate dispersant soluble to an alkali such as polymer particulates copolymerized with methacrylic acid having one or more carboxyl groups is used, it is preferred to add a base such as sodium hydrate to partially dissolve the solid particulate dispersant. The amount of the acid added is preferably from 0.01 to 10 %, and more preferably from 0.1 to 5 % based on the amount thereof by which the whole of the inorganic substance can be totally dissolved.

[0152] Specific examples of the dispersant added during emulsification on a necessity basis include anionic surfactants such as alkylbenzene sulfonic acid salts, α-olefin sulfonic acid salts, and phosphoric acid salts; cationic surfactants such as amine salts (e.g., alkyl amine salts, aminoalcohol fatty acid derivatives, polyamine fatty acid derivatives and imidazoline), and quaternary ammonium salts (e.g., alkyltrimethyl ammonium salts, dialkyldimethyl ammonium salts, alkyldimethyl benzyl ammonium salts, pyridinium salts, alkyl isoquinolinium salts and benzethonium chloride) ; nonionic surfactants such as fatty acid amide derivatives, polyhydric alcohol derivatives; and ampholytic surfactants such as alanine, dodecyldi(aminoethyl)glycin, di(octylaminoethyle)glycin, and N-alkyl-N,N-dimethylammonium betaine.

[0153] By using a surfactant having a fluoroalkyl group, a good dispersion can be prepared even with an extremely small amount thereof. Specific examples of the anionic surfactants having a fluoroalkyl group include fluoroalkyl carboxylic acids having from 2 to 10 carbon atoms and their metal salts, disodium perfluorooctanesulfonylglutamate, sodium 3-{omega-fluoroalkyl(C6-C11)oxy}-1-alkyl(C3-C4) sulfonate, sodium
3-{omega-fluoroalkanoyl(C6-C8)-N-ethylamino}-1-propanesulfonate, fluoroalkyl(C11-C20) carboxylic acids and their metal salts, perfluoroalkylcarboxylic acids and their metal salts, perfluoroalkyl(C4-C12)sulfonate and their metal salts, perfluorooctanesulfonic acid diethanol amides, N-propyl-N-(2-hydroxyethyl)perfluorooctanesulfone amide, perfluoroalkyl (C6-C10)sulfoneamidepropyltrimethylammonium salts, salts of perfluoroalkyl(C6-C10)-N-ethylsulfonyl glycin, and monoperfluoroalkyl(C6-C16)ethylphosphates.

[0154] Market products can be used as the surfactant having a fluoroalkyl group.

[0155] Specific examples of such market products include SURFLON® S-111, S-112 and S-113, which are manufactured by Asahi Glass Co., Ltd.; FRORARD® FC-93, FC-95, FC-98 and FC-129, which are manufactured by Sumitomo 3M Ltd.; UNIDYNE® DS-101 and DS-102, which are manufactured by Daikin Industries, Ltd.; MEGAFACE® F-110, F-120, F-113, F-191, F-812 and F-833 which are manufactured by Dainippon Ink and Chemicals, Inc.; ECTOP® EF-102, 103, 104, 105, 112, 123A, 306A, 501, 201 and 204, which are manufactured by Tohchem Products Co., Ltd.; FUTARGENT® F-100 and F150 manufactured by Neos; etc.

[0156] Specific examples of the cationic surfactants having a fluoroalkyl group include primary, secondary or tertiary aliphatic amino acids, aliphatic quaternary ammonium salts (such as perfluoroalkyl(C6-C10)sulfoneamidepropyltrimethylammonium salts), benzalkonium salts, benzetonium chloride, pyridinium salts, imidazolinium salts, etc., all of which have a fluoroalkyl group Specific examples of commercially available products of these elements include SURFLON® S-121 (from Asahi Glass Co., Ltd.); FRORARD® FC-135 (from Sumitomo 3M Ltd.); UNIDYNE® DS-202 (from Daikin Industries, Ltd.); MEGAFACE® F-150 and F-824 (from Dainippon Ink and Chemicals, Inc.); ECTOP® EF-132 (from Tohchem Products Co., Ltd.); FUTARGENT® F-300 (from Neos); etc.

[0157] It is possible to adjust dispersed droplets using a polymeric protection colloid.

[0158] Specific examples of such polymeric protection colloids include homopolymers and copolymers prepared using monomers such as acids (e. g. , acrylic acid, methacrylic acid, α-cyanoacrylic acid, α -cyanomethacrylic acid, itaconic acid, crotonic acid, fumaric acid, maleic acid and maleic anhydride), acrylic monomers having a hydroxyl group (e.g., β-hydroxyethyl acrylate, β -hydroxyethyl methacrylate, β-hydroxypropyl acrylate, β-hydroxypropyl methacrylate, γ -hydroxypropyl acrylate,γ -hydroxypropyl methacrylate, 3-chloro-2-hydroxypropyl acrylate, 3-chloro-2-hydroxypropyl methacrylate, diethyleneglycolmonoacrylic acid esters, diethyleneglycolmonomethacrylic acid esters, glycerinmonoacrylic acid esters, N-methylolacrylamide and N-methylolmethacrylamide), vinyl alcohol and its ethers (e.g., vinyl methyl ether, vinyl ethyl ether and vinyl propyl ether) , esters of vinyl alcohol with a compound vinyl butyrate); acrylic amides (e.g, acrylamide, methacrylamide and diacetoneacrylamide) and their methylol compounds, acid chlorides (e.g., acrylic acid chloride and methacrylic acid chloride), and monomers or copolymers having a nitrogen atom or an heterocyclic ring having a nitrogen atom (e.g., vinyl pyridine, vinyl pyrrolidone, vinyl imidazole and ethylene imine).

[0159] In addition, polymers such as polyoxyethylene compounds (e.g., polyoxyethylene, polyoxypropylene, polyoxyethylenealkyl amines, polyoxypropylenealkyl amines, polyoxyethylenealkyl amides, polyoxypropylenealkyl amides, polyoxyethylene nonylphenyl ethers, polyoxyethylene laurylphenyl ethers, polyoxyethylene stearylphenyl esters, and polyoxyethylene nonylphenyl esters), and cellulose compounds such as methyl cellulose, hydroxyethyl cellulose and hydroxypropyl cellulose, can also be used as the polymeric protective colloid.

[0160] When a dispersant is used, the dispersant may remain on the surface of a toner particle. However, it is preferred in terms of toner charging that the remaining solid particulate dispersant is dissolved, washed with water, and removed after elongation and/or cross-linking reaction.

[0161] The emulsion (emulsion dispersion body) which has been made to be liquid droplets having a toner particle size in the emulsion process mentioned above is transferred to the next process. Thereafter, the organic solvent contained in the emulsion dispersion body is removed. To remove the organic solvent from the thus prepared emulsified dispersion, a method in which the emulsion is gradually heated to substantially completely evaporate the organic solvent included in the liquid droplets of the oil phase liquid can be used. Alternatively, a method in which the emulsion is sprayed in a dry atmosphere to remove the nonaqueous organic solvent in the liquid droplets, resulting in formation of particulates forming mother toner particles, and thereafter the aqueous dispersant in the dispersion is evaporated, can be used. Specific preferred examples of such a dry atmosphere in which the emulsified dispersion is sprayed include heated gases of air, nitrogen, carbon dioxide, combustion gas, etc. It is especially preferred to use various kinds of air streams heated to a temperature not lower than the boiling point of the solvent having the highest boiling point among the solvents used in the emulsion. Mother toner particles having desired properties can be rapidly prepared by performing this treatment using a spray dryer, a belt dryer, a rotary kiln, or the like.

[0162] The thus obtained dried mother toner particles can be mixed with other foreign particles such as a releasing agent, a charge controlling agent, a fluidizer agent and a colorant to form complex particles. These foreign particles can be fixed and fused on the surface of the complex toner particle to be prevented from detaching from the surface of the complex toner particle by imparting a mechanical impact on the complex toner particle.

[0163] Specific preferred examples of the method include: a method of applying an impact on a mixture with a blade rotating at a high speed and another method of colliding particles against each other or complex particles against a collision board.

[0164] Specific more preferred examples of such mechanical impact applicators include ONG MILL (manufactured by Hosokawa Micron Co., Ltd.), modified I TYPE MILL in which the air pressure for pulverizing is reduced (manufactured by Nippon Pneumatic Mfg. Co., Ltd.), HYBRIDIZATION SYSTEM (manufactured by Nara Machine Co., Ltd.), KRYPTRON SYSTEM (manufactured by Kawasaki Heavy Industries, Ltd.), and automatic mortars.

(Method of manufacturing dry toner)

[0165] After the mother toner particles are mixed with the other foreign particles, the resultant can be further adjusted as a dry toner, i.e., a developer. It is possible to add and mix inorganic particulates such as hydrophobic silica particulate powder to improve fluidity, preservability, developability and transferability.

[0166] In the process of mixing an external additive, a typical powder mixer is used. It is preferred that such a powder mixer is equipped with a jacket and the like to adjust the internal temperatures thereof. To change stresses on the external additive, the external additive may be added in separate times or in a stepwise manner. It is also possible to change the stress by varying the number of rotation, tumbling speed, and mixing time and temperature. For example, a method in which a strong stress is first applied and then a relatively weak stress is applied, or vice versa can be used. Specific preferred examples of mixing facilities include a v-type mixer, a rocking mixer, a LOEDIGE Mixer, a NAUTA mixer and a HENSCHEL mixer.

[0167] There are other various methods of controlling the form of the obtained toner particles as follows: a mechanical pulverization method including the steps of: (1) fusing/kneading the toner components including a toner binder and a colorant, (2) finely pulverizing the kneaded toner components and (3) mechanically controlling the form of finely pulverized toner components using a hybridizer and MECHANOFUSION; a spray drying method including the steps of: (1) dissolving and dispersing toner components in an solvent which can dissolve the toner binder; and (2) removing the solvent using a spray drying device to obtain a toner having a sphere form; and a method including the steps of: heating toner components in an aqueous medium to obtain a toner having a sphere form. The methods of controlling the form of the obtained toner particles are not limited thereto.

(External additive)

[0168] The colored particles obtained by the present invention may be mixed with an external additive to assist in improving the fluidity, developing property, and charging ability of the toner particles. Suitable preferred external additives include particulate inorganic materials.

[0169] Such particulate inorganic materials preferably have a primary particle diameter of from 5 nm to 2 μm, and more preferably from 5 nm to 500 nm. In addition, it is preferred that the specific surface area of such particulate inorganic materials measured by a BET method is from 20 to 500 m^2/g The content of the external additive is preferably from 0.01 to 5 % by weight, and more preferably from 0.01 to 2.0 % by weight, based on the total weight of the toner.

[0170] Specific examples of such inorganic particulate materials include silica, alumina, titanium oxide, barium titanate, magnesium titanate, calcium titanate, strontium titanate, zinc oxide, tin oxide, quartz sand, clay, mica, sand-lime, diatom earth, chromium oxide, cerium oxide, red iron oxide, antimony trioxide, magnesium oxide, zirconium oxide, barium sulfate, barium carbonate, calcium carbonate, silicon carbide, silicon nitride, etc.

[0171] In addition, particles of polymers such as polymers and copolymers of styrene, methacrylate esters, and acrylate esters, which can be prepared by a soap-free emulsion polymerization method, a suspension polymerization method or a dispersion polymerization method; polymers prepared by polycondensation polymerization, such as silicone resins, benzoguanamine resins and nylon resins; and thermosetting resins, can also be used as the external additive.

[0172] These materials for use as the external additive may be subject to a surface treatment to improve hydrophobic property, thereby preventing deterioration of the fluidity and charge properties of the toner even under high humidity conditions. Specific preferred examples of the hydrophobizing agents include silane coupling agents, silylation agents, silane coupling agents including a fluoroalkyl group, organic titanate coupling agents, aluminum coupling agents, silicone oils, modified silicone oils, etc.

[0173] Specific preferred examples of cleanability improving agents for use in removing developer remaining on an image bearing member and/or a primary transfer medium after transfer include fatty acids and their metal salts such as stearic acid, zinc stearate, and calcium stearate; and polymer particulates such as polymethyl methacrylate particulates and polystyrene particulates which are manufactured by a method such as a soap-free emulsion polymerization method. Such particulate polymers preferably have a relatively sharp particle diameter distribution and a volume average particle diameter of from 0.01 to 1 μm.

(Carrier for use in a two component developer)

[0174] The toner obtained by the manufacturing method of the present invention can be used in a two component developer such that the toner is mixed with a magnetic carrier. The weight ratio (T/C) of the toner (T) to the carrier (C) is preferably from 1/100 to 10/100.

[0175] Suitable carriers for use in such two component developers include any known carrier materials such as iron powders, ferrite powders, magnetite powders, magnetic resin carriers, which have a particle diameter of from about 20 μm to about 200 μm.

[0176] In addition, specific preferred examples of resins coating such carriers include amino resins such as urea-formaldehyde resins, melamine resins, benzoguanamine resins, urea resins, and polyamide resins, and epoxy resins. In addition, polyvinyl or polyvinylidene resins such as acrylic resins, polymethylmethacrylate resins, polyacrylonitirile resins, polyvinyl acetate resins, polyvinyl alcohol resins, polyvinyl butyral resins, polystyrene resins, styrene-acrylic copolymers, halogenated olefin resins such as polyvinyl chloride resins, polyester resins such as polyethyleneterephthalate resins and polybutyleneterephthalate resins, polycarbonate resins, polyethylene resins, polyvinyl fluoride resins, polyvinylidene fluoride resins, polytrifluoroethylene resins, polyhexafluoropropylene resins, vinylidenefluoride-acrylate copolymers, vinylidenefluoride-vinylfluoride copolymers, fluoroterpolymers such as a terpolymer of tetrafluoroethylene, vinylidenefluoride and other monomers including no fluorine atom, and silicone resins can be used.

[0177] If desired, an electroconductive powder may be included in the coating resin. Specific preferred examples of such electroconductive powders include metal powders, carbon blacks, titanium oxides, tin oxides, and zinc oxides. The average particle diameter of such electroconductive powders is preferably not greater than 1 μm. When the particle diameter is too small, it is hard to control the resistance thereof.

[0178] In addition, the toner of the present invention can also be used as a single component magnetic toner or a single component non-magnetic toner, in which a carrier is not contained.

[0179] By using an image forming method in which a latent electrostatic image formed on an image bearing member is developed with the toner of the present invention, and the toner developed image is transferred and fixed on a recording medium, especially a quality full color image can be reproduced while truly developing the latent electrostatic image.

[0180] In addition, when a process cartridge detachably attached to the main body of an image forming apparatus, which includes an image bearing member, a developing device a developer containing the toner of the present invention, and optionally at least one of a charging member and a cleaning device is used, especially a quality full color image can be reproduced while the latent electrostatic image formed on the image bearing member is truly developed.

[0181] Further, when an image forming apparatus includes the process cartridge mentioned above, it is possible to make the maintenance easy and the reliability high, and form quality images.

[0182] Having generally described preferred embodiments of this invention, further understanding can be obtained by reference to certain specific examples which are provided herein for the purpose of illustration only and are not intended to be limiting. In the descriptions in the following examples, the numbers represent weight ratios in parts, unless otherwise specified.

EXAMPLES

[0183] The present invention will be specifically described in detail but is not limited thereto.

Example 1

[0184] An emulsion dispersant was prepared by mixing an oil phase (formed of the A oil phase and the B oil phase) and an aqueous phase using a granulation device having the structure described in Figure in Detailed Description to granulate toner particles. After separately adjusting the A oil phase, the B oil phase, and the aqueous phase for granulation as described later, solvent removal, filtration, washing and drying were performed to obtain mother toner particles.
[0185] First, materials to adjust [A oil phase] such as an unmodified polyester resin formed of a low molecular weight polyester, a master batch (MB), and a ketimine were prepared.

<Synthesis of unmodified polyester resin formed of low molecular weight polyester>

[0186] [Unmodified polyester resin 1] was obtained as follows:
(1) Place the following components in a reacting container equipped with a condenser, a stirrer and a nitrogen introducing tube and react for 8 hours at 230 °C under normal pressure:

Adduct of bisphenol A with 2 moles of ethylene oxide	229 parts
Adduct of bisphenol A with 3 moles of propylene oxide	529 parts
Terephtalic acid	208 parts
Adipic acid	46 parts
Dibutyl tin oxide	2 parts

(2) React the resultant for 5 hours under a reduced pressure of from 10 to 15 mmHg, and
(3) Add 44 parts of trimellitic anhydride to the reacting container and react for 2 hours at 180 °C at normal pressure.
[0187] [Unmodified polyester resin 1]. had a number average molecular weight of 2,500, a weight average molecular weight of 6,700, a glass transition temperature (Tg) of 43 °C, and an acid value of 25.
[Unmodified polyester resin 1] represents an unmodified polyester not modified by urea linkage as defined in the Detailed Description mentioned above.

<Synthesis of master batch>

[0188] [Master batch 1] was obtained as follows:

(1) Mix 1,200 parts of water, 540 parts of carbon black (Printe x 35, manufactured by Deggsa Co., Ltd.), and 1,200 parts of a polyester resin with HENSCHEL mixer (manufactured by Mitsui Mining Co., Ltd.).
(2) Mix and knead the mixture with a two-axis roll at 150 °C for 30 minutes, and
(3) Subsequent to flatting and cooling down, pulverize the resultant with a pulverizer.

[0189] Carbon black had a DBP oil absorption amount of 42 ml/100 mg and a PH of 9.5.

<Synthesis of ketimine>

[0190] [Ketimine compound 1] was obtained as follows:

(1) Place 170 parts of isophoron diamine and 75 parts of methyletyl ketone in a reacting container equipped with a stirrer and a thermometer.
(2) React these at 50 °C for 5 hours.

[0191] [Ketimine compound 1] had an amine value of 418. Ketimine serves as an elongation agent for a polyester prepolymer having an isocyanate groups of the B oil phase described below.

[Preparation of A oil phase (black)]

[0192] Using [Unmodified polyester resin 1] , [Master batch 1] , and [Ketimine compound 1] prepared as described above, A oil phase were prepared as follows:
(1) Place the following components in a reacting container equipped with a stirrer and a thermometer:

[Unmodified polyester resin 1]	378 parts
Carnauba wax	110 parts
CCA (salicylic acid metal complex E-84 manufactured by Orient Chemical Industries, Ltd.	22 parts
Ethyl acetate	947 parts

(2) Raise the temperature to 80 °C during stirring and maintain 80 °C for 5 hours.
(3) Cool down the resultant to 30 °C in one hour.
(4) Place and mix 500 parts of [master batch 1] and 500 parts of ethyl acetate in a container for one hour to obtain [material solution 1] .
(5) Move to 1, 324 parts of [material solution 1] to a container and disperse carbon black and wax under the condition of liquid transfer speed of 1 kg/hour, disc circumference speed of 6 m/sec, 80 volume % filling of 0.5 mm zirconia beads, and 3 pass using a beads mill (ULTRAVISCOMILL, manufactured by Aimex Co., Ltd.).
(6) Add 1,324 parts of 65 % ethyl acetate solution of [Unmodified polyester resin 1] and perform 1 pass using the beads mill under the condition mentioned above to obtain [Dye wax dispersion liquid

1] with the solid portion density of [Dye wax dispersion liquid

1] being 50 % (130 °C, 30 minutes).

(7) Place 749 parts of [Dye wax dispersion liquid 1] and 2.9 parts of [Ketimine compound 1] in a container.
(8) Mix [Dye wax dispersion liquid 1] and [Ketimine compound 1] using a Homodisper (manufactured by Tokushu Kika Kogyo Co., Ltd.) at 5,000 rpm for one minute to obtain [A oil phase (black) 1] .

<Synthesis of prepolyester polymer having an isocyanate group>

[0193] Next, a polyester prepolymer having an isocyanate group was prepared for preparation of [B oil phase] .
[0194] [Intermediate polyester 1] was obtained as follows:
(1) Place the following components in a reacting container equipped with a condenser, a stirrer and a nitrogen introducing tube and react for 8 hours at 230 °C under normal pressure:

Adduct of bisphenol A with 2 moles of ethylene oxide	682 parts
Adduct of bisphenol A with 2 moles of propylene oxide	81 parts
Terephtalic acid	283 parts
Trimellitic anhydride	22 parts
Dibutyl tin oxide	2 parts

(2) React the resultant for 5 hours under a reduced pressure of from 10 to 15 mmHg.
[0195] [Intermediate polyester 1] had a number average molecular weight of 2,100, and a weight average molecular weight of 9,500, a glass transition temperature (Tg) of 55 °C, an acid value of 0.5, and a hydroxyl value of 51.
[0196] Next, [Prepolymer 1] was obtained by placing 410 parts of [Intermediate polyester 1], 89 parts of isophoron diisocyanate, and 500 parts of ethyl acetate in a reacting container equipped with a condenser, a stirrer and a nitrogen introducing tube and reacting at 100 °C for 5 hours. Isolated isocyanate weight % of [Prepolymer 1] was 1.53 %. This [Prepolymer 1] was determined to be [B oil phase 1] .

<Preparation of aqueous phase>

[0197] Next, [Aqueous phase] was prepared as follows:
(1) Place the following components in a reacting container equipped with a stirrer and a thermometer and stir 400 rotation/min for 15 minutes to obtain a white emulsion:

Water	683 parts
Sodium salt of sulfuric acid ester of an adduct of methacrylic acid with ethylene oxide (Eleminol RS-30 manufactured by Sanyo Chemical Industries, Ltd.)	11 parts
Styrene	83 parts
Methacrylic acid	83 parts

Table continued

Butyl acrylate	110 parts
Ammonium persulfate	1 part

(2) Heat the white emulsion to raise the temperature of the system to 75 °C and react for 5 hours.
(3) Further, add 30 parts of 1 % ammonium persulfate aqueous solution and age the resultant for 5 hours at 75 °C to obtain an aqueous dispersion liquid [Particulate dispersion liquid 1] of a vinyl based resin (copolymer of styrene - methacrylic acid - butyl acrylate - sodium salt of sulfuric acid ester of an adduct of methacrylic acid with ethylene oxide. The volume average particle diameter of [Particulate dispersion liquid 1] measured by LA-920 was 105 nm.
(4) Partially dry [Particulate dispersion liquid 1] to isolate the resin portion.
(5) The resin portion had a glass transition temperature (Tg) of 59 °C and a weight average molecular weight of 150,000.
(6) Mix and stir the following components to obtain a milky-white liquid, which was defined to be [Aqueous phase 1] :

[Particulate dispersion liquid 1]	83 parts
Water	990 parts
48.5 % aqueous solution of dodecyl diphenyl ether disulfonic sodium (Eleminol MON-7, manufactured by Sanyo Chemical Industries, Ltd.)	37 parts
Ethyl acetate	90 parts

<Granulation by emulsification>

[0198]

(1) Transfer [A oil phase (black) 1] , [B oil phase 1] , and [Aqueous phase 1] obtained above from each raw material supplying tank illustrated in Figure to the emulsification mechanism 4 to perform emulsification. In this regard, [A oil phase 1] and [B oil phase 1] were mixed in advance at the static mixer (STM) 10 before mixed with [Aqueous phase 1] .
(2) The mixing ratio of [A oil phase (black) 1] , [B oil phase 1] , and [Aqueous phase 1] during emulsification was 60.4 parts, 7.4 parts, and 101.6 parts based on weight.

[0199] In addition, the conditions for the emulsification device 2 and the emulsion circulation route 3 forming the emulsification mechanism 4 were as follows.

<Emulsification conditions>

[0200] Stirring Reynolds number (stirring Re): 5118; Shearing energy (E) : 1813; Unit total energy (e) : 4.0 x 10^6; the flow speed (v) of the emulsion in the emulsion circulation route 3; 1.89 m/s; Flow Reynolds number (Flow Re) in the pipe: 851; fluxion energy loss (Eloss) of the emulsion: 125 J/kg; the number of the right angle elbows: 4; Inner diameter (D) of the pipe forming the emulsion circulation route 3: 0.0225 m; Surface roughness (Ra) of the inner side of the pipe forming the emulsion circulation route 3: 0.5; Variation ratio of the inner diameter of the pipe forming the emulsion circulating route 3: 1.0 to 1.2; The ratio (S)/(D) of the length (S) of the straight portion of the pipe between the right angle elbows to the inner diameter (D) of the pipe: 20; and discharging condition of emulsion: via a right angle elbow.

[0201] Under the conditions mentioned above, emulsification was continuously performed to obtain liquid droplets having a toner particle size. Thereafter, the emulsion was transferred to the next process and processed as follows to obtain a toner.

[0202] The solvent removing process of removing the organic solvent contained in the emulsion transferred to the next process was performed as follows:

(1) Raise the temperature of the emulsion to 45 °C.
(2) Remove the organic solvent under atmospheric pressure (101.3 kPa) with the outer circumference speed of the stirring blade of 10.5 m/s.
It took 20 hours to remove the organic solvent. Subsequent to solvent removal, filtration, washing and drying were performed to obtain mother toner particles. Then, toner (black toner) of Example 1 was obtained as follows:

(1) Place 100 parts of the mother toner particle obtained and 0.25 parts of a charge controlling agent (Bontron E-84, manufactured by Orient Chemical Industries, Ltd.) in a Q type mixer (manufactured by Mitsui Mining Co., Ltd.)

(2) Set the circumference speed of the turbine type blade to 50 m/sec and operate the blade in a cycle of two-minute operation and one minute break.
(3) Repeat the cycle 5 times so that the total of operation time was 10 minutes.
(4) Add 0.5 parts of hydrophobic silica (H2000, manufactured by Clariant Japan K.K.).
(5) Operate the turbine type blade in a cycle of 30 second mixing and one minute break.
(6) Repeat the cycle 5 times.
(7) Further, mix 0.5 parts of hydrophobic silica and 0.5 parts of hydrophobized titanium oxide with the resultant using HENSCHEL mixer.
(8) Remove coarse particles with a screen having an opening mesh of 37 μm.

[0203] The emulsification conditions mentioned above for the toner manufacturing are separately shown in Table 1 based on the factors of forming fine particles of liquid droplets and the factors of coalescence of the fine particles. The discharging condition of the emulsion is shown together in Table 1. In addition, the emulsification particle size (Dv, Dv/Dn), and the mother toner particle diameter (hereinafter referred to as the toner particle diameter) (Dv, Dv/Dn) are shown in Table 2 below. In Table 2, the evaluation results of the fine line repeoducibility described below are also shown.

[Evaluation of fine line reproducibility]

[0204] Fine line reproducibility was evaluated using a developer containing the toner of Example 1 in a remodeled marketed color photocopier (imagio color 5000, manufactured by Ricoh Co.) taking an intermediate transfer system from which the oil fixing portion is removed.

[0205] A running was performed for evaluation using 6000 paper manufactured by Ricoh Co. with a printing ratio having an image occupation ratio of 7 %. The fine line portion of the 10th image and the 30,000th image were compared with that of an original. The images were observed by an optical microscope with a magnifying power of 100 to compare the level of omission of the fine line with that of the fine line of 5-ranked samples to scale the results from 1 to 5. In the 1 to 5 ranking system, 5 represented the best. Acceptable scale in the ranking was not less than 3.5. The results are shown in Table 2.

Example 2

[0206] Toner of Example 2 was prepared in the same manner as described in Example 1, where the emulsion was transferred to the next process and solvent removal, filtration, washing and drying were performed to obtain mother toner particles after continuous emulsification was performed to obtain liquid droplets having a toner particle size, except that the emulsification conditions of Example 1 were changed to the following.

<Emulsification condition>

[0207] Stirring Reynolds number (stirring Re) : 13269; Shearing energy (E) : 655; Unit total energy (e) : 2.6 x 10^6; the flow speed (v) of the emulsion in the emulsion circulation route 3; 1.92 m/s; Flow Reynolds number (Flow Re) in the pipe: 4608; Fluxion energy loss (Eloss) of the emulsion: 152 J/kg; the number of the right angle elbows: 5; Inner diameter (D) of the pipe forming the emulsion circulation route 3: 0.12 m; Surface roughness (Ra) of the inner side of the pipe forming the emulsion circulation route 3: 0.91; Variation ratio of the inner diameter of the piper forming the emulsion circulating route 3: 1.4; the ratio (S) / (D) of the length (S) of the straight portion of the pipe between the right angle elbows to the inner diameter (D) of the pipe: 5; and discharging condition of emulsion: via a right angle elbow.

[0208] The emulsification conditions are separately shown in Table 1 based on the factors of forming fine particles of liquid droplets and factors of coalescence of the fine particles as in Example 1. The discharging condition of the emulsion is shown in Table 1 in the same manner as in Example 1. Inaddition, the emulsification particle size and the toner particle diameter are shown in Table 2 below.

[0209] The evaluation results with regard to fine line reproducibility using a developer containing the toner of Example 2 are shown in Table 2 below in the same manner as in Example 1.

Example 3

[0210] Toner of Example 3 was prepared in the same manner as described in Example 2, where the emulsion was transferred to the next process and solvent removal, filtration, washing and drying were performed to obtain mother toner particles after continuous emulsification was performed to obtain liquid droplets having a toner particle size, except that the emulsification conditions of Example 2 were changed to the following. <Emulsification condition>

[0211] Fluxion energy loss (Eloss) of the emulsion: 130 J/kg; The number of the right angle elbows: 3.

[0212] The emulsification conditions are separately shown in Table 1 based on the factors of forming fine particles of liquid droplets and the factors of coalescence of the fine particles as in Example 1. In addition, the emulsification particle size and the toner particle diameter are shown in Table 2 below.

[0213] The evaluation results with regard to fine line reproducibility using a developer containing the toner of Example 3 are shown in Table 2 below in the same manner as in Example 1.

Example 4

[0214] Toner of Example 4 was prepared in the same manner as described in Example 3, where the emulsion was transferred to the next process and solvent removal, filtration, washing and drying were performed to obtain mother toner particles after continuous emulsification was performed to obtain liquid droplets having a toner particle size, except that the emulsification conditions of Example 3 were changed to the following.

<Emulsification conditions>

[0215] Fluxion energy loss (Eloss) of the emulsion: 98 J/kg; Inner diameter (D) of the pipe forming the emulsion circulation route 3: 0. 053 m.

[0216] The emulsification conditions are separately shown in Table 1 based on the factors of forming fine particles of liquid droplets and the factors of coalescence of the fine particles as in Example 1. The discharging condition of the emulsion is shown in Table 1 in the same manner as in Example 1. In addition, the emulsification particle size and the toner particle diameter are shown in Table 2 below.

[0217] The evaluation results with regard to fine line reproducibility using a developer containing the toner of Example 4 are shown in Table 2 below in the same manner as in Example 1.

Example 5

[0218] Toner of Example 5 was prepared in the same manner as described in Example 4, where the emulsion was transferred to the next process and solvent removal, filtration, washing and drying were performed to obtain mother toner particles after continuous emulsification was performed to obtain liquid droplets having a toner particle size, except that the emulsification conditions of Example 4 were changed to the following.

<Emulsification condition>

[0219] Fluxion energy loss (Eloss) of the emulsion: 82 J/kg; Surface roughness (Ra) of the inner side of the pipe forming the emulsion circulation route 3: 0.5.

[0220] The emulsification conditions are separately shown in Table 1 based on the factors of forming fine particles of liquid droplets and the factors of coalescence of the fine particles as in Example 1. The discharging condition of the emulsion is shown in Table 1 in the same manner as in Example 1. In addition, the emulsification particle size and the toner particle diameter are shown in Table 2 below.

[0221] The evaluation results with regard to fine line reproducibility using a developer containing the toner of Example 5 are shown in Table 2 below in the same manner as in Example 1.

Example 6

[0222] Toner of Example 6 was prepared in the same manner as described in Example 5, where the emulsion was transferred to the next process and solvent removal, filtration, washing and drying were performed to obtain mother toner particles after continuous emulsification was performed to obtain liquid droplets having a toner particle size, except that the emulsification conditions of Example 5 were changed to the following.

<Emulsification conditions>

[0223] Fluxion energy loss (Eloss) of the emulsion: 82 J/kg; Variation ratio of the inner diameter of the piper forming the emulsion circulating route 3: 1.0.

[0224] The emulsification conditions are separately shown in Table 1 based on the factors of forming fine particles of liquid droplets and the factors of coalescence of the fine particles as in Example 1. The discharging condition of the emulsion is shown in Table 1 in the same manner as in Example 1. In addition, the emulsification particle size and the toner particle diameter are shown in Table 2 below.

[0225] The evaluation results with regard to fine line reproducibility using a developer containing the toner of Example

6 are shown in Table 2 below in the same manner as in Example 1.

Example 7

[0226] Toner of Example 7 was prepared in the same manner as described in Example 6, where the emulsion was transferred to the next process and solvent removal, filtration, washing and drying were performed to obtain mother toner particles after continuous emulsification was performed to obtain liquid droplets having a toner particle size, except that the emulsification conditions of Example 6 were changed to the following.

<Emulsification condition>

[0227] Fluxion energy loss (Eloss) of the emulsion: 61 J/kg; The ratio (S) / (D) of the length (S) of the portion of the pipe between the right angle elbows to the inner diameter (D) of the pipe: 10.2.

[0228] The emulsification conditions are separately shown in Table 1 based on the factors of forming fine particles of liquid droplets and the factors of coalescence of the fine particles as in Example 1. The discharging condition of the emulsion is shown in Table 1 in the same manner as in Example 1. In addition, the emulsification particle size and the toner particle diameter are shown in Table 2 below.

[0229] The evaluation results with regard to fine line reproducibility using a developer containing the toner of Example 7 are shown in Table 2 below in the same manner as in Example 1.

Example 8

[0230] Toner of Example 8 was prepared in the same manner as described in Example 7, where the emulsion was transferred to the next process and solvent removal, filtration, washing and drying were performed to obtain mother toner particles after continuous emulsification was performed to obtain liquid droplets having a toner particle size, except that the emulsification conditions of Example 7 were changed to the following.

<Emulsification condition>

[0231] Fluxion energy loss (Eloss) of the emulsion: 42 J/kg; Discharging condition of emulsion: not via a right angle elbow.

[0232] The emulsification conditions are separately shown in Table 1 based on the factors of forming fine particles of liquid droplets and the factors of coalescence of the fine particles as in Example 1. The discharging condition of the emulsion is shown in Table 1 in the same manner as in Example 1. In addition, the emulsification particle size and the toner particle diameter are shown in Table 2 below.

[0233] The evaluation results with regard to fine line reproducibility using a developer containing the toner of Example 8 are shown in Table 2 below in the same manner as in Example 1.

Comparative Example 1

[0234] Toner of Comparative Example 1 was prepared in the same manner as described in Example 1, where the emulsion was transferred to the next process and solvent removal, filtration, washing and drying were performed to obtain mother toner particles after continuous emulsification was performed to obtain liquid droplets having a toner particle size, except that the emulsification conditions of Example 1 were changed to the following.

<Emulsification condition>

[0235] Stirring Reynolds number (stirring Re) : 1866; Shearing energy (E) : 241; Unit total energy (e): 2.8×10^5; the flow speed (v) of the emulsion in the emulsion circulation route 3; 2.12 m/s; Flow Reynolds number (Flow Re) in the pipe: 954; fluxion energy loss (Eloss) of the emulsion: 95 J/kg; the number of the right angle elbows: 3; Inner diameter (D) of the pipe forming the emulsion circulation route 3: 0.0225 m; Surface roughness (Ra) of the inner side of the pipe forming the emulsion circulation route 3: 0.72; variation ratio of the inner diameter of the piper forming the emulsion circulating route 3: 1.0; the ratio (S) / (D) of the length (S) of the portion of the pipe between the right angle elbows to the inner diameter (D) of the pipe: 11.5; and discharging condition of emulsion: not via a right angle elbow.

[0236] The emulsification conditions are separately shown in Table 1 based on the factors of forming fine particles of liquid droplets and the factors of coalescence of the fine particles as in Example 1. The discharging condition of the emulsion is shown in Table 1 in the same manner as in Example 1. In addition, the emulsification particle size and the toner particle diameter are shown in Table 2 below.

[0237] The evaluation results with regard to fine line reproducibility using a developer containing the toner of Comparative Example 1 are shown in Table 2 below in the same manner as in Example 1.

Comparative Example 2

[0238] Toner of Comparative Example 2 was prepared in the same manner as described in Example 1, where the emulsion was transferred to the next process and solvent removal, filtration, washing and drying were performed to obtain mother toner particles after continuous emulsification was performed to obtain liquid droplets having a toner particle size, except that the emulsification conditions of Example 1 were changed to the following.

<Emulsification condition>

[0239] Stirring Reynolds number (stirring Re): 2710; Shearing energy (E) : 508; Unit total energy (e) : 3.1 x 10^5; the flow speed (v) of the emulsion in the emulsion circulation route 3; 2.7 m/s; Flow Reynolds number (Flow Re) in the pipe: 1215; fluxion energy loss (Eloss) of the emulsion: 160 J/kg; the number of the right angle elbows: 5; Inner diameter (D) of the pipe forming the emulsion circulation route 3: 0.0225 m; Surface roughness (Ra) of the inner side of the pipe forming the emulsion circulation route 3: 0.26; variation ratio of the inner diameter of the piper forming the emulsion circulating route 3: 0.8 to 1.0; the ratio (S) / (D) of the length (S) of the portion of the pipe between the right angle elbows to the inner diameter (D) of the pipe: 10.2; and discharging condition of emulsion: via a pipe having a different diameter (1D to 1.2D).

[0240] The emulsification conditions are separately shown in Table 1 based on the factors of forming fine particles of liquid droplets and the factors of coalescence of the fine particles as in Example 1. The discharging condition of the emulsion is shown in Table 1 in the same manner as in Example 1. In addition, the emulsification particle size and the toner particle diameter are shown in Table 2 below.

[0241] The evaluation results with regard to fine line reproducibility using a developer containing the toner of Comparative Example 2 are shown in Table 2 below in the same manner as in Example 1.

[Table 1]

Example	Factors involving forming fine particles			Factors involving coalescence of fine particles								Dis-charging condition of emulsion
	Stirring Re	Shearing energy (E)	Unit total energy (e)	Flow speed (v) of emulsion	Flow Re	Fluxion energy loss (Eloss)	Number of the right angle elbows	Inner diameter (D) of the pipe	Surface roughness (Ra) of the inner side of the pipe	Variation ratio of the inner diameter (D)	The length (S) of the pipe /the inner diameter (D)	
	(*1)	(*2)	(*3)	m/sec	(*4)	J/kg		m	-	-	-	-
Example 1	5118	1813	4.0×10^6	1.89	851	125	4	0.0225	0.50	1.0 to 1.2	20	Via right angle elbow
Example 2	13269	655	2.6×10^6	1.92	4608	152	5	0.120	0.91	1.4	5	Via right angle elbow
Example 3	13269	655	2.6×10^6	1.92	4608	130	3	0.120	0.91	1.4	5	Via right angle elbow
Example 4	13269	655	2.6×10^6	1.92	2035	98	3	0.053	0.91	1.4	5	Via right angle elbow
Example 5	13269	655	2.6×10^6	1.92	2035	82	3	0.053	0.50	1.4	5	Via right angle elbow
Example 6	13269	655	2.6×10^6	1.92	2035	70	3	0.053	0.50	1.0	5	Via right angle elbow
Example 7	13269	655	2.6×10^6	1.92	2035	61	3	0.053	0.50	1.0	10.2	Via right angle elbow
Example 8	13269	655	2.6×10^6	1.92	2035	42	3	0.053	0.50	1.0	10.2	Not via right angle elbow
Comparative Example 1	1866	241	2.8×10^6	2.12	954	95	3	0.0225	0.72	1.0	11.5	Not via right angle elbow

Comparative Example 2	2710	508	3.1 × 10^6	2.70	1215	160	5	0.0225	0.92	1.5	10.2	Via pipe having a different diameter 1.0 to 1.2

(*1) unit represented by the relationship (1) in the specification

(*2) unit represented by the relationship (2) in the specification

(*3) unit represented by the relationship (3) in the specification

(*4) unit represented by the relationship (4) in the specification

[Table 2]

Example	Emulsification particle diameter		Toner particle diameter		Image evaluation (fine line reproducibility)
	Volume average particle diameter (Dv)	Ratio (Dv/Dn) of volume average particle diameter (Dv) to number average particle diameter (Dn)	Volume average particle diameter (Dv)	Ratio (Dv/Dn) of volume average particle diameter (Dv) to number average particle diameter (Dn)	
	(μm)	-	(μm)	-	Evaluation (scaling of 1 to 5)
Example 1	3.82	1.35	3.90	1.36	4.5
Example 2	6.21	1.41	6.25	1.39	3.5
Example 3	6.19	1.28	6.20	1.29	3.5
Example 4	6.25	1.25	6.24	1.26	4.0
Example 5	6.05	1.20	6.10	1.21	4.0
Example 6	6.09	1.18	6.08	1.20	4.5
Example 7	6.15	1.17	6.20	1.18	5.0
Example 8	6.03	1.16	6.10	1.14	5.0
Comparative Example 1	12.50	2.61	12.55	2.60	2.5

Comparative Example 2	4.65	1.32	4.72	1.27	3.0

[0242] Judging from the test results on fine line reproducibility shown above, it is found that, when Dv and Dv/Dn satisfy the target value, the evaluation results are good.

[0243] That is, it is found from the test results that there is the following tendency. In the experiments, while the emulsification particle diameter (Dv) (volume average particle diameter) of Example 1 is 3.82 μm, the emulsification particle diameters (Dv) of Examples 2 to 8 are around 6 μm. Therefore, it can be inferred that, since the factors involved in the formation of fine particles are almost the same, the particle diameter does not function as a major factor. However, the particle size distribution (Dv/Dn) varies according as the values involved in the coalescence of the fine particles change. As the number of the factors set in the target range of the coalescence of the fine particles increase, the particle size distribution (Dv/Dn) becomes better. In addition, when the emulsion is transferred via a right angle elbow or a pipe having a different diameter as the discharging condition, it is confirmed that the particle size distribution (Dv/Dn) of the toner particle size to the emulsion particle diameter tends to slightly deteriorate. The particle size distribution is most sharp in Example 8, in which all the factors involved in the formation of fine particles and the coalescence of the fine particles are set in the target range. Therefore, the image evaluation thereof shows a good result, i.e., 5.0. On the other hand, since stirring Re and shearing energy (E) of Comparative Example 1 are not set in the target range, the emulsion particle diameter thereof tends to increase. In addition, in Comparative Example 2, since shearing energy (E) is within the target range, its particle size achieves the target. However, its particle size distribution deteriorates due to other factors which are not set in the target range of the coalescence of the fine particles factors. Therefore, the image evaluation thereof is low.

[Effects of the Invention]

[0244] According to the manufacturing methods of the present invention, conditions such as the structural conditions of the emulsion mechanism forming a granulation device, the conditions of stirring an emulsion, the conditions of circulating an emulsion, the conditions of discharging an emulsion from the emulsion mechanism are regulated to suitably control both of the shearing conditions of forming fine particles and the coalescence conditions of the fine particles. Therefore, by balancing each condition, a toner having a stable particle diameter (volume average particle diameter) satisfying a target value, and a sharp particle size distribution can be manufactured in an easy and efficient manner. According to the manufacturing methods of the present invention; a toner which can truly develop a latent image to reproduce a quality full color image can be obtained, and it is possible to provide an image forming method, a process cartridge and an image forming apparatus by which high grade and quality imaged can be obtained when such a toner is used.

[0245] This document claims priority and contains subject matter related to Japanese Patent Application No. 2004-246852, filed on 26 August 2004.

Claims

1. A method of manufacturing a toner, comprising:

    forming an emulsion by mixing and stirring an aqueous phase and an oil phase, the oil phase comprising one of a dissolved material and a dispersed material which comprises an organic phase comprising at least one of a resin, a resin precursor, and a monomer, in an emulsification mechanism comprising an emulsification circulation route comprising pipes comprising a main portion, and an emulsification device located in the middle of the emulsification circulation route, by a stirring blade provided in the emulsification device,
    wherein the stirring Reynolds number (stirring Re) during stirring is from 3, 000 to 15, 000 when calculated based on the following relationship (1):
    stirring Reynolds number (stirring Re) = $\rho n d^2/\mu$ (1),
    wherein ρ represents the density of the emulsion (kg/m^3), n represents the rotation number (rps) of the stirring blade, d represents the blade diameter (m) of the stirring blade, and μ represents the viscosity (Pa s) of the emulsion.

2. The method of manufacturing a toner according to Claim 1, wherein the pipes have a straight portion.

3. The method of manufacturing a toner according to Claim 1 or 2, wherein the emulsion circulation route has one to four right angle elbows.

4. The method of manufacturing a toner according to Claim 3, wherein the ratio ((S) / (D)) of the length (S) of the straight portion between the right angle elbows to the inner diameter (D) of the emulsion circulation route satisfies the following relationship:

$$(S)/(D) > 10.$$

5. The method of manufacturing a toner according to Claim 3 or 4, wherein the emulsion is discharged from the emulsion circulation route without passing through any one of the right angle elbows.

6. The method of manufacturing a , toner according to any one of Claims 1 to 5, wherein the pipes have the same diameter.

7. The method of manufacturing a toner according to any one of Claims 1 to 6, wherein one of the resin and the resin precursor comprises at least two polymers having a different molecular weight.

8. The method of manufacturing a toner according to Claim 7, wherein the two polymers having a different molecular weight are a modified polyester resin modified by a urea linkage, and an unmodified polyester resin.

9. The method of manufacturing a toner according to any one of Claims 1 to 8, wherein the aqueous phase is an aqueous medium comprising a solid particulate dispersant.

10. The method of manufacturing a toner according to any one of Claims 1 to 9, wherein the shearing energy (E) generated by the rotation of the stirring blade is from 400 to 2,000 based on the following relationship (2):

$$E = (n \times 60)^3 \times d^5/Q \qquad (2),$$

wherein n represents the rotation number (rps) of the stirring blade, d represents the blade diameter (m) of the stirring blade, and Q represents the flow amount (L/min) in the emulsion circulation route.

11. The method of manufacturing a toner according to any one of Claims 1 to 10, wherein the total energy of the emulsion received from the emulsification device based on unit total energy (e) per material feed unit flow amount while the emulsion is circulated and stayed in the emulsion circulation route is from 1×10^6 to 5×10^6 based on the following relationship (3):

$$e = [(n \times 60)^3 \times d^5 \times Q]/F^2 \qquad (3),$$

wherein n represents a rotation number (rps) of the stirring blade, d represents the blade diameter (m) of the stirring blade, Q. represents the flow amount (L/min) in the emulsion circulation route, and F represents the material feed amount (kg/min).

12. The method of manufacturing a toner according to any one of Claims 1 to 11, wherein a flow speed (v) of the emulsion in the emulsion circulation route is from 0.5 to 3 m/sec.

13. The method of manufacturing a toner according to any one of Claims 1 to 12, wherein the pipes forming the emulsion circulation route have an inner diameter (D) of from 0.02 to 0.10 m.

14. The method of manufacturing a toner according to any one of Claims 1 to 13, wherein the emulsion has a flow Reynolds number (flow Re) of from 500 to 4,000 at the straight portion of the pipes forming the emulsion circulation route based on the following relationship (4) :

$$\text{Flow Reynolds number} = \rho v D/\mu \qquad (4),$$

wherein ρ represents the density of the emulsion (kg/m^3), v represents the flow speed (m/s) of the emulsion, D represents an inner diameter (m) of the pipe, and μ represents the viscosity (Pa s) of the emulsion.

15. The method of manufacturing a toner according to any one of Claims 1 to 14, wherein the surface roughness (Ra) of the inner side of the pipes forming the emulsion circulation route is less than 0.8.

16. The method of manufacturing a toner according to any one of Claims 1 to 15, wherein the variation ratio of the inner diameter of the pipes is from 0.8 to 1.2 when the inner diameter of the main portion of the pipes is set to 1.

17. The method of manufacturing a toner according to Claim 16, wherein, in the variation ratio of an inner diameter of the pipes, the flow energy loss (E loss) of the emulsion generated is from 20 to 100 J/kg.

18. A toner, comprising:

toner particles having a volume average particle diameter (Dv) of from 3 to 10 μm,

wherein the toner particles are prepared by the method of manufacturing a toner of any one of Claims 1 to 17.

19. The toner according to Claim 18, wherein the value obtained by dividing the volume average particle diameter (Dv) of the toner with the number average particle diameter (Dn) thereof is 1.05 to 1.25.

20. An image forming method, comprising:

developing a latent electrostatic image formed on an image bearing member with the toner of Claim 18 or 19;
transferring the toner-developed image on a recording medium; and
fixing the transferred.image on the recording medium.

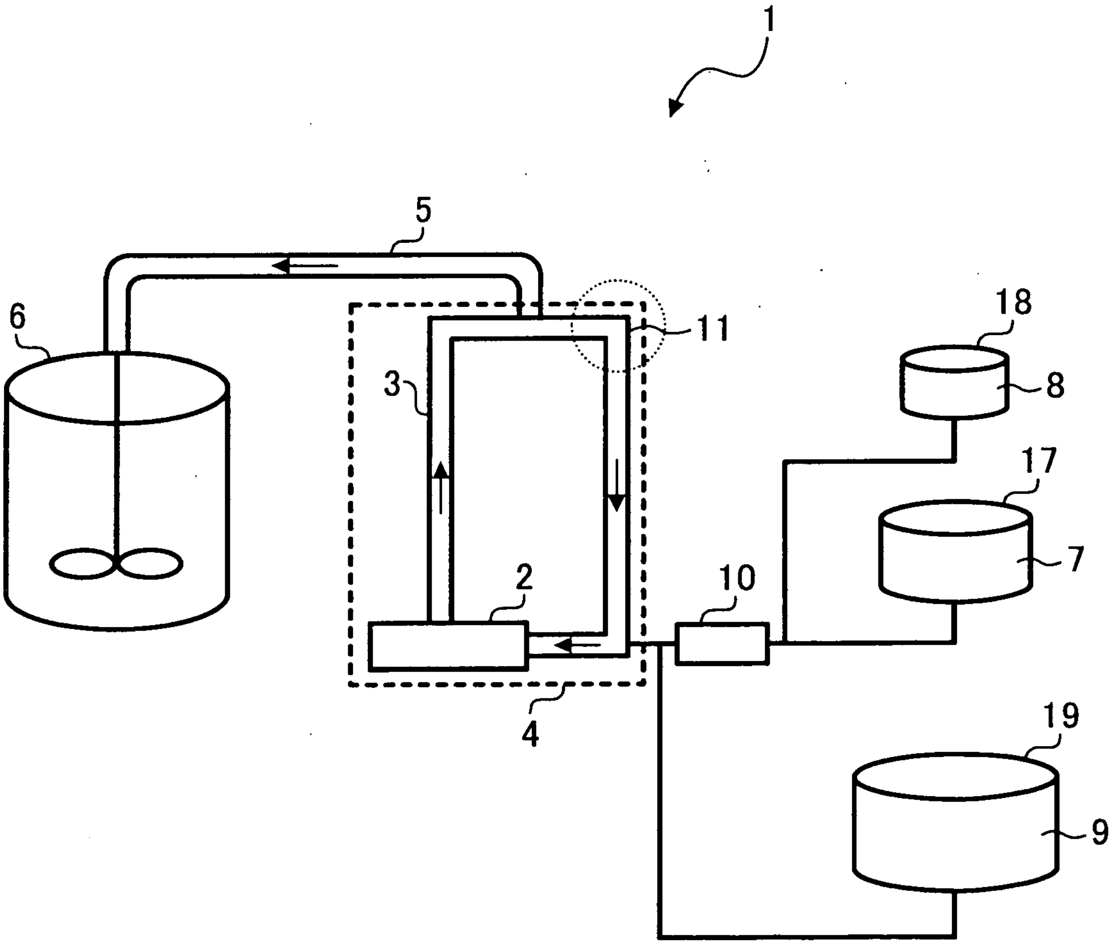
21. A process cartridge, comprising:

an image bearing member;
a developing device holding a developer comprising the toner of Claim 17 or 18; and
optionally at least one of a charging device and a cleaning device;
wherein the process cartridge is integrally and detachably attached to a main body of an image forming apparatus.

22. An image forming apparatus, comprising:

an image bearing member;
a charging device configured to charge the image bearing member;
an irradiator configured to irradiate the image bearing member to form a latent electrostatic image on the image bearing member;
a developing device configured to develop the latent electrostatic image on the image bearing member with the toner of Claim 17 or 18;
a cleaning member configured to remove residual toner on the image bearing member;
a transferring device configured to transfer the developed image on a recording medium; and
a fixing device configured to fix the developed image onto the recording medium,
wherein the image bearing member, the developing device, and optionally at least one of the charging device and the cleaning device are provided as the process cartridge of Claim 21.

FIGURE



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EUROPEAN SEARCH REPORT

Application Number
EP 05 01 8515

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Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
D,A	PATENT ABSTRACTS OF JAPAN vol. 2002, no. 07, 3 July 2002 (2002-07-03) & JP 2002 091071 A (CANON INC), 27 March 2002 (2002-03-27) * abstract * -----	1-22	G03G9/08 B01F7/16
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TECHNICAL FIELDS SEARCHED (IPC)

G03G
B01F

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	1 December 2005	Buscha, A

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