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(54) Toner and process for preparation thereof.

(57) A toner having excellent fixing properties and offset resistance comprising a binder resin and a coloring agent obtainable by suspension polymerization, wherein the median diameter D_{50} of the toner particles based on their volume is in the range of from 3 to 20 μm, the weight average molecular weight (Mw) of the toner particles is at least 100,000 and the dispersion degree (Mw/Mn) thereof expressed by the ratio of the weight (Mw) to the number average molecular weight (Mn) is at least 50.

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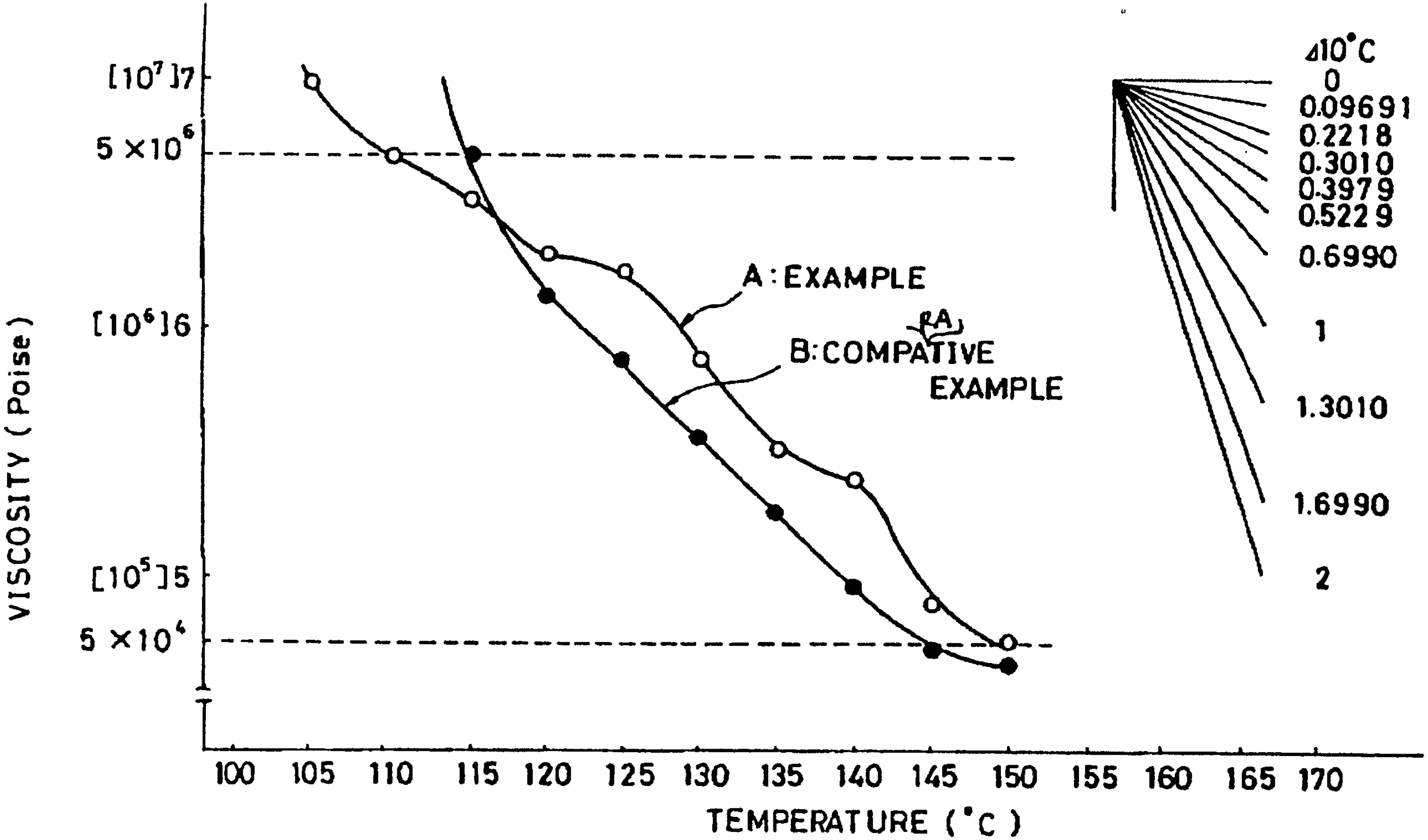
FIG.1


[10⁷]7
5 ×10⁶
[10⁶]6
[10⁵]5
5 ×10⁴
VISCOSITY (Poise)
100
105
110
115
120
125
130
135
140
145
150
155
160
165
170
TEMPERATURE (°C)
A : EXAMPLE
B: COMPATIVE
RA
EXAMPLE
Δ10°C
0
0.09691
0.2218
0.3010
0.3979
0.5229
0.6990
1
1.3010
1.6990
2

TONER AND PROCESS FOR PREPARATION THEREOF

Background of the Invention

(1) Field of the Invention

The present invention relates to a toner for use in the electrophotography. More particularly, the present invention relates to a toner showing excellent fixing property and offset resistance at the development and a process for the preparation of this toner.

(2) Description of the Prior Art

Toners used in the field of the electrophotography are composed of particles comprising a binder resin, a coloring agent and, if necessary, a charge-controlling agent, a magnetic material and a releasing agent. The fixing property to a transfer sheet at the developing step and the offset resistance can be mentioned as functions generally required for toners.

As the means for improving the fixing property and offset resistance in toners, there have been adopted a method in which a low-molecular-weight hydrogenated polybutadiene is incorporated in the binder resin (see Japanese Unexamined Patent Publication No. 60-103354), a method in which a reactive prepolymer is incorporated into the binder resin (see Japanese Unexamined Patent Publication No. 56-110948), and a method in which the ratio between styrene and 2-ethylmetahexyl methacrylate in the binder resin is controlled within a certain range (Japanese Unexamined Patent Publication No.60-57855).

However, even if a low-molecular-weight resin is merely incorporated (made present) in toner particles, the fixing property is not sufficiently improved, and sometimes, a problem of a poor offset resistance is caused at the fixing step. Moreover, the durability of the toner per se is still insufficient and the additives such as the coloring agent, falling from the toner particles during the copying operation, degrade the developing characteristic. Similar defects are observed when the constituent ratio in the binder resin is specified.

At the development, the fixing roller is maintained at a certain uniform temperature to melt toner particles appropriately. In this case, no trouble is caused to occur if the toner particles always undergo uniform melting and the viscosity of entire toner particles is at a constant level. However, it often happens that the heating state of the surface of the fixing roller is inevitably changed delicately during formation of many prints from the start of the copying operation. This temperature change has serious influences on the viscosity at the development, and hot offset of cold offset is readily caused. For obviating this disadvantage, there has been adopted a method in which the molecular weight of the binder resin is changed or a method in which the resin is rendered reactive. However, further improvements of the fixing property and offset resistance are desired.

In the suspension polymerization, the particle size of prepared particles is not uniform, and especially, incorporation of fine particles at a certain ratio cannot be avoided. If such fine particles are present in a toner, scattering of the toner at the development and fogging cannot be prevented.

Summary of the Invention

It is a primary object of the present invention to provide a toner composed of substantially spherical particles having a certain size, which are formed by suspension polymerization, in which a low-molecular-weight component of a binder resin is contained in toner particles in an appropriate state and the fixing property and offset resistance are highly improved, and a process for the preparation of this toner.

Another object of the present invention is to provide a toner composed of particles formed by the suspension polymerization, in which the content of fine particles is reduced and occurrence of scattering or fogging at the development is controlled, and a process for the preparation of this toner.

Still another object of the present invention is to provide a toner comprising a binder resin, the viscosity of which is not substantially changed when the toner is melted at the fixing step, in which the fixing property, offset resistance and apparatus adaptability are highly improved, and a process for the preparation of this toner.

In accordance with the present invention, there is provided a toner comprising a binder resin and a coloring agent and obtained by the suspension polymerization, wherein the median diameter D_{50} based on the volume of toner particles is in the range of from 3 to 20 μm, the weight average molecular weight (Mw) is at least 100,000 and the dispersion degree (Mw/Mn) expressed by the ratio of the weight average molecular weight (Mw) to the number average molecular weight (Mn) is at least 50. This toner can be further characterized in that in the particle size distribution of the toner having the above-mentioned average particle size, the dispersion degree (D_{25}/D_{75}) expressed by the ratio of the 25% cumulative diameter D_{25} based on the volume to the 75% cumulative diameter D_{75} based on the volume is lower than 1.6.

The present invention is based on the finding that if the bulk polymerization is combined with the suspension polymerization, a toner having the above-mentioned characteristics can be obtained. More specifically, the present invention is based on the finding that if a low-molecular-weight component of a binder resin is made present in formed particles in an appropriate state and the particles are used as the toner, the fixing property and offset resistance can be highly improved. Furthermore, the present invention is based on the finding that if the particle size of particles obtained by the suspension polymerization is adjusted within a specific range and also the particle size distribution is adjusted within a specific range, scattering and fogging can be prevented.

In accordance with the present invention, there is provided a toner satisfying the above-mentioned requirements, which is further characterized in that in the temperature range of from 100 to 150°C at which the toner is heated at the fixing step, the temperature difference required for the viscosity of the toner to change from 5×10^6 poise to 5×10^4 poise under heating is at least 32°C.

The binder resin of the above-mentioned toner can have such flow characteristics that the flow-initiating temperature Ti satisfies the requirement of $(Ti-Tg) \leqq 50$ in which Tg represents the glass transition temperature of the binder resin, and the temperature Tm for flow-out of 1/2 of the toner satisfies the requirement of $(Tm-Ti) \geqq 30$.

Furthermore, the average viscosity gradient (absolute value) of the toner of the present invention in the temperature range of from 100 to 150°C is preferably 0.02 to 0.7/°C, and in this temperature region, there is preferably present at least one region where the absolute value of the viscosity gradient is smaller than 0.03/°C.

Incidentally, the viscosity gradient of the toner represents the ratio of the logarithm of the viscosity to the temperature. The change quantity of the viscosity to the temperature difference, $(X + \Delta) - X$°C, is $\log(Y + \Delta)$poise - $\log Y$ poise, and the viscosity gradient K is the value represented by the following formula :

$$K = [\log(Y + \Delta) - \log Y]/°C$$
$$= [\mathrm{Log}(Y + \Delta)/Y]/\Delta°C$$

Incidentally, K monotonously decrease as the temperature is elevated, and the viscosity is the value measured by a flow tester.

Furthermore, there are present two regions where the absolute value of the viscosity gradient is smaller than 0.03/°C, and these two regions can be region of from 115 to 125°C and a region of from 130 to 140°C. Moreover, in the above-mentioned temperature range, the proportion of a region where the viscosity gradient is gentler than the average viscosity gradient is preferably at least 10%.

Investigations have been made on the binder resin in toner particles obtained by the suspension polymerization, and the present invention has been completed based on the finding that if the change of the viscosity of the resin is controlled within a certain range, the fixing property and offset resistance can be highly improved.

In accordance with the present invention, a toner having the above-mentioned characteristics is prepared according to a process for preparing a toner by using a vinyl monomer and a coloring agent, which comprises bulk-polymerizing the vinyl monomer to form a prepolymer syrup having a polymerization degree of 10 to 70%, suspending the prepolymer syrup in a dispersing solvent, carrying out the suspension polymerization and using the formed polymer. In carrying out the suspension polymerization, a crosslinking agent can added together with the prepolymer syrup. Furthermore, in carrying out the suspension polymerization, the suspension granulation temperature can be adjusted within the following range :

suspension polymerization temperature - 30°C <
suspension granulation temperature < suspension
polymerization temperature.

In the present invention, in carrying out the bulk polymerization, an initiator having a half-value period shorter than 40 minutes at a predetermined polymerization temperature can be used, and the process of the present invention can be further characterized in that the bulk polymerization and suspension polymerization are carried out while incorporating at least one member selected from the group consisting of charge-controlling agents, magnetic materials and releasing agents together with the vinyl monomer and coloring agent.

The preparation process of the present invention is suitable for the production of the above-mentioned toner, and the particles have a spherical shape suitable for the toner. Moreover, according to the process of the present invention, a toner having a sharp particles size distribution can be formed without any sieving step.

Brief Description of the drawings

Fig. 1 is a characteristic curve illustrating the relation between the temperature and the change of the viscosity in toner particles of the present invention.

Detailed Description of the Preferred Embodiments

In the toner of the present invention, it is important that the median diameter D_{50} should be in the range of from 3 to 20 µm, especially from 5 to 13 µm. Toner particles having a median diameter D_{50} adjusted within this range provide an excellent toner, and scattering of the toner and fogging can be controlled at the development. A toner composed of these toner particles can be easily obtained by combining the bulk polymerization and suspension polymerization and using specific binder resin components as described hereinafter.

Moreover, in the present invention, it is important that the weight average molecular weight (Mw) of the toner particles should be at least 100,000 and the dispersion degree (Mw/Mn) should be at least 50, especially at least 80. If the weight average molecular weight (Mw) is at least 100,000, the toner particles are appropriately melted when the toner is heated by a fixing roller or the like at the fixing step and a certain cohesive force is attained. This certain cohesive force can effectively prevent hot offset. In this case, if the dispersion degree of the molecular weight in the toner particles is at least 50, a low-molecular-weight component, for example, a resin component having a molecular weight lower than 50,000, can be present in a sufficient amount in the binder resin. This low-molecular-weight binder resin component is promptly melted under heating at the fixing step and penetrates sufficiently in a transfer material, whereby the fixing property is improved.

It is preferred that the dispersion degree (Mw/Mn) in the toner particles be at least 80. As pointed out hereinbefore, the toner is obtained by the bulk polymerization and suspension polymerization. If a crosslinking agent is used at this suspension polymerization, high-molecular-weight component clearly distinguishable from the low-molecular-weight component formed at the bulk polymerization can be formed at the suspension polymerization, with the result that the dispersion degree of the binder resin can be increased to at least 80. A toner having this dispersion degree is highly improved in the fixing property and offset resistance.

In the toner of the present invention, it also is important that the particle size dispersion degree (D_{25}/D_{75}) expressed by the ratio of the 25% cumulative diameter D_{25} based on the volume to the 75% cumulative diameter D_{75} should be lower than 1.6. This feature is based on this finding that if the suspension granulation is carried out at a specific temperature, a toner composed of particles having a uniform particle size can be obtained. In the case where the particle size dispersion degree of the toner particles is within the above-mentioned range, large-diameter particles and fine particles are removed, and scattering of the toner particles or fogging is hardly caused at the development.

In addition to the above-mentioned requirements of the weight average molecular weight (Mw) and dispersion degree of the binder resin, the following requirement should be satisfied in the present invention. Namely, in the temperature region of from 100 to 150°C at which the toner is heated at the fixation, the temperature difference required for the viscosity of the toner to change from 5×10^6 poise to 5×10^4 poise should be at least 32°C, especially at least 35°C. In the toner where such a large temperature difference, since the change of the viscosity of a fixing roller and a transfer material, the fixing property and apparatus adaptability are improved.

Fig. 1 is a characteristic curve showing the relation between the temperature and the viscosity in the toner of the present invention. In Fig. 1, the temperature is plotted on the abscissa and the logarithm of the viscosity is plotted on the ordinate. As is seen from the viscosity change curve A of the toner of the present invention in Fig. 1, Δ 40°C is necessary for the viscosity to change from 5×10^6 poise to 5×10^4 poise while this temperature is smaller than Δ 30°C in the curve B of the conventional toner, and the gradient of the curve A of the toner of the present invention is considerably gentle. Namely, in the conventional toner, in order to change the viscosity from 5×10^6 poise to 5×10^4 poise, it is sufficient if the temperature is elevated only by less than 30°C, but in case of the toner of the present invention, the temperature should be elevated by at least 40°C.

Furthermore, in the present invention, it is preferred that in the temperature range of from 100 to 150°C, the average viscosity gradient of the toner be 0.02 to 0.07/°C. Since the binder resin is gradually melted with elevation of the temperature, the viscosity of the toner monotonously decreases and the viscosity gradient is a negative value. The absolute value of the viscosity gradient had influences on the change of the viscosity of the toner, and the larger is the absolute value, the larger is the change of the viscosity to the temperature. In the present invention, as shown in Fig. 1, in the temperature range of from 100 to 150°C at which the toner is substantially fixed to a transfer sheet, the average viscosity of the toner is in the range of 0.02 to 0.07/°C. As is seen from Fig. 1, in the toner having the viscosity gradient included within this range, the change of the viscosity to the toner is smaller than in the conventional toner particles, and it will be readily understood that an allowance is produced for setting the condition of heating the fixing roller.

In the toner particles of the present invention, it is preferred that the occupancy ratio of the region where in the above-mentioned temperature range, the viscosity gradient is lower than the average viscosity gradient be at least 10%, especially at least 15%. It also is preferred that in the toner particles, there be present at least one region where the viscosity gradient (absolute value) of the toner is lower than 0.03/°C, especially lower than 0.02/°C.

At the fixing step, the toner is heated for a short time by the fixing roller maintained at about 180°C. By this heating, the toner begins to melt at about 100°C, and in an appropriate fused state, the resin penetrates into a transfer sheet and when the fixing roller separates, the resin is left in the transfer sheet by dint of a certain cohesive force and an anchoring effect. In this case, it is understood that components having different physical properties are present in the binder resin, and it is considered that in the temperature range of a steep viscosity gradient of the toner, the component of the binder resin reducing the viscosity of the entire toner under elevation of the temperature acts and in the temperature region of a gentle gradient of the viscosity, the melted state is changed by elevation of the temperature but the component of the binder resin not substantially changing the viscosity characteristics of the entire toner acts.

As shown in Fig. 1, in the viscosity change curve A of the toner of the present invention, in the temperature range of from 115 to 125°C, the gradient is -0.014/°C and in the temperature range of from 130 to 140°C, the gradient is -0.025/°C. In contrast, in the viscosity change curve B of the conventional toner, throughout the temperature range of from 100 to 150°C, the minimum value (absolute value) of the viscosity gradient is larger than 0.05/°C. Accordingly, when the toner is heated by the fixing roller, no substantial change of the viscosity is caused by the viscosity is maintained at a predetermined level. However, in the conventional toner, that is, a toner having a viscosity gradient larger than 0.05/°C, the change of the viscosity is conspicuous. This difference at the time of heating has serious influences on the penetrability, cohesiveness and anchoring effect which are factors having influences on the fixing property and offset resistance.

In the present invention, it is preferred that as shown in Fig. 1, there be present two regions where the viscosity gradient is gentler than 0.030 poise/°C. For example, a first region can be present at temperatures of from 115 to 125°C and a second region can be present at temperatures of from 130 to 140°C. A toner having such viscosity characteristics has a good penetrability to a transfer sheet and shows an excellent cohesiveness when the fixing roller in which the temperature delicately changes separates, with the fixing property is improved, though it is indefinite now the viscosity characteristics act at the transfer step. Accordingly, the fixed toner is not separated from the transfer sheet and contamination or offset is not found on the fixing roller.

In this toner, it is preferred that requirements of (Ti - Tg) ≦ 50 and (Tm - Ti) ≧ 30 be satisfied among the temperature Ti of initiation of flow-out of the toner, the temperature Tm for flow-out of 1/2 of the toner and the glass transition temperature Tg of the binder resin. (Ti - Tg) has a relation to the meltability of the toner particles and the penetrability in a transfer sheet and (Tm - Ti) has a relation to the melted state of the toner and the viscosity of the toner.

If it is tried to reduce the difference (Ti - Tg), also the difference (Tm - Ti) tends to become small (see Table 4). In the toner particles of the present invention, however, by selecting a specific polymerization state and a specific resin, it becomes possible to maintain Ti within the above-mention range and especially satisfy the requirements of (Ti - Tg) ≦ 45 and (Tm - Ti) ≧ 35. If Ti is within the above-mentioned range, the difference (Ti - Tg) of the toner particles is small and the toner particles are easily melted, and the penetration of the toner in a transfer sheet is accelerated. Furthermore, since the difference (Tm - Ti) is large, the mixed state of the melt and the unmelted substance is kept for a long time and the viscosity of the toner is maintained at a relatively high level. Accordingly, offset to the fixing roller or the like is prevented and the anchoring effect to the transfer sheet is maintained.

In principle, the toner of the present invention is prepared by the suspension polymerization. More specifically, a toner having the above-mentioned characteristics can be prepared by combining the suspension polymerization and bulk polymerization and using specific binder resin components.

The above-mentioned requirements of the weight average molecular weight (Mw) and dispersion degree (Mw/Mn) of the toner can be satisfied by bulk-polymerizing a vinyl monomer as the binder resin component and then, carrying out the suspension polymerization. In the bulk polymerization, a low-molecular-weight polymer necessary for the fixing property is formed, and in the suspension polymerization, a high-molecular-weight polymer is formed.

In the bulk polymerization, not only the molecular weight of the polymer but also the polymerization degree, that is, the polymerization ratio, is important. It is preferred that in the bulk polymerization, the polymerization ratio be 10 to 70%, especially 25 to 60%. If the polymerization ratio is within this range, a sufficient amount of a low-molecular-weight polymer is present in the obtained toner particles. The bulk polymerization is carried out so that the content of a polymer having a weight average molecular weight lower than 50,000 is 10 to 70%.

The monomer/polymer mixture obtained by the bulk polymerization is generally a syrup having a high viscosity. The viscosity of the syrup differs according to the kind of the vinyl monomer, but it is preferred that the viscosity of the syrup be such that granulation can be accomplished by a high-speed shearing stirrer such as a homomixer or a homogenizer in a dispersion medium at the subsequent suspension polymerization. It is preferred that in the formation of this prepolymer syrup, that is, in the bulk polymerization, at least one polymerization initiator having a short half-value period be added. A polymerization initiator having a half-value period shorter than 40 minutes, especially shorter than 35 minutes, at a predetermined polymerization temperature, is used. Use of this initiator is preferable for adjusting the weight average molecular weight (Mw) of the binder resin to at least 100,000. The initiator acts at the initial stage of the bulk polymerization and hardly acts at the stage where the above-mentioned desired polymerization ratio is attained. Furthermore, the initiator has no influence on the subsequent suspension polymerization.

As pointed out hereinbefore, the prepolymer syrup is granulated in the dispersion medium and the particle size of the granulated particles is preferably adjusted to 3 to 20 µm. If the particle size of the granulated particles is set within the above-mentioned range, toner particles having a median diameter D_{50} based on the volume of 3 to 20 µm can be directly obtained.

When the suspension polymerization of the prepolymer syrup particles is completed, a polymer having a high molecular weight is mainly formed in the surface layer portion of the granulated particles, and by dint of this feature, the dispersion degree (Mw/Mn) in the entire toner particles can be maintained at a level of at least 50. In this case, the low-molecular-weight component is present in a large amount in the interior of the toner particles.

As pointed out hereinbefore, the prepolymer syrup is subjected to the suspension granulation. It is preferred that the suspension granulation temperature be set so that the relation of $(Tj - 30°C) < Tz < Tj$ is established between the suspension granulation temperature (Tz) and the suspension polymerization temperature (Tj). If the prepolymer syrup us granulated at this suspension granulation temperature, the particle size of the obtained toner particles becomes uniform and the desired dispersion degree can be attained.

The viscosity characteristics of the toner of the present invention can be attained by combining the bulk polymerization and suspension polymerization and selecting fixing resin components while satisfying the requirements of the weight average molecular weight (Mw) and dispersion degree (Mw/Mn).

The materials used in the present invention, and the bulk polymerization and suspension polymerization will not be described.

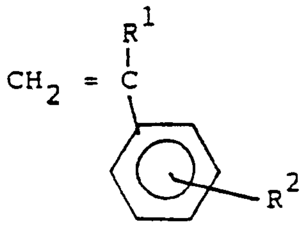
Materials Used

(a) Vinyl monomer

In the polymerization process of the present invention, at least one monomer having an ethylenically unsaturated double bond is used.

For suitable examples of the monomer, there can be mentioned monovinyl aromatic monomers, acrylic monomers, vinyl ester monomers, vinyl ether monomers, diolefin monomers and monoolefin monomers.

As the monovinyl aromatic monomer, there can be mentioned monomers represented by the following formula :

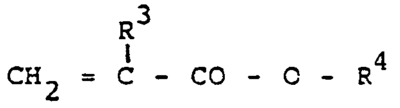


(1)

wherein R^1 represents a hydrogen atom, a lower alkyl group or a halogene atom, and R^2 represents a hydrogen atom, a lower alkyl group, a halogen atom, an alkoxy group, an amino group, a nitro group, a vinyl group or a carboxyl group.

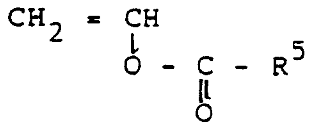
For example, at least one monovinyl aromatic hydrocarbon selected from the group consisting of styrene, α-methylstyrene, vinyltoluene, α-chlorostyrene, o-chlorostyrene, m-chlorostyrene, p-chlorostyrene, p-ethylstyrene, sodium styrene-sulfonate and divinylbenzene is used.

As the other monomer, there can be mentioned acrylic monomers represented by the following formula :



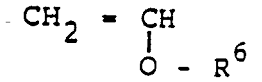
$$CH_2 = \overset{\displaystyle R^3}{\overset{|}{C}} - CO - O - R^4 \qquad (2)$$

wherein R^3 represents a hydrogen atom or a lower alkyl group, and R^4 represents a hydrogen atom, a hydrocarbon group having up to 12 carbon atoms, a hydroxyalkyl group, a vinyl ester group or an aminoalkyl group, such as acrylic acid, methacrylic acid, methyl acrylate, ethyl acrylate, butyl acrylate, 2-ethylhexyl acrylate, cyclohexyl acrylate, phenyl acrylate, methyl methacrylate, hexyl methacrylate, 2-ethylhexyl methacrylate, ethyl 3-hydroxyacrylate, propyl γ-hydroxyacrylate, butyl δ-hydroxyacrylate, ethyl β-hydroxymethacrylate, propyl γ-aminoacrylate, propyl γ-N,N-diethylaminoacrylate, ethylene grlycol dimethacrylic acid ester and tetraethylene glycol dimethacrylic acid ester, vinyl esters represented by the following formula :



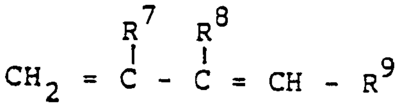
$$CH_2=CH-O-\underset{\underset{O}{\|}}{C}-R^5 \quad (3)$$

wherein R^5 represents a hydrogen atom or a lower alkyl group, such as vinyl formate, vinyl acetate and vinyl propionate, vinyl ethers represented by the following formula :



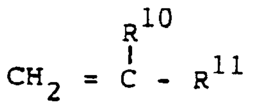
$$CH_2=CH-O-R^6 \quad (4)$$

wherein R^6 represents a monovalent hydrocarbon group having up to 12 carbon atoms, such as vinylmethyl ether, vinylethyl ether, vinyl-n-butyl ether, vinylphenyl ether and vinylcyclohexyl ether, diolefins represented by the following formula :



$$CH_2=\overset{R^7}{\overset{|}{C}}-\overset{R^8}{\overset{|}{C}}=CH-R^9 \quad (5)$$

wherein R^7, R^8 and R^9 each represent a hydrogen atom, a lower alkyl group or a halogen atom, such as butadienne, isoprene and chloroprene, and monoolefins represented by the following formula :



$$CH_2=\overset{R^{10}}{\overset{|}{C}}-R^{11} \quad (6)$$

wherein R^{10} and R^{11} each represent a hydrogen atom or a lower alkyl group, such as ethylene, propylene, isobutylene, butene-1, pentene-1 and 4-methylpentene-1.

(b) Polymerization initiator

In the suspension polymerization of the present invention, a polymerization initiator is used, and as the polymerization initiator, there can be mentioned radical-polymerizable initiators, for example, azo compounds such as 2,2-azobis(2,4-dimethylvaleronitrile), 2,2′-azobisisobutyronitrile, 1,1′-azobis(cyclohexane-1-carbonitrile), 2,2′-azobis-4-methoxy-2,4-dimethylvaleronitrile and 2,2-azobis(2-cyclopropylpropionitrile, and peroxides such as cumene hydroperoxide, t-butyl hydroperoxide, dicumyl peroxide, di-t-butyl peroxide, benzoyl peroxide and lauroyl peroxide. Furthermore, ionizing radiations such as γ-rays and accelerated electron beams, and various sensitizers can be used in combination with the polymerization initiator.

The amount added of the polymerization initiator such as an azo compound or peroxide can be a so-called catalytic compound, and it is generally preferred that the polymerization initiator be used in an amount of 0.1 to 20% by weight based on the charged monomer.

A polymerization initiator having a short half-value period is preferably used for the bulk polymerization, and an initiator showing a half-value period within the above-mentioned range at a predetermined polymerization temperature is selected and used.

(c) Crosslinking agent

A crosslinking agent is added at the suspension polymerization to promote the polymerization of the vinyl monomer and the increase of the bulky polymer.

Any of known crosslinking agents, for example, divinyl compounds such as divinylbenzene, divinyl ether and divinyl sulfone, diallyl compounds such as allyl phthalate and diallylcarbinol, diacryl esters such as diacrylphenol, and ethylene glycol dimethacrylate, trimetylol propane triacrylate, glycidyl methacrylate and glycidyl acrylate, can be used. A diacryl ester is especially preferably used. It is referred that the crosslinking agent be used in an amount of 0.1 to 20% by weight based on the charged monomer.

(d) Other additives used at polymerization step

In the present invention, a polymerization promoter, crosslinking agent and a chain transfer agent can be used according to need. Known additives can be added in appropriate amounts.

Furthermore, in order to perform granulation or the like smoothly, a known surface active agent or dispersant can be added at the polymerization step.

(e) Coloring agent

Known dyes and pigments can be used as the coloring agent. Specific examples are described below.

a. Black pigment

Carbon black, acetylene black, lamp black and aniline black.

b. Yellow pigment

Chrome yellow, cadmium yellow, yellow iron oxide, Mineral Fast Yellow, nickel titanium yellow, naples Naphthol Yellow S, Hansa Yellow 10G, Benzidine Yellow G, Quinoline Yellow Lake, Permanent Yellow NGG and Tartrazine Lake.

c. Orange pigment

Chrome orange, molybdenum orange, Permanent Orange GTR, Pyrazolone Orange, Vulcan Orange, Indanthrene Brilliant Orange EK, Benzidine Orange G and Indanthrene Brilliant Orange GR.

d. Red pigment

Red iron oxide, cadmium red, red lead, mercury cadmium sulfide, Permanent Orange 4R, Lithol Red, Pyrazolone Red, Watching Red calcium salt, Lake RedD, Brilliant Carmine 6B, Eosine Lake, Rhodamine Lake B, Alizaline Lake and Brilliant Carmine 3B.

e. Violet pigment

Manganese violet, Fast Violet B and Methyl Violet Lake.

f. Blue pigment

Iron blue, cobalt blue, Alkali Blue Lake, Victoria Blue Lake, Phthalocyanine Blue, metal-free Phthalocyanine Blue, partially chlorinated Phthalocyanine Blue, Fast Sky Blue and Indanthrene Blue BC.

g. Green pigment

Chrome green, chromium oxide, Pigment Green B, Marachite Green Lake and Final Yellow Green G.

h. White pigment

Zinc flower, titanium oxide, antimony white and zinc sulfide.

i.Extender pigment

Baryte powder, barium carbonate, clay silica, white carbon, talc and aluminum white.

The coloring pigment can be added in an amount of 1 to 20 parts by weight, preferably 5 to 15 parts by weight, per 100 parts by weight of the polymerizable monomer.

(f) other additives to be incorporated into toner

As the magnetic pigment, there are known triiron tetroxide (Fe_3O_4), diiron trioxide (γ-Fe_2O_3), zinc iron oxide ($ZnFe_2O_4$), yttrium iron oxide ($Y_3Fe_5O_{12}$), cadmium iron oxide ($Gd_3Fe_5O_{12}$), copper iron oxide ($CuFe_2O_4$), lead iron oxide ($PbFe_{12}O_{19}$), neodium iron oxide ($NbFeO_3$), barium iron oxide ($BaFe_{12}O_{19}$), magnesium iron oxide ($MgFe_2O_4$), manganese iron oxide ($MnFe_2O_4$), lanthanum iron oxide ($LaFeO_3$), iron powder (Fe), cobalt powder (Co) and nickel powder (Ni). In the present invention, any of fine powders of these known magnetic materials can be optionally used.

Known charge-controlling agents such as a metal-containing azo dye, a metal compound of (alkyl)salicylic acid, a metal soap of naphthenic acid, a metal soap of a fatty acid and a soap of a resin acid can be added to adjust the chargeability of the toner. The charge-controlling agent can be used in an amount of 0.1 to 10 parts by weight, preferably 0.5 to 5 parts by weight, per 100 parts by weight of the polymerizable monomer.

Releasing agents such as low-molecular-weight polyethylene, low-molecular-weight polypropylene, various waxes and silicone oils can be incorporated into the toner so as to impart an offset-preventing effect to the toner. The releasing agent can be added in an amount of 0.1 to 10 parts by weight, preferably 1 to 8 parts by weight, per 100 parts by weight of the polymerizable monomer.

Bulk Polymerization

In the bulk polymerization, the above-mentioned monomer, coloring agent and initiator, optionally together with other additives, are stirred. The reaction temperature is not particularly critical but appropriate conditions are selected according to the kind of the vinyl monomer. For example, the bulk polymerization is carried out at room temperature, under cooling or under heating.

It is important that the bulk polymerization should be carried out so that the polymerization degree of the vinyl monomer is 10 to 70%, especially 25 to 60%. If the polymerization ratio is low below the above-mentioned range, a low-molecular-weight polymer is not sufficiently formed by the bulk polymerization. If the polymerization ratio is high and exceeds the above-mentioned range, the amount of the low-molecular-weight polymer formed by the bulk polymerization is too large, and the durability and offset resistance of the obtained toner particles are degraded.

The vinyl monomer-bulky polymer mixture is a syrup having a certain viscosity. The viscosity of this syrup differs according to the vinyl monomer used. However, if the polymerization ratio is within the above-mentioned range, the granulation is easily accomplished at the suspension polymerization. From the view point of the fixing performance, it is preferred that a low-molecular-weight component having a molecular weight lower than 50,000 be contained in an amount 10 to 70%.

A polymerization initiator is added at the bulk polymerization, and it is preferred and important that a polymerization initiator having a short half-value period, as mentioned above, be used. A polymerization initiator having a half-value period shorter than 40 minutes, especially shorter than 35 minutes, is preferably used. If such an initiator is used, a component having a relatively low molecular weight can be easily obtained by the polymerization reaction, and the polymerization ratio can be easily adjusted and the subsequent suspension polymerization is not influenced.

Suspension Polymerization

In the suspension polymerization, the above-mentioned syrup is added to a dispersion medium and granulated. A water-soluble dispersion medium is ordinarily used. For example, water and alcohols are used as the dispersion medium. A surface active agent or a dispersion stabilizer is used for the suspension granulation. Known surface active agents and dispersion stabilizers can be used, and an anionic surface active agent of the fatty acid or sulfonic acid type is preferably used as the surface active agent and a hardly soluble inorganic salt is preferably used as the dispersion stabilizer.

The suspension granulation in the dispersion medium is accomplished by a high-speed shearing stirrer such as a homomixer or a homogenizer, and it is preferred that the size of granulated particles be 3 to 20 μm. If the size of the granulated particles is adjusted within this range, toner particles having an appropriate particle size can be obtained.

At the suspension polymerization, a crosslinking agent as mentioned above is preferably used. It is preferred that the crosslinking agent be added to the prepolymer syrup in an amount of 0.01 to 10% by weight, especially 0.1 to 5% by weight, based on the vinyl monomer. If the amount of the crosslinking agent is too large and exceeds the above-mentioned range, the fixing property of the resin component is degraded.

Furthermore, as pointed out hereinbefore, it is important that the particle size distribution of the granulated particles should be sharp. A sharp particle size distribution of the granulated particles means that toner particles having a certain and uniform particle size distribution are finally obtained, and in a toner having such a particle size distribution, scattering or fogging is controlled at the development, though the reason has not been clarified.

In order to prepare a toner having such a uniform particle size, it is important that a specific granulation temperature condition should be set. Namely, it is important that the granulation temperature should be lower than the temperature adopted at the subsequent suspension polymerization but should be higher than the temperature lower by 30°C than the suspension polymerization temperature. If the granulation temperature exceeds the above range, bad influences are imposed on the initiator and other additives at the granulation step and it often happens that the subsequent suspension polymerization cannot be smoothly conducted. If the granulation temperature is too low and below the above-mentioned range, granulation becomes difficult because of the influences of the viscosity and granulated particles having a uniform particle size cannot be obtained.

The obtained toner particles comprise a low-molecular-weight polymer formed by the bulk polymerization and a high-molecular-weight polymer formed by the suspension polymerization, and the additives such as the coloring agent are included in the polymer chains.

In the finally obtained toner particles, the median diameter D_{50} based on the volume is 3 to 20 μm and the weight average molecular weight is at least 100,000, especially 150,000 to 1,000,000. The dispersion degree (Mw/Mn) expressed by the ratio of the weight average molecular weight (Mw) to the number average molecular weight (Mn) is at least 50, especially 80 to 200. If these requirements are satisfied. The low-molecular-weight component and the high-molecular-weight component are broadly present, and the durability, fixing property and offset resistance are highly improved.

Furthermore, in the obtained toner particles, the ratio (D_{25}/D_{75}) of the 25% cumulative diameter (D_{25}) based on the volume to the 75% cumulative diameter (D_{75}) based on the volume is lower than 1.6, especially lower than 1.55, and the flowability and charge stability are improved and a high-density sharp image can be obtained without fogging. In order to obtain particles satisfying the foregoing requirements, it is important that the suspension granulation temperature should be controlled within the above-mentioned range.

Therefore, according to the present invention, by obtaining toner particles by carrying out the suspension polymerization so that the weight average molecular weight (Mw) and dispersion degree (Mw/Mn) of the toner particles are arranged within specific ranges, a toner having excellent fixing property and offset resistance can be obtained. Furthermore, since the particle size distribution is adjusted within a specific range, scattering of the toner and fogging can be prevented.

Still further, in the toner of the present invention, the viscosity characteristics of the toner particles at temperatures in the range of from 100 to 150°C, at which the toner is heated at the fixing step, are adjusted within a specific range, and therefore, the fixing property and offset resistance can be improved in the toner and the toner shows a good apparatus adaptability.

The present invention will now be described in detail with reference to the following examples that by no means limit the scope of the invention.

Example 1

A mixture comprising 80 parts by weight of styrene, 20 parts by weight of 2-ethylhexyl methacrylate, 5 parts by weight of carbon black (#-1000 supplied by Mitsubishi Kasei), 0.5 part by weight of divinylbenzene, 1 part by weight of a charge-controlling agent (Bontron S-40 supplied by Orient Kagaku) and 1 part by weight of 2,2'-azobis(2,4-dimethylvaleronitrile)(the half-value period at 85°C is about 7 minutes) as the polymerization initiator was bulk-polymerized at 85°C for 40 minutes to obtain a prepolymer syrup having a polymerization ratio of 45%. The weight average molecular weight of the polymer was 15,000.

Then, 3 parts by weight of ADVN as the polymerization initiator was added to the prepolymer syrup, and the prepolymer syrup was added into a continuous phase comprising 400 parts by weight of water, 6 parts by weight of tricalcium phosphate and 0.01 part by weight of sodium dodecylbenzene-sulfonate, and the mixture was granulated by using a homomixer. The temperature was elevated to 60°C and polymerization was carried out for 7 hours. The obtained polymer was treated with a dilute acid, washed with water and dried to obtain toner particles. When the particles size characteristics were determined by using a Coulter counter, it was found that the median diameter D_{50} based on the volume was 11.2 µm, and when the molecular weight distribution was measured by GPC, it was found that the weight average molecular weight (Mw) of the entire particles was 170,000, and the dispersion degree (Mw/Mn) expressed by the ratio of the weight average molecular weight to the number average molecular weight was 70.

Hydrophobic silica was added in an amount of 0.1 part by weight per 100 parts by weight of the obtained toner, and then, the toner was mixed with a carrier comprising ferrite particles coated with a silicone resin so that the toner concentration was 3%, whereby a developer was prepared. The obtained developer was subjected to the printing test for obtaining 10,000 prints in an electrophotographic copying machine (Model DC-1205 supplied by Mita Kogyo), and the fixing property and offset resistance were evaluated. Incidentally, the fixing property was examined in the following manner. Namely, a transfer sheet having a toner image formed thereon was passed through fixing means to fix the toner image, and an adhesive tape was press-bonded to the obtained fixed image and the adhesive tape was peeled. The density of the fixed image was measured before and after the peeling by a reflection densitometer (supplied by Tokyo Denshoku), and the fixing ratio was calculated according to the following formula and the fixing property was evaluated based on this fixing ratio :

$$\text{Fixing ratio (\%)} = \frac{\text{image density after peeling}}{\text{image density before peeling}} \times 100$$

The offset resistance was evaluated based on whether or not the offset phenomenon took place during the continuous copying operation. Furthermore, the image characteristics were evaluated. The obtained results are shown in Table 1.

Example 2

A mixture comprising 80 parts by weight of styrene, 20 parts by weight of n-butyl methacrylate, 5 parts by weight of carbon black (#-1000 supplied by Mitsubishi Kasei), 1 part by weight of a charge-controlling agent (Bontron S-40 supplied by Orient Kagaku), 0.5 part by weight of divinylbenzene and 1 part by weight of 2,2′-azobisisobutyronitrile (the half-value period at 95°C is about 10.5 minutes) as the polymerization initiator was bulk-polymerized at 95°C for 1 hour. The polymerization ratio was 40% and the weight average molecular weight of the polymer was 22,000. Then, 3 parts by weight of ADVN as the polymerization initiator was added to the prepolymer syrup, and the suspension polymerization was carried out in the same manner as described in Example 1 to obtain toner particles.

The median diameter D_{50} based on the volume of the obtained toner was 10.5 μm, and by GPC, it was confirmed that the weight average molecular weight was 200,000 and the dispersion degree (Mw/Mn) was 55.

A developer was prepared by using the obtained toner in the same manner as described in Example 1, and the developer was similarly tested. The obtained results are shown in Table 1.

Example 3

A mixture comprising 70 parts by weight of styrene, 30 parts by weight of 2-ethylhexyl methacrylate, 5 parts by weight of carbon black (#-1000 supplied by Mitsubishi Kasei), 1 part by weight of a charge-controlling agent (Bontron S-40 supplied by Orient Kagaku), 0.6 part by weight of divinylbenzene and 1.5 part by weight of 2,2′-(4-methoxy-2, 4-dimethyl valeronitrile) (the half-value period at 65°C is about 6 minutes) as the polymerization initiator was bulk-polymerized at 65°C for 40 minutes. The polymerization ratio was 50% and the weight average molecular weight of the polymer was 11,000. Then, 3 parts by weight of ADVN as the polymerization initiator was added to the prepolymer syrup, and the suspension plymerization was carried out in the same manner as described in Example 1 to obtain toner particles.

The median diameter D_{50} based on the volume of the obtained toner was 10.0 μm, and by GPC, it was confirmed that the weight average molecular weight was 180,000 and the dispersion degree (Mw/Mn) was 85.

A developer was prepared by using the obtained toner in the same manner as described in Example 1, and the developer was similarly tested. The obtained results are shown in Table 1.

Comparative Example 1

The bulk polymerization was carried out in the same manner as described in Example 1 except that the amount of ADVN as the polymerization initiator was changed to 0.1 part by weight and the polymerization was conducted at 85°C. At the polymerization ratio of 6%, the polymerization was terminated. The weight average molecular weight of the obtained polymer was 18,000. Then, the suspension polymerization was carried out in the same manner as described in Example 1. The median diameter D_{50} based on the volume of the obtained toner was 10.2 μm. By GPC, it was confirmed that the weight average molecular weight was 250,000 and the dispersion degree (Mw/Mn) was 6.4. A developer was prepared by using the obtained toner in the same manner as described in Example 1, and the developer was similarly tested. The obtained results are shown in Table 1.

Table 1

	Particle Size Characteristics	Molecular Weight Characteristics		Fixing Property	Offset Resistance	Image Characteristics	
	median diameter (µm) based on volume	weight average molecular weight (Mw)	dispersion degree (Mw/Mn)			density-retaining property	image fogging
Example 1	11.2	170,000	70	○	○	○	○
Example 2	10.5	200,000	55	○	○	○	○
Example 3	10.0	180,000	85	○	○	○	○
Comparative Example 1	10.2	250,000	6.4	x	○	○	△

From Table 1, it is seen that the toners of the Examples were excellent in the fixing property and offset resistance, and variations of the development characteristics were small and sharp images having a high density were obtained without fogging. On the other hand, the fixing ratio was low in the toner obtained in the Comparative Example, and therefore, no fixing property could be maintained, and fogging was caused even if the development characteristics were slightly changed.

In Table 1, in the column of the fixing property, O indicates a fixing ratio of at least 95%, Δ indicates a fixing ratio of at least 90%, and X indicates a fixing ratio lower than 90%.

In the column of the wear resistance, O indicates that fine particles were not formed in the developing machine, Δ indicates that slight formation of fine particles in the developing machine was observed, and X indicates that formation of fine particles in the developing machine was conspicuous.

Comparative Example 2

The bulk polymerization was carried out in the same manner as described in Example 1 except that the amount of ADVN as the polymerization initiator was changed to 3 parts by weight and the polymerization reaction was conducted at 85°C. The polymerization ratio was 80% and the weight average molecular weight of the polymer was 9,500. Since the viscosity of the prepolymer syrup was high, granulation to particles having a toner particle size was impossible even if the suspension polymerization was tried in the same manner as described in Example 1.

Example 4

A mixture comprising 70 parts by weight of styrene, 30 parts by weight of2-ethylhexyl methacrylate, 5 parts by weight of carbon black (#-1000 supplied by Mitsubishi Kasei), 1 part by weight of a charge-controlling agent (Bontron S-40 supplied by Orient Kagaku) and 1 part by weight of 2,2′-azobis(2,4-dimethylvaleronitrile) (the half-value period at 85°C is about 7 minutes) as the polymerization initiator was bulk-polymerized at 85°C for 40 minutes to obtain a prepolymer syrup having a polymerization degree of 43%. The weight average molecular weight of the polymer was 11,000.

Then, 3 parts by weight of azobis(2,4-dimethylvaleronitrile) as the polymerization initiator and 0.6 part by weight of divinylbenzene as the crosslinking agent were added to the preliminary syrup, and the mixture was added into a continuous phase comprising 400 parts by weight of water, 6 parts by weight of tricalcium phosphate and 0.01 part by weight of sodium dodecylbenzene-sulfonate, and the mixture was granulated by using a homomixer. The temperature was elevated to 60°C and polymerization was carried out for 7 hours. The obtained polymer was treated with a dilute acid, washed with water and dried to obtain toner particles. When the particle size characteristics were determined by using a Coulter counter, it was found that the median diameter D_{50} based on the volume was 9.8 μm. By GPC, it was confirmed that the weight average molecular weight (Mw) was 250,000 and the dispersion degree (Mw/Mn) expressed by the ratio of the weight average molecular weight to the number average molecular weight was 100.

The obtained toner was evaluated in the same manner as described in Example 1.

The offset resistance was evaluated based on whether or not the offset phenomenon took place during the continuous copying operation. Furthermore, the antiblocking property was evaluated in the following manner. Namely, 20 g of the toner was charged in a glass cylinder having an inner diameter of 26.5 mm in an oven maintained at a temperature of 60°C, and a weight of 100 g was placed on the toner and the toner was allowed to stand still in this state for 30 minutes. Then, the cylinder was removed and the antiblocking property was evaluated whether or not the toner collapsed.

The obtained results are shown in Table 2.

Example 5

A mixture comprising 80 parts by weight of styrene, 20 parts by weight of n-butyl methacrylate, 5 parts by weight of carbon black (#-1000 supplied by Mitsubishi Kasei), 1 part by weight of a charge-controlling agent (Bontron S-40 supplied by Orient Kagaku) and 1 part by weight of 2,2′-azobis(4-methoxy-2,4-dimethylvaleronitrile) (the half-value period at 85°C is about 7 minutes) as the polymerization initiator was bulk-polymerized at 65°C for 40 minutes. The polymerization ratio was 40% and the weight average molecular weight of the polymer was 18,000. Then, 3 parts by weight of ADVN as the polymerization initiator, 2.5 parts by weight of 2-ethylene glycol dimethacrylate as the crosslinking agent and 0.2 part by weight of divinylbenzene were added to the prepolymer syrup, and the suspension polymerization was carried out at 75°C for 6 hours in the same manner as described in Example 1 to obtain toner particles.

The median diameter D_{50} based on the volume of the obtained toner was 10.3 μm, and by GPC, it was confirmed that the weight average molecular weight was 350,000 and the dispersion degree (Mw/Mn) was 135.

A developer was prepared by using the obtained toner in the same manner as described in Example 1, and the developer was similarly tested. The obtained results are shown in Table 2.

Example 6

A mixture comprising 90 parts by weight of styrene, 10 parts by weight of 2-ethylhexyl methacrylate, 5 parts by weight of carbon black (#-1000 supplied by Mitsubishi Kasei), 1 part by weight of a charge-controlling agent (Bontron S-40 supplied by Orient Kagaku) and 1.5 parts by weight of AIBN (the half-value period at 100°C is about 7 minutes) as the polymerization initiator was bulk-polymerized at 100°C for 40 minutes. The polymerization ratio was 35 and the weight average molecular weight of the polymer was 20,000. Then, 3 parts by weight of 2,2'-azobis(4-methoxy-2,4-dimethylvaleronitrile) as the polymerization initiator was added to the polymer syrup, 0.6 part by weight of divinylbenzene was further added as the crosslinking agent and the suspension polymerization was carried out at 60°C for hours in the same manner as described in Example 1 to obtain toner particles.

The median diameter D_{50} based on the volume of the obtained toner was 9.3 μm, and by GPC, it was confirmed that the weight average molecular weight was 100,000 and the dispersion degree (Mw/Mn) was 30.

A developer was prepared by using the obtained toner in the same manner as described in Example 1, and the developer was similarly tested. The obtained results are shown in Table 2.

Comparative Example 3

A toner was prepared in the same manner as described in Example 4 except that divinylbenzene as the crosslinking agent was not used. The median diameter (D_{50}) based on the volume of the obtained toner was 10.3 μm, and by GPC, it was confirmed that the weight average molecular weight was 230,000 and the dispersion degree (Mw/Mn) was 90. In the same manner as described in Example 1, a developer was prepared by using the obtained toner and was tested. The obtained results are shown in Table 2.

Comparative Example 4

A mixture comprising 70 parts by weight of styrene, 30 parts by weight of 2-ethylhexyl methacrylate, 5 parts by weight of carbon black (#-1000 supplied by Mitsubishi Kasei), 1 part by weight of a charge-controlling agent (Bontron S-40 supplied by Orient Kagaku), 0.6 part by weight of divinylbenzene and 4 parts by weight of 2,2'-azobis(2,4-dimethylvaleronitrile) as the polymerization initiator was added into a continuous phase comprising 400 parts by weight of water, 6 parts by weight of tricalcium phosphate and 0.01 part by weight of sodium dodecylbenzene-sulfonate, and the mixture was granulated by using a homomixer. The temperature was evaluated to 60°C and polymerization was carried out for 8 hours. The obtained polymer was treated with a dilute acid, washed with water and dried to obtain toner particles. When the particle size characteristics were determined by using a Coulter counter, it was found that the median diameter D_{50} based on the volume was 10.3 μm and by GPC, it was confirmed that the weight average molecular weight (Mw) was 120,000 and the dispersion degree (Mw/Mn) expressed by the ratio of the weight average molecular weight to the number average molecular weight was 2.1.

In the same manner as described in Example 1, a developer was prepared by using the obtained toner particles and the developer was tested. The obtained results are shown in Table 2.

Comparative Example 5

The bulk polymerization was carried out in the same manner as described in Example 4 except that the amount of the polymerization initiator was changed to 3 parts by weight and the polymerization reaction was conducted at 85°C. The polymerization ratio was 78 and the weight average molecular weight of the polymer was 9,000. Since the viscosity of the prepolymer syrup was high, granulation to particles having a toner particle size was impossible even if the suspension polymerization was tried in the same manner as described in Example 4.

Table 2

	Particle Size Characteristics	Molecular Weight Characteristics		Fixing Property	Offset Resistance	Anti-blocking Property	Wear Resistance
	median diameter (μm) based on volume	weight average molecular weight (Mw)	dispersion degree (Mw/Mn)				
Example 4	9.8	250,000	100	○	○	○	△
Example 5	10.3	350,000	130	○	○	○	○
Example 6	9.3	230,000	90	○	○	△	△
Comparative Example 3	10.3	100,000	30	○	x	x	x
Comparative Example 4	9.6	120,000	2.1	△	x	x	x

Example 7

A mixture comprising 80 parts by weight of styrene, 20 parts by weight of 2-ethylhexyl methacrylate, 5 parts by weight of carbon black (#-1000 supplied by Mitsubishi Kasei), 1 part by weight of a charge-controlling agent (Bontron S-40 supplied by Orient Kagaku), 1.0 part by weight of divinylbenzene and 2 parts by weight of 2,2'-azobis(2,4-dimethylvaleronitrile) (the half-value period at 85°C is about 7 minutes) as the polymerization initiator was bulk-polymerized at 85°C for 60 minutes. The polymerization ratio was 63 and the weight average molecular weight of the polymer was 12,000. Then, 3 parts by weight of 2,2'-azobis(2,4-dimethylvaleronitrile) was added as the polymerization initiator, and the prepolymer syrup was added into a continuous phase comprising 400 parts by weight of water, 6 parts by weight of tricalcium phosphate and 0.01 part by weight of sodium dodecylbenzene-sulfonate, and the mixture was granulated at 50°C by using a homomixer. The temperature was elevated to 60°C and polymerization was carried out for 7 hours. The obtained polymer was treated with a dilute acid, washed with water and dried to obtain toner particles. When the particle size characteristics were determined by using a Coulter counter, it was found that the median diameter D_{50} based on the volume was 11.0 µm, the dispersion degree represented by the ratio (D_{25}/D_{75}) of the 25% cumulative diameter to the 75% cumulative diameter was 1.47 and the particle size distribution was sharp. By GPC, it was confirmed that the weight average molecular weight (Mw) was 220,000 and the dispersion degree (Mw/Mn) expressed by the ratio of the weight average molecular weight to the number average molecular weight was 88.

The obtained toner was evaluated as described in Example 1 and Example 4. The obtained results are shown in Table 3.

Example 8

A mixture comprising 85 parts by weight of styrene, 15 parts by weight of n-butyl methacrylate, 5 parts by weight of carbon black (#-1000 supplied by Mitsubishi Kasei), 1 part by weight of a charge-controlling agent (Bontron S-40 supplied by Orient Kagaku), 3 parts by weight of 2-ethylene glycol methacrylate and 1 part by weight of 2,2'-azobis(2,4-dimethylvaleronitrile) (the half-value period at 85°C is about 7 minutes) as the polymerization initiator was bulk-polymerized at 65°C for 40 minutes. The polymerization ratio was 40% and the weight average molecular weight of the polymer was 20,000. Then, 2.5 parts by weight of AIBN as the polymerization initiator was added to the prepolymer syrup. In the same manner as described in Example 7, the prepolymer syrup was added into the continuous phase at 70°C to effect the granulation. Then, the suspension polymerization was carried out at 75°C for 6 hours to obtain toner particles.

The median diameter D_{50} based on the volume of the obtained toner was 10.8 µm, the dispersion degree (D_{25}/D_{75}) was 1.49 and the particle size distribution was sharp. By GPC, it was confirmed that the weight average molecular weight was 350,000 and the dispersion degree (Mw/Mn) was 93.

In the same manner as described in Example 1, a developer was prepared by using the obtained toner and the developer was tested. The obtained results are shown in Table 3.

Example 9

A mixture comprising 80 parts by weight of styrene, 20 parts by weight of 2-ethylhexyl methacrylate, 5 parts by weight of carbon black (#-1000 supplied by Mitsubishi Kasei), 1 part by weight of a charge-controlling agent (Bontron S-40 supplied by Orient Kagaku), 0.5 part by weight of divinylbenzene and 2 parts by weight of 2,2'-azobis(4-methoxy-2, 4-dimethylvaleronitrile) (the half-value period at 65°C is about 6 minutes) as the polymerization initiator was bulk-polymerized as 65°C for 40 minutes. The polymerization ratio was 50% and the weight average molecular weight of the polymer was 18,000. Then, 3 parts by weight of 1,1'-azobis(cyclohexane-1-carbonitrile) as the polymerization initiator was added to the prepolymer syrup, and in the same manner as described in Example 1, the prepolymer syrup was added into the continuous phase at 80°C to effect the granulation. Then, the suspension polymerization was carried out at 85°C for 7 hours.

The median diameter D_{50} based on the volume of the obtained toner was 10.5 µm, the dispersion degree (D_{25}/D_{75}) was 1.51 and the particle size distribution was sharp. By GPC, it was confirmed that the weight average molecular weight was 350,000 and the dispersion degree (Mw/Mn) was 75.

In the same manner as described in Example 1, a developer was prepared by using the obtained toner and the developer was tested. The obtained results are shown in Table 3.

Comparative Example 6

A toner was prepared in the same manner as described in Example 7 except that the temperature of the continuous phase was changed to 20°C at the granulation and the suspension polymerization temperature was changed to 60°C.

The median diameter D_{50} based on the volume of the obtained toner was 11.2 μm, the dispersion degree (D_{25}/D_{75}) was 1.67 and the particle size distribution was broad. By GPC, it was confirmed that the weight average molecular weight was 130,000 and the dispersion degree (Mw/Mn) was 35.

In the same manner as described in Example 1, a developer was prepared by using the obtained toner and the developer was tested. The obtained results are shown in Table 3.

Comparative Example 7

In Example 7, if the temperature of the continuous phase at the granulation was changed to 80°C, the polymerization was promoted during the granulation and the polymer adhered to vanes of the homomixer, and therefore, the granulation could not be performed stably.

Comparative Example 8

The bulk polymerization was carried out in the same manner as described in Example 7 except that the amount incorporated of the polymerization initiator was changed to 2.5 parts by weight and the polymerization reaction was conducted at 85°C.

The median diameter D_{50} based on the volume of the obtained toner was 12.0 μm, the dispersion degree (D_{25}/D_{75}) was 1.75 and the particle size distribution was broad. By GPC, it was confirmed that the weight average molecular weight was 110,000 and the dispersion degree (Mw/Mn) was 12.

In the same manner as described in Example 1, a developer was prepared by using the obtained toner and the developer was tested. The obtained results are shown in Table 3.

Comparative Example 9

A mixture comprising 100 parts by weight of a styrene-acrylic copolymer, 7 parts by weight of carbon black (MA-100 supplied by Mitsubishi Kasei) and 0.5 part by weight of a charge-controlling agent (Bontron S-40 supplied by Orient Kagaku) was mold-kneaded on a roll mill at about 150°C. The kneaded composition was cooled, pulverized by an air jet mill and subjected to air classification to obtain a toner having a median diameter based on the volume of 11.3 μm. The viscosity change gradient curve of the obtained toner particles is a monotonous decrease curve as shown in B of Fig. 1. The viscosity gradient was larger than 0.030/°C over the entire temperature range of from 115 to 145°C.

In the same manner as described in Example 7, a developer was prepared by using the obtained toner and the developer was tested. The obtained results are shown in Table 3.

The viscosity change gradient curves of the obtained toner particles in Examples 7, 8, and 9 were similar to a gentle monotonous decrease curve as shown in Fig. 1. The gradient at temperatures of from 120 to 125°C was from -0.0121°C to -0.0161°C and the gradient at temperatures of from 135 to 140°C was from -0.0231°C to -0.0271°C.

Table 3

	Viscosity Characteristics		Molecular Weight Characteristics		Fixing Property	Offset Resistance	Anti-blocking Property	Wear Resistance	Image Characteristics	
	medium diameter (μm) based on volume	dispersion degree (D_{25}/D_{75})	weight average molecular weight (Mw)	dispersion degree (Mw/Mn)					density-retaining property	image fogging
Example 7	11.0	1.47	220,000	88	○	○	○	△	○	○
Example 8	10.8	1.49	350,000	93	○	○	○	○	○	○
Example 9	10.5	1.51	230,000	75	○	○	○	○	○	○
Comparative Example 6	11.2	1.67	130,000	35	○	○	○	△	○	△
Comparative Example 7	12.0	1.75	110,000	12	○	x	x	x	△	x
Comparative Example 9	11.3	—	—	—	x	x	△	—	—	—

From the results shown in Table 3, it is seen that in the present invention (examples), the fixing characteristics, mechanical strength and development characteristics are imporved.

From the results shown in Table 1, it is seen that the toner prepared according to the present invention is excellent in the fixing property, offset resistance and image characteristics. It also is seen that if a crosslinking agent is incorporated at the suspension polymerization (Examples 4, 5 and 6 in Table 2), the dispersiondegree (Mw/Mn) can be broadened as compared with the case where any crosslinking agent is not incorporated (Examples 1, 2 and 3 in Table 1), and the antiblocking property and wear resistance can be further improved.

With respect to the toners of Examples 7, 8, and 9 and Comparative Example 8 shown in Table 3, the copying test for obtaining 20,000 prints was carried out at a copying speed of 32 A-4 sheets/minute (transverse feeding) in an electrophotographic copying machine (Model PC-3255). As is seen from the results shown in Table 3, the toners of Examples 7, 8, and 9 were excellent in all of fixing property, offset resistance, antiblocking property, wear resistance and image characteristics. In contrast, in the toner of Comparative Example 8, the fixing property was worsened and the image-retaining property was degraded.

Values Tg, Ti and Tm of the toners of Examples 7, 8, and 9 and comparative Example 8 are shown in Table 4.

Table 4

	Tg (°C)	Ti (°C)	Tm (°C)
Example 7	66	106	149
Example 8	67	108	151
Example 9	67	107	150
Comparative Example 8	64	116	145

Claims

1. A toner comprising a binder resin and a coloring agent obtainable by suspension polymerization, wherein the median diameter D_{50} of the toner particles based on their volume is in the range of from 3 to 20 μm, the weight average molecular weight (Mw) of the toner particles is at least 100,000 and the dispersion degree (Mw/Mn) thereof expressed by the ratio of the weight (Mw) to the number average molecular weight (Mn) is at least 50.

2. A toner according to claim 1 wherein in the particle size distribution of the toner, the dispersion degree (D_{25}/D_{75}), expressed by the ratio of the 25% cumulative diameter D_{25} based on the volume to the 75% cumulative diameter D_{75} based on the volume, is lower than 1.6.

3. A toner according to claim 1 or claim 2 wherein the toner comprises from 10 to 70% by weight of a component having a weight average molecular weight (Mw) tower than 50,000.

4. A toner according to any one of claims 1 to 3 wherein in the temperature range of from 100 to 150°C at which the toner is heated at the fixing step, the temperature difference required for the viscosity of the toner to change from 5×10^5 Pas to 5×10^3 Pas under heating is at least 32°C.

5. A toner according to any one of claims 1 to 4 wherein the flow-initiating temperature Ti satisfies the require-

ment of (Ti - Tg) $\leqq$ 50 in which Tg represents the glass transition temperature of the binder resin, and the temperature Tm for flow-out of half of the toner satisfies the requirement of (Tm - Ti) $\geqq$ 30.

6. A toner according to any one of claims 1 to 5 having an average viscosity gradient (absolute value), in the temperature range of from 100 to 150°C, of 0.02 to 0.7/°C, and in this temperature range having at least one region wherein the absolute value of the viscosity gradient is smaller than 0.03/°C.

7. A toner according to claim 6 having two regions where the absolute value of the viscosity gradient is smaller than 0.03/°C, these two regions being a region of from 115 to 125°C and a region of from 130 to 140°C.

8. A toner according to claim 6 or claim 7 wherein the region(s) where the viscosity gradient is gentler than the average viscosity gradient is at least 10% of the temperature range.

9. A process for preparing a toner which comprises bulk-polymerizing the vinyl monomer to form a prepolymer syrup having a polymerization degree of 10 to 70%, suspending the prepolymer syrup in a dispersing solvent, carrying out the suspension polymerization.

10. A process according to claim 9, wherein a crosslinking agent is added to the prepolymer syrup prior to or during suspension polymerization.

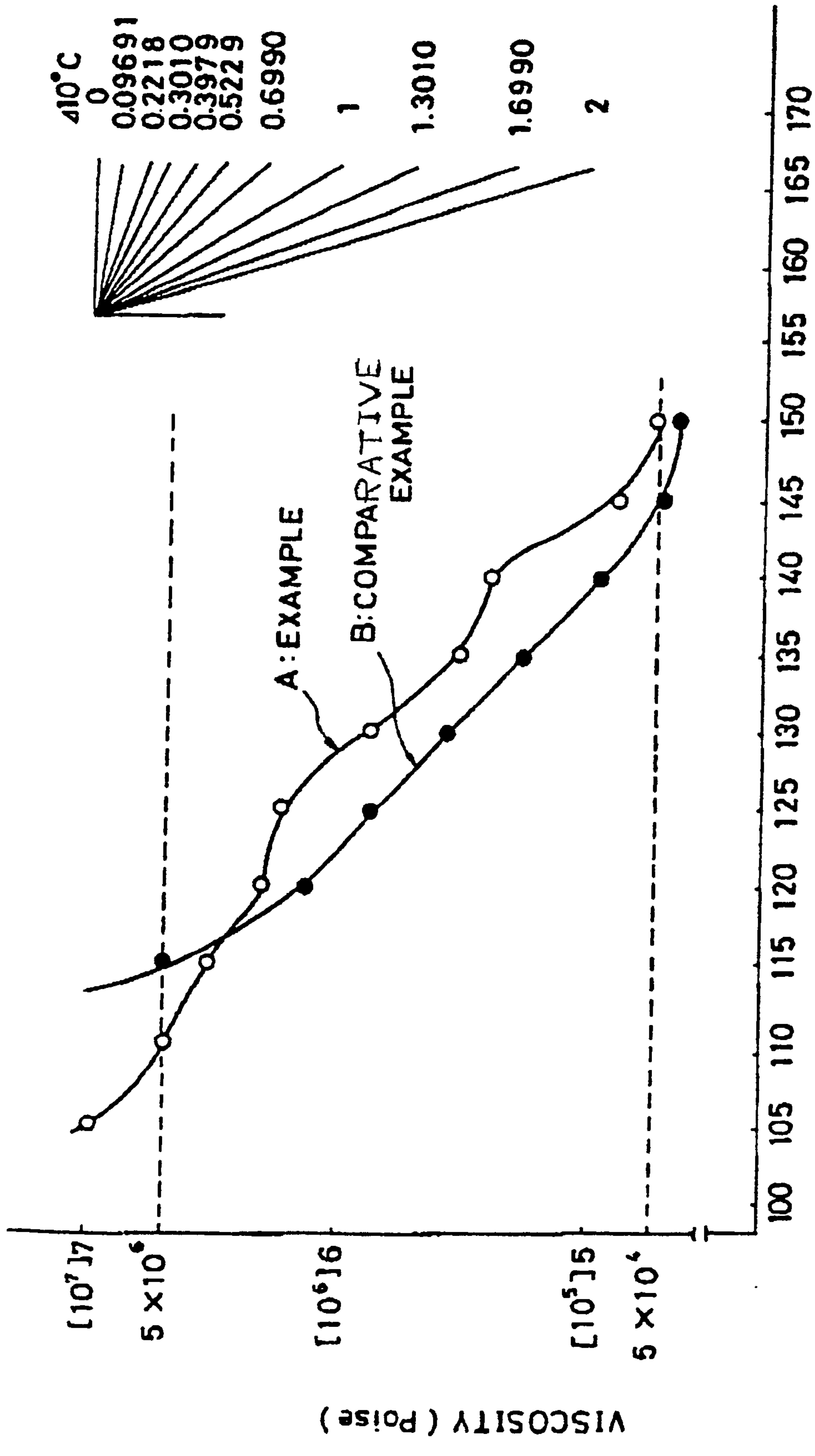
11. A process according to claim 9 or claim 10 wherein in carrying out the suspension polymerization, the suspension granulation temperature is adjusted within the following range :
    suspension polymerization temperature -30°C <
    suspension granulation temperature <
    suspension polymerization temperature.

12. A process according to any of claims 9 to 11, wherein in carrying out the bulk polymerization, an initiator having a half-value period shorter than 40 minutes at a predetermined polymerization temperature is used.

13. A process according to any one of claims 9 to 12, wherein the bulk polymerization and suspension polymerization are carried out while incorporating at least one charge-controlling agent, magnetic material or releasing agent together with the vinyl monomer and coloring agent.

14. A process according to any one of claims 9 to 13 for producing a toner according to any one of claims 1 to 8.

FIG. 1


VISCOSITY (Poise)
[10⁷]7
5 ×10⁶
[10⁶]6
[10⁵]5
5 ×10⁴
TEMPERATURE (°C)
100
105
110
115
120
125
130
135
140
145
150
155
160
165
170
A : EXAMPLE
B:COMPARATIVE EXAMPLE
⊿10°C
0
0.09691
0.2218
0.3010
0.3979
0.5229
0.6990
1
1.3010
1.6990
2

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EUROPEAN SEARCH REPORT

Application Number

EP 90 31 4397

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Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
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			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			G 03 G

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	26-03-1991	HILLEBRECHT D.A.O.

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