Description

The present invention relates to a process for producing a toner for use in development of electrostatic latent images to provide visual images through suspension polymerization.

Conventionally, toners for development of electrostatic charges have been manufactured by fusion-mixing colorants and other additives into thermoplastic resins to be dispersed uniformly therein, followed by pulverization and classification into desired particle sizes by means of a micropulverizer and a classifier. This preparation method is capable of producing considerably excellent toners but accompanied with potential problems arising from the pulverization step. As for a toner produced through the pulverization process, the material therefor is required to be sufficiently fragile so as to be readily pulverized to some extent. However, too fragile a material is pulverized beyond a resonable extent, so that separation of a fine powder portion is necessitated in order to obtain a toner with an appropriate particle size distribution, whereby there results in an increase in production cost. Further, the toner can be further pulverized in a developing apparatus of a copying machine in some cases. Further, in a case where a low-melting point material is used in order to improve a heat fixability or a pressure-fixable material is used, an agglomeration phenomenon can occur in a pulverizer or classifier, thus failing to effect continuous production in some cases.

There are other requisite conditions for a toner such that it has a triboelectric charging characteristic suitable for development, that it provides excellent images, that it causes no change in property when left standing, that it causes no coagulation (blocking), that it has an appropriate characteristic for heat fixation, heat-pressure fixation or pressure fixation, and that it causes no staining on the surface of a photosensitive member. Especially in respect of fixation, an offset phenomenon that a toner sticks onto a fixing roller and then be re-transferred onto a subsequently coming sheet of paper, has been a problem. In order to prevent the phenomenon, application of a release agent such as silicone oil has been practiced. In recent years, however, there has been used a method wherein the offset is prevented by incorporating a polyolefin such as polypropylene or polyethylene in a toner and no or only a reduced amount of release agent is applied on a fixing roller. However, this method still involves a problem for exhibiting a sufficient offset prevention effect for a long period. When a larger amount of a polyolefin is added or a polyolefin with a lower melting point is used in order to improve the anti-offset property for this reason, there arises a problem that agglomeration occurs in a pulverizer or a classifier, that blocking occurs because a low-melting polyolefin is exposed to the surface of a toner, or that the resultant toner is caused to have a poor fluidity to remarkably degrade the developing characteristic.

In order to overcome the problems accompanying the pulverization process, there has been proposed a process for producing a toner from a monomer composition comprising a polymerizable monomer and a colorant through suspension polymerization.

This process has characteristics that the material used is not required to have fragility because no pulverization step is involved, and the resultant toner has a shape close to a sphere to be excellent in fluidity, so that it is excellent in triboelectric charging characteristic.

However, it is technically difficult to effect polymerization of a monomer composition by providing a system wherein particles of the monomer composition are stably suspended in an aqueous medium with little coalescence of the particles and to obtain fine polymer particles with a uniform particle size distribution.

There is a method of using a suspension stabilizer in order to prevent the coalescence of particles of a monomer composition and polymer particles which can occur with the progress of polymerization in suspension polymerization of the monomer composition in water. As the suspension stabilizer, a hardly water-soluble or substantially water-insoluble fine powdery inorganic compound or a water-soluble polymer has been used. Examples of the suspension stabilizer include hardly water-soluble salts such as $BaSO_4$, $CaSO_4$, $MgCO_3$, $BaCO_3$, $CaCO_3$ and $Ca_3(PO_4)_2$; inorganic macromolecules such as diatomaceous earth, talc, silicic acid and clay; powder of metal oxides; and water-soluble polymers such as polyvinyl alcohol, gelatin and starch.

The document "Research Disclosures, Prod. Lic. Index, No. 100, August 1972, pages 54-56, abstract No. 10020" describes a process for producing toner particles in which toner-precursor particles of a desired size and shape are suspended in a "hydrophile, liquid vehicle" wherein a cationic compound having a hydrophobic moiety is dispersed. The toner-precurser material contains a thermoplastic resin composition, colorants and vinyl monomers and optionally other ingredients. The hydrophilic liquid such as water or alcohols may further contain in a dispersed form insoluble, inorganic particles, such as clay, $MgCO_3$, and water-soluble gums. By solidification of the suspension the hydrophobic moiety of the cationic compound migrates into an outermost liquid stratum of the toner-precursor particles. After separation from the

hydrophilic liquid vehicle, dry toner particles are obtained having positively charging triboelectric properties.

However, even by these methods, it is difficult to obtain fine particles with a satisfactory size for a toner, i.e., a number-average particle size of 30 μm or smaller. This is because coalescence of particles of a monomer composition cannot sufficiently be prevented according to the methods of the prior art.

An object of the present invention is to provide a process for producing a toner through suspension polymerization (hereinafter sometimes referred to as "polymerization toner"), by which the problems of the prior art as described above have been solved.

A specific object of the present invention is to provide a process for producing a polymerization toner with a sharp particle size distribution.

Another object of the present invention is to provide a process for producing a polymerization toner such that the polymerization toner can exhibit an excellent anti-blocking characteristic even when it contains an anti-offset agent of a low melting point.

Another object of the present invention is to provide a process for producing a polymerization toner such that the polymerization toner can be fixed at lower pressure-lower temperature conditions by means of hot-press rollers.

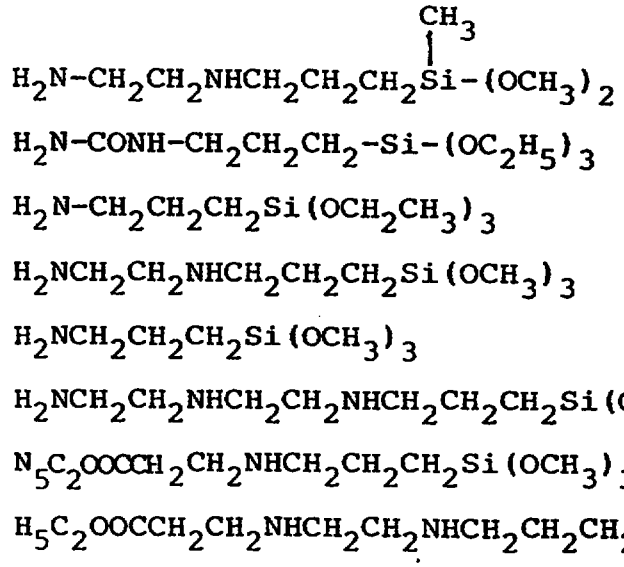
According to the present invention, there is provided a process for producing a toner, comprising: adding a monomer composition comprising at least a polymerizable monomer, an anionic polymer, a polymerization initiator and a colorant, into an aqueous medium to which a cationic dispersion stabilizer composed of inorganic fine powder provided with a nitrogen-containing organic group and a water-soluble acidic substance have been added, dispersing the monomer composition into particles with a prescribed particle size in the aqueous medium, and subjecting the particles of the monomer composition to suspension polymerization to produce toner particles to which said dispersion stabilizer is attached, and removing the dispersion stabilizer which is attached to the suspension-polymerized toner particles.

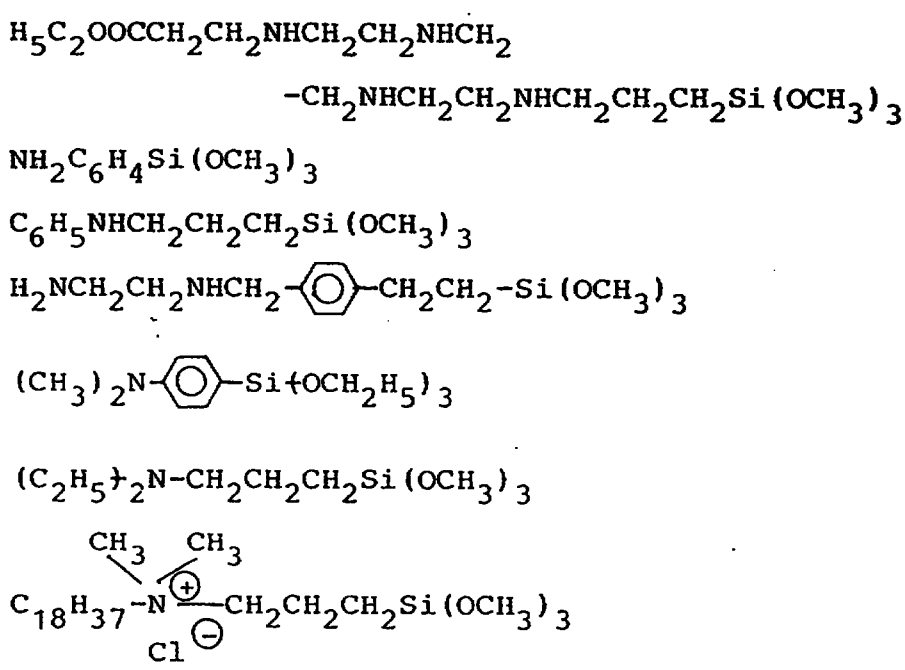
In the present invention, a dispersion stabilizer composed of inorganic fine powder provided with a nitrogen (atom)-containing organic group is added into an aqueous dispersion medium in which a monomer composition is to be dispersed and suspended. The dispersion stabilizer to be used in the present invention is a cationic dispersion stabilizer and is charged with $\delta^{\oplus}$ in water. Herein, "$\delta^{\oplus}$" means a charge which can move a particle having the $\delta^{\oplus}$ to a $\ominus$ electrode in electrophoresis in an aqueous medium for suspension polymerization under the conditions of a distance between electrodes of 1 cm and an applied voltage of 500 V between the electrodes. The nitrogen-containing organic group may be one which is capable of forming



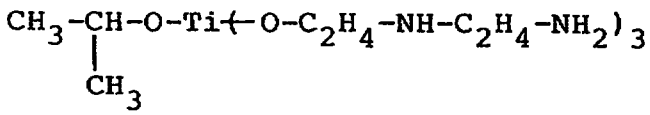
in the presence of an acidic substance in the aqueous medium. Inorganic fine powder is used as a dispersion stabilizer because the post treatment after polymerization becomes easier. As the inorganic fine powder, dry-process silica powder or wet-process silica powder is preferred because of particle size and hydrophilic characteristic. A nitrogen-containing organic group may be suitably provided onto the inorganic fine powder as the substrate by a coupling agent such as a nitrogen-containing silane coupling agent, a nitrogen-containing titanate coupling agent, or a nitrogen-containing zircoaluminate coupling agent.

Examples of the nitrogen-containing silane coupling agent include those having primary to quaternary amino group and those having a nitrogen-containing aromatic ring. In this regard, one that extremely lowers the hydrophilic characteristic of the substrate inorganic fine powder is not desirable because it degrades the function of the dispersant in an aqueous dispersion medium. For this reason, silane coupling agents having a primary to quarternary amino group are preferred. Specific examples of such silane coupling agents include the following:





Further, polyaminoalkyltrialkoxysilane may also be used. Examples of the titanate coupling agent having an amino group may include:



Other examples are zircoaluminate coupling agents having an amino group. These coupling agents may used either singly or as a mixture of two or more species.

In order to treat the inorganic fine powder with such a coupling agent, a coupling agent alone or a solution thereof in a volatile organic solvent may be added little by little to silica fine powder, for example, under stirring. It may also be possible to vaporize a coupling agent or a solution thereof and blow it against

silica fine powder in a gaseous phase. The coupling agent may preferably be used in an amount of 0.1 to 20 wt. parts, particularly 0.5 to 10 wt. parts, with respect to 100 wt. parts of the inorganic fine powder in respects of maintenance of cationic characteristic and hydropholic characteristic.

The thus treated dispersion stabilizer can exhibit a preferred performance when a water-soluble acidic substance is present in the aqueous medium. The acidic substance has a function of cationizing the nitrogen-containing organic group and may preferably be a Broensted acid such as hydrochloric acid or acetic acid. By adding a Broensted acid, the stability of particles of the monomer composition can be further improved, coalescence of the particles is suppressed, and improvement in desirable toner characteristics may be observed. It is considered that the water-soluble acidic substance acts on the dispersion stabilizer having a nitrogen-containing organic group in the following manner.

Inorganic fine powder treated with a substance having a nitrogen-containing organic group or a coupling agent having a nitrogen-containing organic group may contain remaining unreacted hydroxyl groups. As a result, the function or effect attributable to the cationic characteristic thereof is diminished through inter-particle bonding or particle-particle bonding due to some force like a hydrogen bond acting between the amino group in the coupling agent and the hydroxyl groups in the aqueous medium. Further, the bonding between particles causes so-called secondary agglomeration, so that individual particles are prevented from sufficiently exhibiting their function. When a water-soluble organic substance is caused to be present in such a system, the above mentioned inter-particle bonding and particle-particle bonding are removed to disintegrate the agglomerates, so that the individual particles are sufficiently suspended to improve the function and effect as a dispersion stabilizer.

The stabilization of dispersion provides desirable effects in decreasing the time for dispersion down to a desirable particle size and also in preventing the formation of scale or fine powder by-produced during the polymerization. While the effects are exhibited for both an anionic monomer and an anionic polymer (inclusive of copolymer), a monomer composition containing an anionic polymer is more advantageous than a monomer composition containing no anionic polymer because of substantial freeness from elution into water of the anionic substance, so that it provides better results in respects of scale prevention and shortening of dispersion time and better toner characteristics.

The anionic polymer contained in the monomer composition exerts an electrostatic attraction with the dispersion stabilizer composed of inorganic fine powder provided with a nitrogen-containing organic group which is a cationic dispersant in the aqueous medium to be localized at the surface of the monomer composition particles. As a result, coalescence of the particles during the dispersion and polymerization is prevented, and the toner obtained after the polymerization is improved in negatively charging characteristic. Further, the dispersion stabilizer having a cationic characteristic according to the present invention may be improved in dispersibility in the aqueous medium through ionization due to the addition of a water-soluble acidic substance or protons (H^+) formed therefrom.

The water-soluble acidic substance is a substance which can generate hydrogen ions and neutralize a base to form a salt, shows an acidity, and can preferably quaternarize a nitrogen-containing organic group such as an amino group. For example, an inorganic acid such as hydrochloric acid, sulfuric acid, nitric acid, and phosphoric acid, or an organic acid such as formic acid, acetic acid and lactic acid, may be used. Among these, hydrochloric acid is particularly preferred because it is a strong acid and can be easily removed after the reaction by washing with water or heating. The amount of addition of the acidic substance is adjusted so that the aqueous medium in which the treated dispersant is dispersed is caused to have a pH of 7 - 1, preferably 6.5 - 2, further preferably 6.5 - 3.5.

When the pH is 7 or higher, the cationization of the dispersion stabilizer becomes insufficient. When the pH is below 1, there results in an increased tendency that a magnetic material in the monomer composition is eluted and the reaction vessel and the stirrer are corroded. In order to increase the ionization of the dispersion stabilizer, it is preferred to adjust the addition amount of the water-soluble acidic substance so as to provide a difference in pH of 0.1 - 5.5, particularly 0.5 - 4.0, of the aqueous medium before and after the addition of the water-soluble acidic substance.

The anionic polymer used in the present invention is a polymer which moves to a ⊕ electrode in electrophoresis under the condition of pH 1 - 7. Examples thereof include homopolymers or copolymers of the following anionic monomers. For example, monomers containing a nitrile group such as acrylonitrile, methacrylonitrile, α-chloroacrylonitrile, and vinylidene cyanide; halogen-containing monomers such as vinyl chloride, vinylidene chloride, vinyl bromide, vinyl flouride, chlorostyrene, dichlorostyrene, and bromostyrene; carboxyl group-containing monomers such as acrylic acid, methacrylic acid, and α-chloroacrylic acid; unsaturated dibasic acids and derivatives thereof such as maleic acid, maleic anhydride and maleic acid half ester; nitro group-containing monomers such as o-nitrostyrene, m-nitrostyrene, and p-nitrostyrene; monomers containing a hydroxyl group, ethylene glycol group, propylene glycol group, sulfonic acid group,

phosphoric acid group or glycidyl group such as 2-acrylamide-2-methylpropanesulfonic acid, N-methylolacrylamide, 2-hydroxyethyl acrylate, 2-hydroxypropyl methacrylate, glycidyl methacrylate, polypropylene glycol monomethacrylate, tetrahydrofurfuryl methacrylate, and acid phosphoxyethyl methacrylate. Copolymers of an anionic monomer as described with one or more of the following monomers copolymerizable therewith may also be used.

For example, styrene and its derivatives such as styrene, o-methylstyrene, m-methylstyrene, p-methylstyrene, p-methoxystyrene, p-phenylstyrene, p-chlorostyrene, 3,4-dichlorostyrene, p-ethylstyrene, 2,4-dimethylstyrene, p-n-butylstyrene, p-tert-butylstyrene, p-n-hexylstyrene, p-n-octylstyrene, p-n-nonylstyrene, p-n-decylstyrene, and p-n-dodecylstyrene; ethylenically unsaturated monolefins such as ethylene, propylene, butylene, and isobutylene; halogenated vinyls such as vinyl chloride, vinylidene chloride, vinyl bromide, and vinyl fluoride; vinyl esters such as vinyl acetate, vinyl propionate, and vinyl benzoate; α-methylene aliphatic monocarboxylic acid esters such as methyl methacrylate, ethyl methacrylate, propyl methacrylate, n-butyl methacrylate, isobutyl methacrylate, n-octyl methacrylate, dodecyl methacrylate, 2-ethylhexyl methacrylate, stearyl methacrylate, and phenyl methacrylate; acrylic acid esters such as methyl acrylate, ethyl acrylate, n-butyl acrylate, isobutyl acrylate, propyl acrylate, n-octyl acrylate, dodecyl acrylate, 2-ethylhexyl acrylate, stearyl acrylate, 2-chloroethyl acrylate, and phenyl acrylate; vinyl ethers such as vinyl methyl ether, vinyl ethyl ether, and vinyl isobutyl ether; vinyl ketones such as vinyl methyl ketone, vinyl hexyl ketone, and methyl isopropenyl ketone; N-vinyl compounds such as N-vinylpyrrole, N-vinylcarbazole, N-vinylindole, and N-vinylpyrrolidone; vinylnaphthalenes; derivatives of acrylic acid and methacrylic acids such as acrylonitrile, methacrylonitrile, and acrylamide. Further, polyester resins, cyclic rubber, phenol resin, phenol-modified rosin ester resin, epoxy resin, and silicone resin may also be used. Among these, cyclic rubber is especially preferred when a negatively chargeable toner is produced, because it provides a good negatively chargeable characteristic.

The anionic polymer may preferably be used in an amount of 1 - 30 wt. parts per 100 wt. parts of the polymerizable monomer. Below 1 wt. part, the particle size uniformization effect due to the anionic polymer is not sufficiently exhibited. Above 30 wt. parts, the monomer composition is caused to have too high a viscosity and the particulation becomes difficult. It is preferred that the anionic polymer has a weight-average molecular weight of 5,000 - 500,000 in view of the prevention of coalescence of particles during the polymerization and the anti-blocking property of the toner obtained after the polymerization.

Examples of the polymerizable monomer may include unsaturated dibasic acids and derivatives thereof such as maleic acid, maleic anhydride, and maleic acid half esters; styrene and its derivatives such as styrene, o-methylstyrene, m-methylstyrene, p-methylstyrene, p-methoxystyrene, p-phenylstyrene, p-chlorostyrene, 3,4-dichlorostyrene, bromostyrene, p-ethylstyrene, 2,4-dimethylstyrene, p-n-butylstyrene, p-tert-butylstyrene, p-n-hexylstyrene, p-n-octylstyrene, p-n-nonylstyrene, p-n-decylstyrene, p-n-dodecylstyrene, o-nitrostyrene, m-nitrostyrene, and p-nitrostyrene; ethylenically unsaturated monoolefins such as ethylene, propylene, butylene, and isobutylene; halogenated vinyls such as vinyl chloride, vinylidene chloride, vinyl bromide, and vinyl fluoride; vinyl esters such as vinyl acetate, vinyl propionate, vinyl benzoate; α-methylene-aliphatic monocarboxylic acid esters such as methyl methacrylate, ethyl methacrylate; 2-hydroxyethyl methacrylate, propyl methacrylate, 2-hydroxypropyl methacrylate, n-butyl methacrylate, isobutyl methacrylate, n-octyl methacrylate, dodecyl methacrylate, 2-ethylhexyl methacrylate, stearyl methacrylate, phenyl methacrylate, glycidyl methacrylate, polypropylene glycol monomethacrylate, tetrahydrofurfuryl methacrylate, acid phosphoxyethyl methacrylate, dimethylaminoethyl methacrylate, and diethylaminoethyl methacrylate; acrylic acid esters such as methyl acrylate, ethyl acrylate, n-butyl acrylate, isobutyl acrylate, propyl acrylate, n-octyl acrylate, dodecyl acrylate, 2-ethylhexyl acrylate, stearyl acrylate, 2-chloroethyl acrylate, and phenyl acrylate; vinyl ethers such as vinyl methyl ether, vinyl ethyl ether, and vinyl isobutyl ether; vinyl ketones such as vinyl methyl ketone; vinyl hexyl ketone, and methyl isopropenyl ketone; N-vinyl compounds such as N-vinylpyrrole, N-vinylcarbazole, N-vinylindole, and N-vinylpyrrolidone; vinyl naphthalenes; derivatives of acrylic acid or methacrylic acid such as acrylonitrile, methacrylonitrile, α-chloroacrylonitrile, acrylamide, N-methylolacrylamide, and 2-acrylamide-2-methylpropanesulfonic acid. Among these, styrene; styrene having a substituent; combination of styrene and acrylic acid; combination of styrene and methacrylic acid; or combination of styrene and an acrylic acid ester; is particularly preferred as a polymerizable monomer in view of the developing characteristic and the durability of the resultant polymerization toner.

It is also possible to have a crosslinking agent as exemplified below in the polymerization system to produce a crosslinked polymer.

Examples of the crosslinking agent may appropriately include: divinylbenzene, divinylnaphthalene, divinyl ether, divinyl sulfone, diethylene glycol dimethacrylate, triethylene glycol dimethacrylate, ethylene glycol dimethacrylate, polyethylene glycol dimethacrylate, diethylene glycol diacrylate, triethylene glycol

diacrylate, 1,3-butylene glycol dimethacrylate, 1,6-hexane glycol dimethacrylate, neopentyl glycol dimethacrylate, dipropylene glycol dimethacrylate, polypropylene glycol dimethacrylate, 2,2'-bis(4-methacryloxydiethoxyphenyl)propane, 2,2'-bis(4-acryloxydiethoxyphenyl)propane, trimethylolpropane trimethacrylate, trimethylolpropane triacrylate, tetramethylolmethane tetraacrylate, dibromoneopentyl glycol dimethacrylate, and diallyl phthalate. Among these, diethylene glycol dimethacrylate, triethylene glycol dimethacrylate and ethylene glycol dimethacrylate are preferred in view of the anti-offset characteristic and hot-press fixability.

If such a crosslinking agent is used in an excessive amount, the resultant toner particles lose fusibility to show a poor fixability. If the amount is too small, properties such as anti-offset characteristic, anti-blocking characteristic and durability become poor, so that it becomes difficult to prevent the offset phenomenon that, in hot-press roller fixation, a portion of a toner is not completely fixed onto paper but fixed onto a roller surface, and is then re-transferred onto a subsequent sheet of paper. For these reasons, the amount of use of the crosslinking agent may suitably be 0.001 - 15 wt.%, preferably 0.1 - 10 wt.%, of the total amount of the monomer.

The polymerization of the monomer may be effected by using a polymerization initiator such as azobisisobutyronitrile (AIBN), benzoyl peroxide, methyl ethyl ketone peroxide, isopropyl peroxycarbonate, cumene hydroperoxide, 2,4-dichlorobenzoyl peroxide, lauroyl peroxide, azobis-(2,4-dimethylvaleronitrile), and a mixture of these. The initiator is generally used in an amount of about 0.5 - 5 wt.% of the monomer.

It is preferable to add a release agent to a toner in order to improve the fixability and the offset characteristic of the toner. The release agent used in the present invention may be a substance which reduces a friction between the fixing roller and the toner at the time of fixation or improves the fluidity at the time of melting. Examples of the release agent include polyethylene fluoride, fluorinated resin, fluorinated carbon oil, silicone oil, low-molecular weight polyethylene, low-molecular weight polypropylene, and long chain compounds having carbon chains. The release agent may preferably be used in an amount of 0.5 - 15. wt. parts per 100 wt. parts of the monomer. Below 0.5 wt. parts, the effect is not sufficient, while above 15 wt. parts, there increases a tendency that the anti-blocking characteristic and the fixation characteristic are lowered.

Examples of the long chain compounds having carbon chains include hydrocarbons, chlorinated hydrocarbons, fluorinated hydrocarbons; aliphatic acids, aliphatic acid esters, aliphatic acid metal salts; aliphatic alcohols; polyhydric alcohols; amides; and bisamides. These materials are commercially available as a single substance or a mixture. These substances are generally known as paraffin wax, microcrystalline wax, montan wax, ceresine wax, ozocerite, carnauba wax, rice wax, shellac wax, sasol wax, melallic soap, amide wax, and lubricant. Examples of commercially available products include the following: Paraffin Wax (Nihon Sekiyu K.K.), Paraffin Wax (Nihon Seiro K.K.), Microwax (Nihon Sekiyu K.K.), Microcrystalline Wax (Nihon Seiro K.K.), Hoechst Wax (Hoechst A.G.), Diamond Wax (Shinnihon Rika K.K.), Santite (Seiko Kagaku K.K.), and Panasete (Nihon Yushi K.K.).

Representative grades of paraffin wax include those shown in the following Tables 1 and 2.

Table 1

Paraffin wax and Microwax (produced by Nippon Sekiyu K.K.)	
Trade Name	m.p. °C
Nisseki No. 1 Candle wax	59.7
Nisseki No. 2 Candle wax	62.0
125° Paraffin	54.3
130° Paraffin	56.5
135° Paraffin	59.7
140° Paraffin	61.9
145° Paraffin	63.2
125° FD Paraffin	53.8
Paraffin wax (M)	54.1
125° Special paraffin	54.2
Nisseki Microwax 155	70.0
Nisseki Microwax 180	83.6

Table 2

Paraffin wax (produced by Nippon Seiro K.K.)				
Trade Name	m.p. °C	Trade Name	m.p. °C	Trade Name
155	70	SP-0145	62	NCW-5
150	66	SP-1035	58	NCW-10
140	60	SP-1030	56	NCW-35
135	58	SP-3040	63	NCW-38
130	55	SP-3035	60	NCW-40
125	53	SP-3030	57	NCW-42
120	50	FR-0120	50	NCW-45
115	47			NCW-50
				NCW-55
				NCW-60
				NCW-110
				NCW-120
				NCW-125

As a monomer readily soluble in water simultaneously causes emulsion polymerization to contaminate the resultant suspension polymerizate with finer emulsion polymer particles, it is effective to add a water-soluble polymerization inhibitor such as a metal salt to prevent the emulsion polymerization in the aqueous phase. It is also possible to add a salt such as NaCl, KCl or Na_2SO_4 in order to decrease the solubility of a readily water-soluble monomer in water.

After the completion of the reaction, the dispersion stabilizer attached to the produced toner particles is removed. This can be carried out by dissolution through by washing with water, an alkaline aqueous solution or an acidic aqueous solution in a known manner. Especially in a case of treated colloidal silica, after the reaction, the toner particles formed are changed in a prescribed concentration of an alkaline aqueous solution or a prescribed weight of alkali is charged into the reaction vessel, and the mixture is stirred for 3 - 24 hours at room temperature to 40 °C, followed by filtration, sufficient washing with water and drying to obtain a toner.

In the suspension polymerization, a monomer composition obtained by uniformly dissolving or dispersing a polymerization initiator, a colorant, a monomer, an anionic polymer and other optional additives, may be dispersed in an aqueous phase containing a dispersion stabilizer and an acidic substance by means of an ordinary stirrer, homomixer or homogenizer. Preferably, the speed and time for stirring may be adjusted so that the droplets of the monomer composition have the desired toner particle size of generally 30 μm or below, and after that, the stirring is effected to such an extent that the dispersion state is substantially maintained as such while preventing the sedimentation of the particles. The polymerization temperature may be set to a temperature of 50 °C or above, generally 70 - 90 °C. The suspension polymerization reaction may suitably be conducted for a period of 0.5 - 24 hours. After the completion of the reaction, the resultant toner particles are washed, recovered by an appropriate method such as filtration, decantation and centrifugation, and dried.

Examples of the colorant may include dyes or pigments such as carbon black, iron black, phthalocyanine blue, ultramarine, quinacridone, and benzidine yellow. The colorant may be ordinarily used in an amount of 0.5 - 20 wt. parts per 100 wt. parts of the monomer.

In a case of providing a magnetic toner by incorporating magnetic powder, a substance magnetizable when placed in a magnetic field, may be used as the magnetic material. The magnetic powder comprise powder of a ferromagnetic metal such as iron, cobalt and nickel, or an alloy or a compound thereof such as magnetite, hematite and ferrite. The magnetic powder may also pay a role of colorant. The magnetic powder may be added in such an amount as to constitute 15 - 70 wt.% of the toner. It is possible that the magnetic powder may be coated with a resin or an appropriate treating agent. It is also possible to add a known additive for dispersing magnetic powder. A magnetic material (powder) showing a hydrophobicity through treatment with a resin or an appropriate treating agent may be particularly preferred.

A charge controller and a fluidity improver may be added as desired in the monomer composition in order to improve the charge controllability and fluidity of the polymerization toner. The charge controller and the fluidity improver may also be mixed with (externally added to) the toner particles. The charge controller may for example be a metal-containing dye or nigrosine. The fluidity improver may for example be colloidal

silica or an aliphatic acid metal salt. It is also possible to incorporate a filler such as calcium carbonate or fine powdery silica in an amount of 0.5 - 20 wt.% in the toner for the purpose of extension. Further, it is possible to add a fluidity improver such as polytetrafluoroethylene fine powder in order to disintegrate the agglomerate of the toner particles and improve the fluidity.

The developing method using the toner produced as described above may be any of the known methods including the two-component developing methods such as the cascade method, the magnetic brush method, and the microtoning method; the one-component developing methods using a toner containing a magnetic material such as the electroconductive one-component developing method, the insulating one-component developing method and the jumping developing method; the powder cloud method and the fur brush method; and the non-magnetic one-component developing method wherein the toner is carried on a toner-carrying member to be conveyed to a developing position and subjected to developing thereat.

Hereinbelow, the present invention will be explained by way of examples.

Example 1

Styrene monomer	160 g
n-Butyl methacrylate monomer	40 g
Styrene-acrylonitrile-methacrylic acid copolymer (St./AT/MAA = 85/15/5, $\overline{Mw}$ = 50,000)	10 g
Paraffin wax 155°F	8 g
Lipophilized magnetic material (average particle size: 0.3 μ)	120 g

The above ingredients were heated at 70°C to dissolve the copolymer in the styrene monomer and uniformly disperse the insoluble. Thereafter, the monomer composition was mixed for about 5 minutes while being heated at about 70°C in a vessel provided with a high-shearing force mixer (TK homomixer, mfd. by Tokushu Kika Kogyo K.K.). Then, 10 g of azobisisobutyronitrile was dissolved therein.

Separately, 10 g of silica (Aerosil #200) treated with 5 % of γ-aminopropylethoxysilane was dispersed in 1000 ml of water, and 20 g of 0.1N-HCl was added thereto. The aqueous phase showed pH 7.4 before the addition of 0.1N-HCl and pH 6 after the addition, according to measurement by use of pH test paper. Then, while heating the aqueous phase at 70°C, the above monomer composition was charged thereinto under stirring by means of the TK homomixer, and the system was further stirred at 8000 rpm for about 30 minutes. Then, the system was stirred by means of a paddle blade stirrer to complete the polymerization. The dispersant was removed by adding sodium hydroxide into the aqueous phase, and the remaining particles were subjected to filtration, washing with water, and drying to obtain a toner. Fine powder portion (scale) was removed by passing the toner through a 200-mesh sieve and measured to be below 1 %. The resultant toner showed a volume-average particle size of 11.5 μm. Hydrophobic silica (R-972) in an amount of 0.4 g was added to and mixed with 100 g of the toner to form a developer. The developer was used for image formation by means of an electrophotographic copier (NP-270RE, mfd. by Canon K.K.), whereby sharp images were obtained. In continuous image formation, no practical deterioration in images was observed, and sharp images of high density were continually obtained. Even under high temperature-high humidity environmental conditions, no practical problem was observed as compared with the image formation under the normal temperature-normal humidity conditions to obtain a high image density.

10 g of the toner produced above was charged in a 100 ml-polyethylene container and left standing for 3 days under the environmental conditions of a temperature of 50°C and a relative humidity of 60 ± 5 %, whereby no agglomeration block to such an extent as to exert ill effects to developing was observed, and the toner was found to have an excellent anti-blocking characteristic. This is considered because the styrene-acrylonitrile-methacrylic acid copolymer having a $\delta^{\ominus}$ charge was electrostatically attracted by the $\delta^{\oplus}$ charge of the amino group present at the surface of the silica used as the dispersion stabilizer to be localized at the surface of the toner particles.

Comparative Example 1

The suspension polymerization was conducted in the same manner as in Example 1 except that the 20 g of 0.1N-HCl was not added into the aqueous phase. In order to obtain the same particle size as in Example 1, 45 minutes of stirring with a homomixer rotating at 45 minutes. Fine scale portion was removed by a 200-mesh sieve and measured to be 4 wt.%.

10 g of the resultant toner was charged in a 100 ml-polyethylene container and left standing for 3 days under the environmental conditions of a temperature of 50°C and a relative humidity of 60 ± 5 %, whereby agglomeration blocks of 1 - 5 mm were found to be formed. This is considered because the electrostatic attraction exerted by the amino group on the silica surface was weakened and the degree of localization of the styrene-acrylonitrilemethacrylic acid copolymer at the toner particle surfaces was lowered so that the anti-blocking property was deteriorated as compared with that in Example 1.

At the same time, when the developer including the toner was subjected to image formation by means of the NP-270RE copier, sharp images were obtained at the initial stage, whereas fog increased gradually during continuous image formation. Further, under the environmental conditions of high temperature and high humidity, fog was noticeably observed from the initial stage.

Example 2

Styrene monomer	160 g
2-Ethylhexyl methacrylate monomer	40 g
Cyclic rubber (CK-450, mfd. by Hoechst A.G.)	10 g
Paraffin wax 155°F	8 g
Magnetite (BL-250, Titan Kogyo K.K.)	120 g
Stearic acid	2 g

The above ingredients were heated at 80°C to effect dissolution and dispersion. The monomer composition was subjected to mixing at 60°C for about 10 minutes in a vessel provided with a TK homomixer. Then, 10 g of azobis-(2,4-dimethylvaleronitrile) was dissolved therein.

Separately, 10 g of silica (Aerosil #200) treated with 5 wt.% of γ-aminopropylmethoxysilane was dispersed in 1000 ml of water, and 19 g of 0.1N-HCl was added thereto. The measurement with pH test paper showed pH 7.4 before the addition and pH about 6.3 after the addition. Then, the polymerization was conducted at 60°C to obtain a toner. The amount of scale contained in the toner was below 1 %.

Image formation was conducted similarly as in Example 1, whereby good images were obtained.

Example 3

A toner was obtained in the same manner as in Example 1 except that 120 g of the lipophilized magnetic material was replaced by 10 g of phthalocyanine blue. The content of the scale was below 1 %. The toner was mixed with iron powder carrier (EFV 250/400, mfd. by Nihon Teppun K.K.) so as to obtain a developer having a toner content of 10 wt.%, which was then subjected to image formation by means of a copier (NP-5500, mfd. by Canon K.K.), whereby good images were obtained.

Example 4

Styrene	160 g
n-Butyl methacrylate	40 g
Methacrylic acid	2 g
Cyclic rubber	5 g
Phthalocyanine Blue	10 g
Azobisisobutylonitrile	10 g

A toner was prepared in the same manner as in Example 3 by using the above composition. The resultant polymerization toner showed a good negative chargeability and was excellent in anti-blocking characteristic.

As described hereinabove, the polymerization toner produced according to the present invention provides sharp images of high density and also provides images of high quality even under continuous use and under enrivonmental conditions of high temperature and high humidity. Further, the toner has a sharp particle size distribution and is also excellent in anti-blocking characteristic.

Claims

1. A process for producing a toner, comprising:
adding a monomer composition comprising at least a polymerizable monomer, an anionic polymer, a polymerization initiator and a colorant, into an aqueous medium to which a cationic dispersion stabilizer composed of inorganic fine powder provided with a nitrogen-containing organic group and a water-soluble acidic substance have been added, dispersing the monomer composition into particles with a prescribed particle size in the aqueous medium, and
subjecting the particles of the monomer composition to suspension polymerization to produce toner particles to which said dispersion stabilizer is attached, and
removing the dispersion stabilizer which is attached to the suspension-polymerized toner particles.

2. A process according to Claim 1, wherein said water-soluble acidic substance is a Broensted acid.

3. A process according to Claim 2, wherein said water-soluble substance is an inorganic acid selected from the group consisting of hydrochloric acid, sulfuric acid, nitric acid, and phosphoric acid.

4. A process according to Claim 2, wherein said water-soluble acidic substance is formic acid or lactic acid.

5. A process according to Claim 1, wherein said dispersion stabilizer comprises dry-process silica or wet-process silica treated with a coupling agent having a primary to quaternary amino group.

6. A process according to Claim 1, wherein said aqueous medium shows a pH of 7 to 1.

7. A process according to Claim 6, wherein said aqueous medium shows a pH of 6.5 to 2.

8. A process according to Claim 7, wherein said aqueous medium shows a pH of 6.5 to 3.5.

9. A process according to Claim 1, wherein said monomer composition comprises 1 - 30 wt. parts of the anionic polymer per 100 wt. parts of the polymerizable monomer.

10. A process according to Claim 1, wherein said anionic polymer has a weight-average molecular weight of 5,000 - 500,000.

11. A process according to Claim 1, wherein said polymerizable monomer is a vinyl monomer.

12. A process according to Claim 1, wherein said polymerizable monomer comprises a vinyl monomer selected from the group consisting of styrene, acrylic acid, alkyl acrylate ester, methacrylic acid, alkyl methacrylate ester, and mixtures of these.

13. A process according to Claim 1, wherein said monomer composition further comprises a crosslinking agent.

14. A process according to Claim 13, wherein said crosslinking agent is a monomer having at least two vinyl groups.

15. A process according to Claim 14, wherein said monomer composition contains 0.001 - 15 wt. % of the crosslinking agent based on the total amount of the polymerizable monomer.

16. A process according to Claim 15, wherein said monomer composition contains 0.1 - 10 wt.% of the crosslinking agent based on the total amount of the polymerizable monomer.

17. A process according to Claim 16, wherein the suspension polymerization is carried out at a temperature of 50 °C or higher.

18. A process according to Claim 17, wherein the suspension polymerization is carried out at a temperature of 70 - 90 °C.

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19. A process according to claim 1, wherein the dispersion stabilizer attached to the toner particles is removed by washing with water.

20. A process according to claim 1, wherein the dispersion stabilizer attached to the toner particles is removed by washing with an alkaline aqueous solution.

21. A process according to claim 1, wherein the dispersion stabilizer attached to the toner particles is removed by washing with an acidic aqueous solution.

22. A process according to claim 1, wherein the dispersion stabilizer comprises colloidal silica having a nitrogen-containing organic group.

23. A process according to claim 1, wherein said monomer composition further comprises a release agent.

24. A process according to claim 23, wherein said release agent is selected from the group consisting of polyethylene fluoride, fluorinated resin, fluorinated carbon oil, silicone oil, low-molecular weight polyethylene, low-molecular weight polypropylene, and long chain carbon compounds.

25. A process according to claim 24, wherein said release agent is contained in an amount of 0.5 - 15 wt. parts per 100 wt. parts of said polymerizable monomer in said monomer composition.

26. A process according to claim 24, wherein said long chain carbon compound is selected from the group consisting of hydrocarbons, chlorinated hydrocarbons, fluorinated hydrocarbons, aliphatic acids, aliphatic acid esters, aliphatic acid metal salts, aliphatic alcohols, polyhydric alcohols, amides and bisamides.

27. A process according to claim 26, wherein said long chain carbon compound is selected from the group consisting of paraffin wax, microcrystalline wax, montan wax, ceresine wax, ozocerite, carnauba wax, rice wax, shellac wax, sasol wax, metallic soap, amide wax, and lubricant.

Patentansprüche

1. Verfahren zur Herstellung eines Toners **dadurch gekennzeichnet,** daß es folgendes umfasst:
die Zugabe einer Monomerzusammensetzung, die mindestens ein polymerisationsfähiges Monomer, ein anionisches Polymer, einen Polymerisationsinitiator und ein Färbemittel umfasst, in ein wässriges Medium, zu dem ein kationischer Dispersionsstabilisator, der aus anorganischem, feinem Pulver besteht und mit einer stickstoffhaltigen, organischen Gruppe ausgestattet ist und eine wasserlösliche, saure Substanz zugegeben wurden,
die Dispersion der Monomerzusammensetzung in dem wässrigen Medium in Teilchen mit einer vorgeschriebenen Teilchengröße, und
die Durchführung von Suspensionspolymerisation mit den Teilchen der Monomerzusammensetzung unter Herstellung von Tonerteilchen, mit denen der Dispersionsstabilisator verbunden ist, und
die Entfernung des Dispersionsstabilisators der mit den suspensionspolymerisierten Tonerteilchen verbunden ist.

2. Verfahren nach Anspruch 1 **dadurch gekennzeichnet,** daß die wasserlösliche, saure Substanz eine Brönsted-Säure ist.

3. Verfahren nach Anspruch 2 **dadurch gekennzeichnet,** daß die wasserlösliche Substanz eine anorganische Säure ist, ausgewählt aus Salzsäure, Schwefelsäure, Salpetersäure und Phosphorsäure.

4. Verfahren nach Anspruch 2 **dadurch gekennzeichnet,** daß die wasserlösliche, saure Substanz Ameisensäure oder Milchsäure ist.

5. Verfahren nach Anspruch 1 **dadurch gekennzeichnet,** daß der Dispersionsstabilisator Siliziumdioxid, das nach einem trockenen Verfahren hergestellt wurde oder Siliziumdioxid, das nach einem nassen Verfahren hergestellt wurde, umfasst, das mit einem Kopplungsmittel mit einer primären bis quartären Aminogruppe behandelt wurde.

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6. Verfahren nach Anspruch 1 **dadurch gekennzeichnet,** daß das wässrige Medium einen pH von 7 bis 1 hat.

7. Verfahren nach Anspruch 6 **dadurch gekennzeichnet,** daß das wässrige Medium einen pH von 6,5 bis 2 hat.

8. Verfahren nach Anspruch 7 **dadurch gekennzeichnet,** daß das wässrige Medium einen pH von 6,5 bis 3,5 hat.

9. Verfahren nach Anspruch 1 **dadurch gekennzeichnet,** daß die Monomerzusammensetzung 1 bis 30 Gewichtsteile des anionischen Polymers pro 100 Gewichtsteilen des polymerisationsfähigen Monomers umfasst.

10. Verfahren nach Anspruch 1 **dadurch gekennzeichnet,** daß das anionische Polymer ein gewichtsbezogenes, mittleres Molekulargewicht von 5000 bis 500000 besitzt.

11. Verfahren nach Anspruch 1 **dadurch gekennzeichnet,** daß das polymerisationsfähige Monomer ein Vinylmonomer ist.

12. Verfahren nach Anspruch 1 **dadurch gekennzeichnet,** daß das polymerisationsfähige Monomer ein Vinylmonomer umfasst, ausgewählt aus Styrol, Acrylsäure, Alkylacrylatester, Methacrylsäure, Alkylmethacrylatester und Mischungen davon.

13. Verfahren nach Anspruch 1 **dadurch gekennzeichnet,** daß die Monomerzusammensetzung ferner ein Quervernetzungsmittel umfasst.

14. Verfahren nach Anspruch 13 **dadurch gekennzeichnet,** daß das Quervernetzungsmittel ein Monomer mit mindestens zwei Vinylgruppen ist.

15. Verfahren nach Anspruch 14 **dadurch gekennzeichnet,** daß die Monomerzusammensetzung 0,001 bis 15 Gew.-% des Quervernetzungsmittels, bezogen auf die Gesamtmenge des polymerisationsfähigen Monomers, enthält.

16. Verfahren nach Anspruch 15 **dadurch gekennzeichnet,** daß die Monomerzusammensetzung 0,1 bis 10 Gew.-% des Quervernetzungsmittels, bezogen auf die Gesamtmenge des polymerisationsfähigen Monomers, enthält.

17. Verfahren nach Anspruch 16 **dadurch gekennzeichnet,** daß die Suspensionspolymerisation bei einer Temperatur von 50 °C oder mehr ausgeführt wird.

18. Verfahren nach Anspruch 17 **dadurch gekennzeichnet,** daß die Suspensionspolymerisation bei einer Temperatur von 70 bis 90 °C ausgeführt wird.

19. Verfahren nach Anspruch 1 **dadurch gekennzeichnet,** daß der mit den Tonerteilchen verbundene Dispersionsstabilisator durch Waschen mit Wasser entfernt wird.

20. Verfahren nach Anspruch 1 **dadurch gekennzeichnet,** daß der mit den Tonerteilchen verbundene Dispersionsstabilisator durch Waschen mit einer alkalischen, wässrigen Lösung entfernt wird.

21. Verfahren nach Anspruch 1 **dadurch gekennzeichnet,** daß der mit den Tonerteilchen verbundene Dispersionsstabilisator durch Waschen mit einer sauren, wässrigen Lösung entfernt wird.

22. Verfahren nach Anspruch 1 **dadurch gekennzeichnet,** daß der Dispersionsstabilisator kolloidales Siliziumdioxid mit einer stickstoffhaltigen, organischen Gruppe umfasst.

23. Verfahren nach Anspruch 1 **dadurch gekennzeichnet,** daß die Monomerzusammensetzung ferner ein Freisetzungsmittel umfasst.

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24. Verfahren nach Anspruch 23 **dadurch gekennzeichnet,** daß das Freisetzungsmittel ausgewählt wird aus Polyethylenfluorid, fluoriertem Harz, fluoriertem Karbonöl, Silikonöl, Polyethylen mit niedrigem Molekulargewicht, Polypropylen mit niedrigem Molekulargewicht und langkettigen Kohlenstoffverbindungen.

25. Verfahren nach Anspruch 24 **dadurch gekennzeichnet,** daß das Freisetzungsmittel in der Monomerzusammensetzung in einer Menge von 0,5 bis 15 Gewichtsteilen pro 100 Gewichtsteilen des polymerisationsfähigen Monomers enthalten ist.

26. Verfahren nach Anspruch 24 **dadurch gekennzeichnet,** daß die langkettige Kohlenstoffverbindung ausgewählt wird aus Kohlenwasserstoffen, chlorierten Kohlenwasserstoffen, fluorierten Kohlenwasserstoffen, aliphatischen Säuren, aliphatischen Säureestern, aliphatischen, sauren Metallsalzen, aliphatischen Alkoholen, mehrwertigen Alkoholen, Amiden und Bisamiden.

27. Verfahren nach Anspruch 26 **dadurch gekennzeichnet,** daß die langkettige Kohlenstoffverbindung ausgewählt wird aus Paraffinwachs, Mikrokristallinwachs, Montanwachs, Ceresinwachs, Ozokerit, Karnaubawachs, Reiswachs, Schellackwachs, Sasolwachs, Metallseife, Amidwachs und Schmiermittel.

Revendications

1. Procédé de production d'un toner, qui consiste :
à introduire une composition de monomère comprenant au moins un monomère polymérisable, un polymère anionique, un initiateur de polymérisation et un colorant dans un milieu aqueux auquel ont été ajoutés un stabilisant de dispersion cationique composé d'une fine poudre inorganique portant un groupe organique contenant de l'azote et d'une substance acide hydrosoluble,
à disperser la composition de monomère en particules de diamètre prédéterminé dans le milieu aqueux et
à soumettre les particules de la composition de monomère à une polymérisation en suspension pour produire des particules de toner auxquelles ledit stabilisant de dispersion est attaché, et
à éliminer le stabilisant de dispersion qui est attaché aux particules de toner polymérisées en suspension.

2. Procédé suivant la revendication 1, dans lequel la substance acide hydrosoluble est un acide de Broensted.

3. Procédé suivant la revendication 2, dans lequel la substance hydrosoluble est un acide inorganique choisi dans le groupe comprenant l'acide chlorhydrique, l'acide sulfurique, l'acide nitrique, l'acide phosphorique.

4. Procédé suivant la revendication 2, dans lequel la substance acide hydrosoluble est l'acide formique ou l'acide lactique.

5. Procédé suivant la revendication 1, dans lequel le stabilisant de dispersion comprend de la silice obtenue par voie sèche ou de la silice obtenue par voie humide traitée avec un agent de couplage portant un groupe amino primaire à quaternaire.

6. Procédé suivant la revendication 1, dans lequel le milieu aqueux a un pH de 7 à 1.

7. Procédé suivant la revendication 6, dans lequel le milieu aqueux a un pH de 6,5 à 2.

8. Procédé suivant la revendication 7, dans lequel le milieu aqueux a un pH de 6,5 à 3,5.

9. Procédé suivant la revendication 1, dans lequel la composition de monomère comprend 1 à 30 parties en poids du polymère anionique pour 100 parties en poids du monomère polymérisable.

10. Procédé suivant la revendication 1, dans lequel le polymère anionique a une moyenne pondérale du poids moléculaire de 5000 à 500 000.

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11. Procédé suivant la revendication 1, dans lequel le monomère polymérisable est un monomère vinylique.

12. Procédé suivant la revendication 1, dans lequel le monomère polymérisable comprend un monomère vinylique choisi dans le groupe formé du styrène, de l'acide acrylique, d'un acrylate d'alkyle, de l'acide méthacrylique, d'un méthacrylate d'alkyle et de mélanges de ces monomères.

13. Procédé suivant la revendication 1, dans lequel la composition de monomère comprend en outre un agent de réticulation.

14. Procédé suivant la revendication 13, dans lequel l'agent de réticulation est un monomère portant au moins deux groupes vinyle.

15. Procédé suivant la revendication 14, dans lequel la composition de monomère contient 0,001 à 15 % en poids de l'agent de réticulation sur la base de la quantité totale du monomère polymérisable.

16. Procédé suivant la revendication 15, dans lequel la composition de monomère contient 0,1 à 10 % en poids de l'agent de réticulation sur la base de la quantité totale du monomère polymérisable.

17. Procédé suivant la revendication 16, dans lequel la polymérisation en suspension est conduite à une température égale ou supérieure à 50 °C.

18. Procédé suivant la revendication 17, dans lequel la polymérisation en suspension est conduite à une température de 70 à 90 °C.

19. Procédé suivant la revendication 1, dans lequel le stabilisant de dispersion attaché aux particules de toner est éliminé par lavage à l'eau.

20. Procédé suivant la revendication 1, dans lequel le stabilisant de dispersion attaché aux particules de toner est éliminé par lavage avec une solution aqueuse alcaline.

21. Procédé suivant la revendication 1, dans lequel le stabilisant de dispersion attaché aux particules de toner est éliminé par lavage avec une solution aqueuse acide.

22. Procédé suivant la revendication 1, dans lequel le stabilisant de dispersion comprend de la silice colloïdale portant un groupe organique contenant de l'azote.

23. Procédé suivant la revendication 1, dans lequel la composition de monomère comprend en outre un agent de décollement.

24. Procédé suivant la revendication 23, dans lequel l'agent de décollement est choisi dans le groupe comprenant un polymère de fluorure d'éthylène, une résine fluorée, une huile carbonée fluorée, une huile de silicone, un polyéthylène de bas poids moléculaire, un polypropylène de bas poids moléculaire et des composés carbonés à longue chaîne.

25. Procédé suivant la revendication 24, dans lequel l'agent de décollement est contenu en quantité de 0,5 à 15 parties en poids pour 100 parties en poids dudit monomère polymérisable dans la composition de monomère.

26. Procédé suivant la revendication 24, dans lequel le composé carboné à longue chaine est choisi dans le groupe comprenant des hydrocarbures, des hydrocarbures chlorés, des hydrocarbures fluorés, des acides aliphatiques, des esters d'acides aliphatiques, des sels métalliques d'acides aliphatiques, des alcools aliphatiques, des alcools polyhydroxyliques, des amides et des bisamides.

27. Procédé suivant la revendication 26, dans lequel le composé carboné à longue chaîne est choisi dans le groupe comprenant une cire paraffinique, une cire microcristalline, la cire montane, la cire cérésine, l'ozocérite, la cire de carnauba, la cire de riz, la gomme-laque, la cire sasol, un savon métallique, une cire amidique et un lubrifiant.

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