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(54) Electrophotographic toner and developer

(57) The present invention provides a toner comprising at least a fixing resin and a colorant, wherein a graft polymer consisting of a main chain of a styrene polymer and a graft chain represented by the following general formula (1) is formulated. This toner is superior in low-temperature fixing properties without causing blocking or offset. Furthermore, when the colorant is retained in or on the graft polymer particle, the dispersion properties of the colorant are also improved. In addition, a developer obtained by using the above toner in combination with a magnetic carrier wherein the surface of a magnetic particle is coated with a coat layer of a silicone resin or a fluororesin is superior in charging properties of the toner.

Fig. 1

Printed by Jouve, 75001 PARIS (FR)

Description

BACKGROUND OF THE INVENTION

The present invention relates to an electrophotographic toner which is used in image forming apparatus such as electrostatic copying machines, plain paper facsimile apparatus, laser beam printers, etc.

The electrophotographic toner is normally produced by dispersing a colorant, an electric charge controlling material, etc. in a suitable fixing resin, followed by pulverizing and additional classification.

One of the important characteristics of such an electrophotographic toner include fixing properties to paper, etc. That is, the toner transferred on the paper surface is molten by passing through heated fixing rollers in the image forming apparatus, and then fixed on the paper surface. However, the fixing temperature is liable to decrease according to recent demands on the image forming apparatus, such as miniaturization, speeding-up, electric power saving, etc. Therefore, a toner showing good fixing properties at low temperature has been required in response to the above demands.

On the other hand, it has been well known that, when a low-melting point substance as a fixing auxiliary is added in the toner, the fixing temperature can be easily decreased. That is, in Japanese Laid-Open Patent Publication No. 4-277753, there is disclosed a toner for flash fusing wherein a polymer having a glass transition temperature of not more than 8 °C as a low-Tg additive and a fatty acid bisamide wax are contained in a predetermined fixing resin, together with a colorant. In Japanese Laid-Open Patent Publication No. 62-191858, there is disclosed a toner composition wherein a styrene polymer oligomer having a number-average molecular weight of not more than 1,000 is contained in a fixing resin comprising a styrene copolymer as a main component.

However, when these low-melting point substances are added to the toner, there are problems that so-called blocking wherein toners are fused each other, or so-called offset such as back contamination of papers, contamination of fixing rollers, etc. are generated.

These problems are caused by using the low-melting point substance which are miscible with the fixing resin for toner so as to prevent fracture of the toner. That is, since the low-melting point substance is miscible with the fixing resin of the toner, it exists on the whole of the toner surface uniformly, thereby causing blocking of the toner, offset, etc.

In addition, it has been suggestedthat the low-melting point substance is embedded in the toner by capsulating it. However, there is a problem that it is not produced easily because of its complicated structure.

Another one of important characteristics of the electrophotographic toner includes dispersion properties of the colorant. Among the carbon blacks which have widely been used as the colorant for black toner, particularly a carbon black having a particle size of not more than 40 nm, which has high coloring properties, is not easily uniformly dispersed in the toner. Therefore, the above carbon black is liable to agglomerate in the toner to form a huge mass. It has been studied to use the above carbon black for a toner wherein the particle size is liable to decrease in response to the accomplishment of high-quality image of the formed image.

If the above mass is formed, the carbon black falls out from the above mass part or a fracture is formed on the toner when the toner is stirred repeatedly in a developing vessel of the image forming apparatus. As a result, the magnetic carrier circulating in the developing vessel together with the toner or the interior of developing vessel is contaminated with the fragments of toner particles, fallen-out carbon black.

Therefore, there is a problem that the life of the developer is shortened to cause unstabilization of the image density due to a change in the charged amount of the toner as well as image failures such as toner scattering, image fog, etc., or contamination of the image or apparatus.

In addition, there is also a problem that sufficient coloring cannot be obtained, although carbon black having a particle size of not more than 40 nm, which has high coloring properties, is used because of its insufficient dispersion properties.

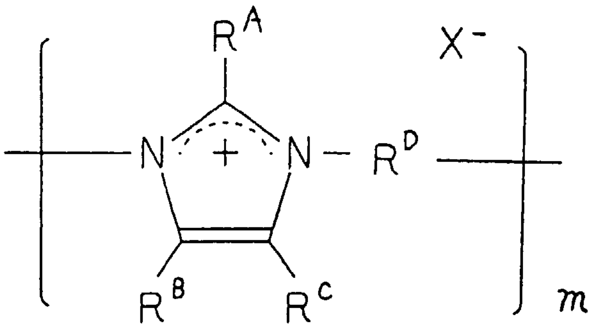
In Japanese Laid-Open Patent Publication No. 2-52362, there is disclosed a toner wherein a terminal amide-modified polyester is contained in a fixing resin as a pigment surface treating agent, so as to improve the dispersion properties of the pigment. However, the pigment surface treating agent to be used is expensive and an amine is used for amidation of the terminal end of the polyester as this treating agent and, therefore, the toner is positively charged by the residual amine, thereby causing a problem of lack of toner density due to over charging. Also, there is a problem that it is inferior in environmental resistance (humidity resistance).

In Japanese Laid-Open Patent Publication No. 3-155568 (EP-A-402882), it is disclosed that a fixing resin, a colorant and an organic solvent in which the fixing resin can be dissolved are mixed and pulverized or granulated to obtain a masterbatch (coloring material wherein a high concentration of a pigment is dispersed and incorporated in a resin), and then, the rest of the fixing resin and other additives are added and the mixture is pulverized to form a toner, so as to disperse the colorant into the toner particles uniformly. However, the toner is produced via the preparation process of the masterbatch and, therefore, the production process of the toner becomes complicated, which results in high cost of the toner.

On the other hand, various compounds such as dyes, etc. have been used for the above electric charge controlling material contained in the fixing resin of the toner according to the charged polarity of the toner. Taking the environmental and correspondence to color toners into consideration, the use as the positive charging tone of a white quaternary ammonium salt containing no metal has recently been studied.

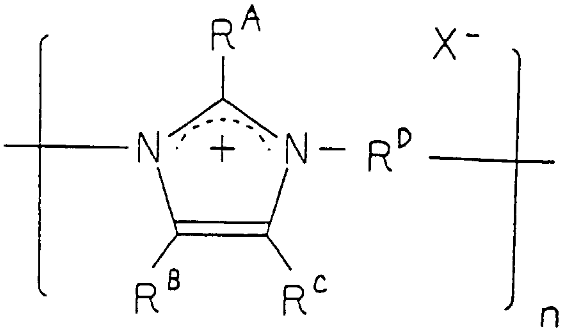
However, since a normal low-molecular weight quaternary ammonium salt has high crystallizability and insufficient dispersion properties to the fixing resin, the charging properties are inferior. Therefore, a low-charging toner having a charged amount lower than a predetermined value, reversal-charging toner which is charged to a reversal polarity, etc. are liable to be formed. As a result, image failures such as so-called image fog wherein the toner is adhered to the margin part of the formed image, toner scattering, etc. are likely to be generated. In addition, there is a problem of charging stability, i.e. the image density varies when the image is formed repeatedly.

In Japanese Laid-Open Patent Publication No. 5-165259, there is disclosed an electric charge controlling material comprising a graft polymer consisting of a polystyrene main chain and a graft chain having a skeleton represented by the following general formula (5):



(5)

wherein R^A is a C_{11}-C_{17} hydrocarbon group; R^B and R^C independently indicate a hydrogen atom or a C_1-C_8 hydrocarbon group, and R^B and R^C may bond together to form an aromatic ring; R^D is a C_1-C_{12} alkylene group which may contain an ether bond; X^- is an anion; and m is an integer of 2 to 100, or an electric charge controlling material comprising this glaft polymer and a polymer represented by the following general formula (6):



(6)

wherein R^A to R^D and X^- are as defined above; and n is an integer of 2 to 100.

The above electric charge controlling material is superior in dispersion properties of the toner to the fixing resin. In addition, a toner using this electric charge controlling material can obtain a sharp charged amount distribution, and is also superior in stability to an environmental change such as temperature, etc.

However, this electric charge controlling material has a drawback that the charged amount is not sufficient. There is a problem that, when the amount of the electric charge controlling material to be added is increased so as to improve the charged amount, the heat resistance of the toner deteriorates, to cause blocking, offset, etc.

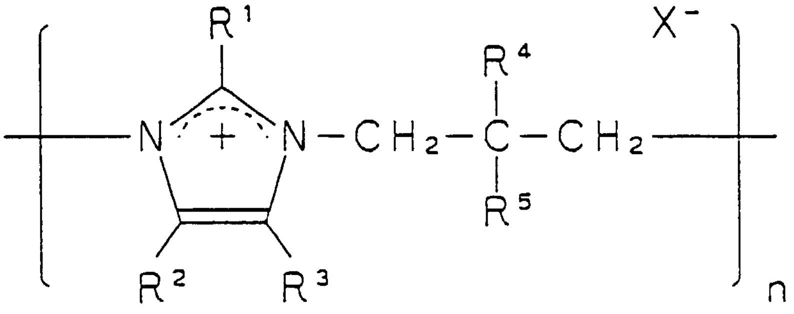
SUMMARY OF THE INVENTION

It is a main object of the present invention to provide an electrophotographic toner wherein low-temperature fixing properties can be improved without causing blocking and offset.

It is another object of the present invention to provide an electrophotographic toner which can be superior in dispersion properties of colorants such as carbon black, etc.

It is still another object of the present invention to provide an electrophotographic developer which can be superior in charging properties.

The present inventors have studied intensively in order to accomplish the above objects. As a result, it has been found that the low-temperature fixing properties can be improved without causing blocking, offset, etc. when a graft polymer consisting of a main chain of a styrene polymer having a glass transition temperature Tg of 30 to 60 °C and a number-average molecular weight Mn of 2,000 to 10,000 and a graft chain represented by the general formula (1):



(1)

wherein R^1 is a hydrogen atom, an alkyl having 11 to 17 carbon atoms or an aryl group; R^2 and R^3 are the same or different and indicate a hydrogen atom or an alkyl group having 1 to 17 carbon atoms; R^4 is an alkyl group having 1 to 12 carbon atoms; R^5 is a hydrogen atom, a hydroxyl group or a methyl group; X^- is an anion; and n is an integer of not less than 2, is contained in a fixing resin in the amount of 1 to 10 parts by weight, based on 100 parts by weight of the fixing resin. The above graft polymer serves, so to speak, as a fixing auxiliary.

That is, the above graft polymer is not miscible with the fixing resin, like a conventional low-melting point substance. However, the dispersion properties to the fixing resin are improved by adjusting the glass transition temperature, polymerization degree, etc. of a styrene polymer constituting the main chain. Therefore, if only the graft polymer is molten and kneaded, together with the fixing resin, colorant, etc., it can be uniformly dispersed in the toner as fine particles.

A graft polymer is scarcely exposed on the surface of an electrophotographic toner wherein the graft polymer is blended. Even if the graft polymer is exposed, a part comprising fine particles of the graft polymer is exposed only sporadically. Accordingly, it is possible to effectively improve the low-temperature fixing properties of the toner alone without generating blocking, offset, etc.

In addition, the above graft polymer in the present invention also functions as a dispersant for the colorant agent and is of superior effect in uniformlydispersing a colorant which is not easily dispersed in the fixing resin uniformly. (e. g. a carbon black having a particle size of 40 nm or less, etc.).

In order to make the above graft polymer function effective as a dispersant, it is preferred that the graft polymer defined in claim 1 is present in an amount within the range of 1 to 20 parts by weight, based on 100 parts by weight of the fixing resin, in a particulately dispersed state and, at the same time, the colorant is retained in or on the fine particles of the above graft polymer.

For example, a graft polymer wherein the colorant is uniformly dispersed therein, and/or is adhered on the surface thereof is dispersed in the fixing resin. As a result, there can be obtained a structure wherein the graft polymer as a lot of fine particles is dispersed in the fixing resin and a large amount of the colorant is retained in the interior or on the surface of the above fine particles, thereby further improving dispersion properties of the colorant in the toner.

In addition, the above graft polymer in the present invention has improved dispersion properties to the fixing resin in comparison with the low-molecular weight quaternary ammonium salt to be used as the electric charge controlling material for a conventional positive charging toner, and has charging properties.

The present inventors have studied intensively in order to make the above graft polymer develop a function as the electric charge controlling material, effectively. As a result, it has been found that, when using a magnetic carrier wherein the surface of magnetic particles is coated with a coat layer of a silicone resin or a fluororesin as a carrier to be used in combination with the toner containing the above graft polymer, the charged amount of the toner can be improved to a level enough to put to practical use. The reason is assumed that the above coating type carrier is superior in action of positively charging the toner because of its high negative charging properties.

On the other hand, the polymer having a repeating unit represented by the above formula (1) is superior in affinity with colorants such as carbon black, etc. Accordingly, a function as the dispersant of the colorant is expected, similar to the above graft polymer. However, the above polymer has a problem that the dispersion properties are not sufficient and it is liable to agglomerate in the fixing resin.

Thus, the present inventors have studied intensively in order to eliminate the drawback of the above polymer. As a result, it has been found that the dispersion properties of the polymer in the fixing resin are improved when the polymer having a repeating unit represented by the above formula (1) is contained in the fixing resin in the proportion of 1 to 10 parts by weight, based on 100 parts by weight of the fixing resin and, at the same time, the inorganic fine particles are contained in the proportion of 0.1 to 10 parts by weight, based on 100 parts by weight of the fixing resin, thereby improving the dispersion properties of the colorant in the toner.

The reason why the dispersion properties of the polymer are improved by containing the inorganic fine particles is assumed as follows. That is, when the polymer where colorants such as carbon black are dispersed is mixed with the inorganic fine particles, it is finely ground by the inorganic fine particles, and the inorganic fine particles adhered on the surface of the ground product prevent the ground product from reagglomerating. As a result, the dispersion properties of the polymer to the fixing resin is improved, thereby improving the dispersion properties of the colorant.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. **1** is a transmission electron micrograph (15,000X magnification) showing the section of the electrophotographic toner of Example 4.

Fig. **2** is a transmission electron micrograph (15,000X magnification) showing the section of the electrophotographic toner of Comparative Example 1.

Fig. **3** is a transmission electron micrograph (30,000X magnification) showing the section of the electrophotographic toner of Example 11.

Fig. **4** is a transmission electron micrograph (30,000X magnification) showing the section of the electrophotographic toner of Comparative Example 19.

DETAILED DESCRIPTION OF THE INVENTION

The electrophotographic toner of the present invention can be formed by formulating the above-described graft polymer comprising the styrene chain and graft chain represented by the general formula (1), colorant and, if necessary, other additives such as electric charge controlling material, etc. in the fixing resin. Since the electric charge controlling material has a moiety corresponding to the quaternary ammonium salt in the graft chain, it also has a function as the electric charge controlling material in case of positive charging toner. Accordingly, when using this positive charging toner containing the graft polymer in combination with the above-described specific coating type carrier, the other electric charge controlling material is not required necessarily, but an electric charge controlling material which has hitherto been known may be formulated, together with the graft polymer. In case of positive charging toner, negative charging toner and one-component toner to be used in combination with a carrier other than the above specific coating type carrier, it is necessary to formulate an electric charge controlling material which has hitherto been used, in order to obtain the predetermined charged amount.

The electrophotographic toner of the present invention can be produced by melting and kneading a mixture, obtained by preliminary mixing the above respective components using a dry blender, Henshel mixer, ball mill, etc., using a Banbury mixer, roll, single-screw or twin-screw extruder, etc., cooling the resulting kneaded product, followed by pulverizing and optional classifying.

In addition, when it is the purpose to disperse the colorant, the electrophotographic toner can be produced by melting and kneading the graft polymer and colorant according to the same manner as that described above to give a mixture wherein the colorant is uniformly dispersed in the graft polymer, preliminary mixing the mixture with the fixing resin, electric charge controlling material and other additives, melting and kneading them, cooling the resulting kneaded product, followed by optional classification.

Examples of the fixing resin include styrene resin (homopolymer or copolymer containing styrene or a styrene substitute) such as polystyrene, chloropolystyrene, poly-α-methylstyrene, styrene-chlorostyrene copolymer, styrene-propylene copolymer, styrene-butadiene copolymer, styrene-vinyl chloride copolymer, styrene-vinyl acetate copolymer, styrene-maleic acid copolymer, styrene-acrylate copolymer (e.g. styrene-methyl acrylate copolymer, styrene-ethyl acrylate copolymer, styrene-butyl acrylate copolymer, styreneoctyl acrylate copolymer, styrene-phenyl acrylate copolymer, etc.), styrene-methacrylate copolymer (e.g. styrene-methyl methacrylate copolymer, styrene-ethyl methacrylate copolymer, styrene-butyl methacrylate copolymer, styrene-phenyl methacrylate copolymer, etc.), styrene-α-chloromethyl acrylate copolymer, styrene-acrylonitrile-acrylate copolymer, etc., polyvinyl chloride, low-molecular weight polyethylene, low-molecular weight polypropylene, ethylene-ethyl acrylate copolymer, polyvinyl butyral, ethylene-vinyl acetate copolymer, rosin-modified maleic acid resin, phenol resin, epoxy resin, polyester resin, ionomer resin, polyurethane resin, silicone resin, ketone resin, xylene resin, polyamide resin, etc. These may be used alone or in any combination thereof.

It is particularly preferred to use styrene-acrylic resins such as styrene-acrylate copolymer, styrene-methacrylate copolymer, etc. among them, as the fixing resin.

As the colorant to be formulated in the fixing resin, there can be used various dyes, pigments, etc., which have hitherto been known. In case of black toner, a carbon black is mainly used.

As the carbon black, there can be used various carbon blacks which have hitherto been known, such as channel black, roller black, disc black, gas furnace black, oil furnace black, thermal black or acetylene black. A carbon black having a particle diameter of not more than 40 nm is suitably used in view of coloring properties, as described above. As a matter of course, another normal type carbon black may be used.

Since the carbon black itself has a conductivity, it also plays a role as control means of electric characteristics related to charging of the toner. Accordingly, it is preferred to set a preferable range of the amount to be formulated according to the objective toner performances. It is preferred in view of charging properties of the electrophotographic toner that the amount of the carbon black to be formulated is normally about 1 to 15 parts by weight, based on 100 parts by weight of the fixing resin.

The electric charge controlling material is formulated so as to control the friction charging properties of the electrophotographic toner, and any one of electric charge controlling materials for controlling positive electric charge and negative electric charge may be used according to the charged polarity of the toner.

Among them, as the electric charge controlling material for controlling positive electric charge, there are various electric charge controlling materials which have hitherto been known, such as organic compounds containing a basic nitrogen atom, e.g. basic dyes, aminopyridine, pyrimidine compounds, polynuclearpolyamino compounds, aminosilanes, etc.

On the other hand, as the electric charge controlling material for controlling negative electric charge, there are oil-soluble dyes such as nigrosine base (CI5045), oil black (CI26150), bonthrone S, spiron black, etc.; electric charge controlling resins such as styrene-styrenesulfonic acid copolymer, etc.; compounds containing a carboxyl group, such as metal chelate alkyl salicylate, etc.; metal complex dye, fatty metal soap, fatty acid soap, metal naphthenate, etc.

The electric charge controlling material is used in the proportion of 0.1 to 10 parts by weight, preferably 0.5 to 8 parts by weight, based on 100 parts by weight of the fixing resin.

The graft polymer in the present invention is composed of a main chain of a styrene polymer having a glass transition temperature Tg of 30 to 60 °C and a number-average molecular weight Mn of 2,000 to 10,000, and a graft chain represented by the above general formula (1).

In the styrene polymer constituting the main chain in such a graft polymer, the proportion of styrene by which the monomer is occupied is preferably not less than 50 molar %. Regarding the graft polymer using a main chain having a proportion of styrene of less than 50 mol %, the dispersion properties to the fixing resin are likely to become insufficient, thereby making it impossible to disperse uniformly, although they vary depending on the value of the glass transition temperature Tg and number-average molecular weight Mn of the main chain, kind of the binding resin, etc. When it is not dispersed uniformly, a large mass of the graft polymer is formed and the toner is liable to be fractured, or the above mass of the graft polymer is exposed on the surface of the toner to cause blocking, offset, etc.

Examples of the other monomers constituting the above main chain, together with styrene, include styrene derivatives, acrylic monomers, viny ester monomers, vinyl ether monomers, diolefin monomers, monoolefin monomers, olefin halide monomers, polyvinyl monomers, etc.

Among them, examples of the styrene derivative include α-methylstyrene, vinyltoluene, α-chlorostyrene, o-chlorostyrene, m-chlorostyrene, p-chlorostyrene, p-ethylstyrene, sodium styrene sulfonate, etc.

Examples of the acrylic monomer include acrylic acid, methyl acrylate, ethyl acrylate, butyl acrylate, acrylic acid-2-ethylhexyl, cyclohexyl acrylate, phenyl acrylate, methacrylic acid, methyl methacrylate, ethyl methacrylate, butyl methacrylate, methacrylic acid-2-ethylhexyl, cyclohexyl methacrylate, phenyl methacrylate, β-hydroxyethyl methacrylate, γ-aminopropyl acrylate, γ-N,N-diethylaminopropyl acrylate, ethylene glycol dimethacrylate, tetraethylene glycol dimethacrylate, etc.

Examples of the vinyl ester monomer include vinyl formate, vinyl acetate, vinyl propionate, etc.

Examples of the vinyl ether monomer include vinyl methyl ether, vinyl ethyl ether, vinyl-n-butyl ether, vinyl phenyl ether, vinyl cyclohexyl ether, etc.

Examples of the diolefin monomer include butadiene, isoprene, chloroprene, etc.

Examples of the monoolefin monomer include ethylene, propylene, butene-1, pentene-1, 4-methylpentene-1, etc.

Examples of the olefin halide include vinyl chloride, vinylidene chloride, etc.

Furthermore, examples of the polyvinyl monomer include divinylbenzene, diallyl phthalate, trivinylcyanurate, etc.

The reason why the glass transition temperature Tg and number-average molecular weight Mn of the above main chain are limited within the above range is as follows. That is, when the glass transition temperature Tg of the main chain is less than the above range or the number-average molecular weight Mn is less than the above range, the heat resistance of the electrophotgraphic toner deteriorates to cause problems such as offset, blocking, fusing onto the photo-conductor, drum, etc. On the other hand, when the glass transition temperature Tg of the main chain exceeds the above range or the number-average molecular weight Mn exceeds the above range, the dispersion properties of the graft polymer to the fixing resin are deteriorated. As a result, a large mass of the graft polymer is formed as described above, and fracture of the toner, blocking, offset, etc. are liable to be generated. In addition, when the dispersion properties to the fixing resin are deteriorated, the charging properties of the toner itself also deteriorate.

Further, it is particularly preferred that the number-average molecular weight of the main chain is about 2,000 to 8,000 within the above range, taking a function of the graft polymer as the fixing auxiliary into consideration.

In the graft chain represented by the above general formula (1), examples of the alkyl group having 11 to 17 carbon atoms, which corresponds to the group R^1, include straight-chain or branched alkyl groups such as undecyl group, dodecyl group, tridecyl group, tetradecyl group, pentadecyl group, hexadecyl group, heptadecyl group, etc.

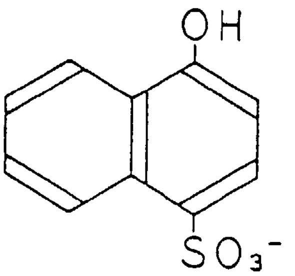
Examples of the aryl group include phenyl group, biphenyl group, naphtyl group, anthryl group, a phenanthryl group, o-terphenyl group, etc.

Examples of the alkyl group having 11 to 17 carbon atoms among alkyl groups having 1 to 17 carbon atoms, which correspond to the groups R^2 and R^3, include the same groups as those described above.

Examples of the alkyl group having 1 to 10 carbon atoms include straight-chain or branched alkyl groups such as methyl group, ethyl group, normal propyl group, isopropyl group, normal butyl group, isobutyl group, secondary butyl group, tertiary butyl group, pentyl group, hexyl group, heptyl group, octyl group, nonyl group, decyl group, etc.

Examples of the alkyl group having 1 to 12 carbon atoms, which corresponds to the group R^4, include groups from methyl group to dodecyl group among the above groups.

Examples of the anion corresponding to X^- include halogen ions such as chlorine ion, bromine ion, fluorine ion, iodine ion, etc.; sulfonic ions such as hydroxynaphthosulfonic ion represented by the formula (2):



(2)

p-toluenesulfonic ion, methylsulfonic ion, etc.; sulfuric ion, nitric ion, phosphoric ion, boric ion, oxo ion, carboxylic ion, etc.

The polymerization degree corresponding to n is limited to 2 or more. When n is 1, it becomes miscible with the toner and blocking, offset, etc. are liable to be generated. Even if polymerization degree may be not less than 2, the upper limit is not specifically limited. When the polymerization degree is too high, the dispersion properties of the graft polymer to the fixing resin deteriorate and a large mass of the graft polymer is likely to be formed, as described above, to cause fracture of the toner, blocking, offset, etc. Therefore, it is preferred that the polymerization degree is about 2 to 100.

It is preferred that the molar ratio (M:G) of the main chain M to graft chain G in the above graft polymer is within a range of 2:1 to 18:1.

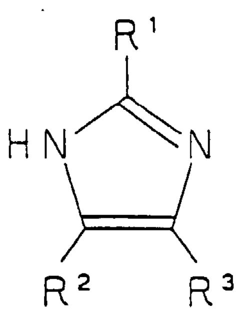
When the ratio (M:G) of the main chain M to the graft chain G deviates to the direction where the amount of the graft chain is larger than the above range (M/G < 2/1), the glass transition temperature Tg of the whole graft polymer becomes high, which may result in insufficient effect of improving the low-temperature fixing properties. There can also be caused a problem that the fluidity of the toner deteriorates or the graft polymer is fused onto the blades of a mixer at the time of premixing before the respective components are molten and kneaded in the process of producing the toner.

When the above ratio M:G deviates to the direction where the amount of the graft chain is smaller than the above range (M/G > 18/1), the graft chain is related to an affinity with the colorant and, therefore, the dispersion properties of the colorant in the toner may deteriorate to fracture the toner, and thereby to form a mass of the toner, which causes image failures such as toner scattering, image fog. In addition, the number-average molecular weight of the main chain becomes smaller than the above range because the molecular weight of the whole graft polymer is inhibited. Therefore, the heat resistance of the toner may deteriorate to cause problems such as offset, blocking, fusing onto the photoconductor drum, etc.

Further, it is the purpose to improve the dispersion properties of the colorant, the molar ratio (M:G) of the main chain M to graft chain G is preferably within a range of 3:1 to 10:1.

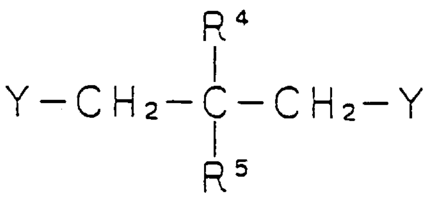
When the above graft polymer is synthesized, functional groups such as chlorine, bromine, etc. are firstly introduced into a styrene polymer corresponding to the main chain. In order to introduce the above functional group into the styrene polymer, a monomer having the functional group is normally copolymerized with styrene, but the functional group may also be introduced into the polymer after polymerization.

Next, the above polymer may be reacted with an imidazole derivative represented by the general formula (3):



(3)

wherein R¹, R² and R³ respectively indicate the same group as that described above, and a dihalide represented by the general formula (4):



$$Y-CH_2-\overset{\displaystyle R^4}{\underset{\displaystyle R^5}{C}}-CH_2-Y$$

(4)

wherein Y is a halogen atom such as chlorine, bromine, etc.; and R^4 and R^5 respectively indicate the same group as that described above.

The reaction may be conducted in a solvent which is inert to the imidazole derivative and dihalide. Examples of the above solvent include aromatic solvents such as benzene, toluene, xylene, etc.; ketone solvents such as acetone, methyl ethyl ketone, etc.; aprotic solvents such as dimethylformamide, dimethylacetamide, dimethyl sulfoxide, etc.; mixed solvents of these solvents and alcohol solvents such as methanol, ethanol, isopropanol, etc. or water, etc.

Monohalide or N-substituted imidazole may be optionally added to the above reaction system so as to block the terminal end of the graft group.

In addition, alkalis such as sodium hydroxide, potassium hydroxide, sodium carbonate, etc. may be added to the reaction system so as to neutralize hydrogen halide generated by the reaction.

The procedure of the reaction is as follows.

①A dihalide is added dropwise to a solution wherein a polymer and an imidazole derivative and, if necessary, an alkali were dissolved.
②The above respective components are dissolved in the solution, simultaneously.
③The imidazole derivative is reacted with the dihalide, and then the polymer is added to the reactant.

It is preferred that the monohalide or N-substituted imidazole for terminal blocking is added to the reaction system at the point of time where the reaction has proceeded to some extent, not at the beginning of the reaction.

The reaction may be conducted at a temperature of 30 to 200 °C, preferably 60 to 180 °C, for about 2 to 20 hours.

The reaction product obtained by the above reaction is that in which the anion corresponding to X^- in the general formula (1) is a halogen. Therefore, in order to substitute an anion other than the halogen for it, the reaction product may be added to an aqueous solution of a salt of the anion (e.g. alkali metal salt, ammonium salt, etc.), followed by stirring.

After the completion of the reaction, extraction of the nonreacted component due to water and reprecipitation due to water are conducted and, further, a homopolymer of the graft chain is removed to obtain a graft polymer.

The amount of the above graft polymer is 1 to 10 parts by weight, preferably 0.5 to 8 parts by weight, based on 100 parts by weight of the fixing resin. However, when the colorant is dispersed in the graft polymer, it is permitted that the amount of the graft polymer exceeds the above range, e.g. 1 to 20 parts by weight.

When the amount of the graft polymer is less than the above broadest range, the effect of improving the low-temperature fixing properties cannot be obtained. In addition, the effect of dispersing the colorant into the toner becomes insufficient to form a mass of the toner, which can cause fracture of the toner, and image failures due to it, such as toner scattering due to it or image fog. On the contrary, when the amount of the graft polymer exceeds the above broadest range, the heat resistance of the toner deteriorates to cause problems such as offset, blocking, fusing onto the photoconductor drum, etc.

Various additives such as release agents (anti-offset agents), magnetic material powders, etc. may be formulated in the electrophotographic toner, in addition to the above respective components.

Examples of the release agent (anti-offset agent) include aliphatic hydrocarbons, aliphatic metal salts, higher fatty acids, fatty acid esters or partially saponified material thereof, silicone oil, various waxes, etc. Among them, aliphatic hydrocarbons having a weight-average molecular weight of about 1,000 to 10,000 are particularly preferred. Examples thereof include low-molecular weight polypropylene, low-molecular weight polyethylene, paraffin wax, low-molecular weight olefin polymer of an olefin unit having carbon atoms of not less than 4, etc., and they may be suitably used alone or in combination thereof.

The anti-offset agent may be used in the amount of 0.1 to 10 parts by weight, preferably 0.5 to 8 parts by weight, based on 100 parts by weight of the fixing resin.

When the magnetic material powder is added, a magnetic toner as the one-component developer can be obtained. The magnetic material is a substance which is strongly magnetized by the magnetic field in the direction thereof. Those which are chemically stable are preferred and they may be fine powders having a particle size of about not more than 1 μm, particularly about 0.01 to 1 μm. Examples of the typical magnetic material include iron oxides such as magnetite, hematite, ferrite, etc.; metals such as iron, cobalt, nickel, etc.; alloys or mixtures of these metals and aluminum, cobalt, copper, lead, magnesium, tin, zinc, antimony, beryllium, bismuth, cadmium, calcium, manganese, selenium, titanium, tungsten, vanadium, etc.

The amount of the magnetic material powder to be formulated is preferably 20 to 300 parts by weight, more preferably 50 to 150 parts by weight, based on 100 parts by weight of the fixing resin.

In addition, other additives such as a stabilizer, etc. may be formulated in the appropriate amount.

The particle size of the electrophotographic toner is preferably 3 to 30 μm, particularly 4 to 20 μm. In case of small-particle size toner for the purpose of accomplishing high-image quality of the formed image, the particle size is preferably about 4 to 10 μm.

In addition, a surface treating agent can be added to the resulting toner particles for the purpose of improving the fluidity.

As the surface treating agent, there can be used various surface treating agents which have hitherto been used, such as inorganic fine particles, fluororesin particles, etc. Particularly, silica surface treating agents containing hydrophobic or hydrophilic silica fine particles, e.g. ultrafine-particulate anhydrous silica or colloidal silica, etc. may be suitably used.

The amount of the surface treating agent to be added is preferably about 0.1 to 3.0 parts by weight, based on 100 parts by weight of the electrophotographic toner particles. In some case, it may deviate from this range.

The electrophotographic toner of the present invention can be used alone as a non-magnetic one-component developer, or applied for various toners which have hitherto been known, such as non-magnetic toner constituting a magnetic two-component developer together with a magnetic carrier, magnetic toner to be used alone as a magnetic one-component toner, photosensitive toner which itself has a photosensitivity, etc.

The toner concentration in the case of a magnetic two-component developer is typically the same as that of a conventional one, i.e. about 2 to 15% by weight. In the case of magnetic toner, a magnetic pigment may be formulated in a fixing resin. Furthermore, in case of photosensitive toner, a photoconductive pigment and a cyanine pigment etc. as a sensitizing component thereof may be blended in the fixing resin.

As the magnetic carrier to be used in combination with the above toner, there can be suitably used a coating type carrier of which surface is coated with a coat layer of a silicone resin or a fluororesin, as described above.

As the magnetic particle as the base of the coating type carrier, there can be used a magnetic particle having various constructions which have hitherto been known. Examples of the magnetic particle include particles of iron, iron subjected to an oxidation treatment, reduced iron, magnetite, copper, silicon steel, ferrite, nickel, cobalt, etc.; particles of alloys of these materials and manganese, zinc, aluminum, etc.; particles of iron-nickel alloy, iron-cobalt alloy, etc.; particles wherein fine powders of the above various materials are dispersed in a binding resin; particles of ceramics such as titanium oxide, aluminum oxide, copper oxide, magnesium oxide, lead oxide, zirconium oxide, silicon carbide, magnesium titanate, barium titanate, lithium titanate, lead titanate, lead zirconate, lithium niobate, etc.; particles of high dielectric constant substances such as ammonium dihydrogen phosphate ($NH_4H_2PO_4$), potassium dihydrogen phosphate (KH_2PO_4), Rochelle salt, etc.

Among them, iron powders (e.g. iron oxide, reduced iron, etc.) or ferrite particles are particularly preferred. These particles can form an image having a good image quality because a change in electric resistance due to an environmental change or a change with time is small and a head of a magnetic brush is soft, and they are also cheap.

Examples of the ferrite particle include particles of zinc ferrite, nickel ferrite, copper ferrite, nickel-zinc ferrite, manganese-magnesium ferrite, copper-magnesium ferrite, manganese-zinc ferrite, manganese-copper-zinc ferrite, etc.

The particle size of the magnetic carrier to be formed is preferably about 10 to 200 μm, more preferably about 30 to 150 μm. Furthermore, the saturation magnetization of the magnetic carrier is not specifically limited, but is preferably about 35 to 70 emu/g.

As the silicone resin which is a material of the coat layer for coating the surface of the magnetic particles, there can be used various thermosetting type silicone resin. Particularly, a methyl silicone resin, more particularly, a methyl-dimethyl silicone resin having $CH_3SiO_{3/2}$ and $(CH_3)_2SiO$ as a main structural unit can be suitably used. Examples of the methyl-dimethyl silicone resin include products No. SR2400, SR2410 and SR2411 (manufactured by Toray-Dow Corning Co.,Ltd.) or product No. KR251 and KR255 (manufactured by Shinetsu Kagaku Co., Ltd.).

The coat layer of the silicone resin is formed by applying a coating material, obtained by dissolving the silicone resin in a suitable solvent, on the surface of a magnetic carrier, heating the solvent to remove it, and then subjecting the resin to a curing reaction. Further, if a hydroxy group remains in the coat layer, the negative charging properties thereof may deteriorate and the effect of positively charging the toner is likely to become insufficient. Therefore, it is preferred to exclude the hydroxyl group to the utmost by setting the heating temperature at the time of curing to a temperature higher than a normal value.

On the other hand, as the coat layer of the fluororesin, there can be used those in which fine particles of fluororesins such as ethylene tetrafluoride resin, etc. are dispersed in binding resins such as polyamideimide or epoxy resin.

Among these fluororesins, those wherein the amount of the polyamideimide is 10 to 40 % by weight are preferred in those using the polyamideimide as the binding resin. Examples thereof include Teflon S958-207, Teflon S958P-10255 (trade name, manufactured by Du Pont Co.), etc.

Those wherein the amount of the epoxy resin is 10 to 40 % by weight are preferred in those using the epoxy resin as the binding resin. Examples thereof include Teflon 5954-100, Teflon S954-101 (trade name, manufactured by Du Pont Co.), etc.

The coat layer of the fluororesin is formed by applying a coating material, obtained by dissolving the fluororesin in a suitable solvent, on the surface of a magnetic carrier, heating to remove the solvent, and then subjecting a polyamideimide or an epoxy resin as the binding resin to a curing reaction.

As the method for applying the coating material, there can be used any method, such as

①mechanical mixing, comprising uniformly mixing a magnetic carrier with a coating material using a mixer such as V-type blender, naughter mixer, etc.,
②spraying, comprising spraying a coating material to a magnetic carrier,
③dipping, comprising dipping a magnetic carrier in a coating material,
④the so-called fluidized bed method, comprising charging a magnetic carrier in a fluidized bed type coating apparatus, supplying air from the lower part of the coating apparatus to float the magnetic carrier, thereby changing into a fluidized state, and then spraying a coating material to the magnetic carrier in a floated/fluidized state, from the upper of the coating apparatus,
⑤the tumbling bed method, comprising bringing a magnetic carrier in a tumbling state into contact with a coating material, etc.

The film thickness of the coat layer is preferably about 0.05 to 1 μm, more preferably about 0.1 to 0.7 μm.

Additives for adjusting the characteristics of the coat layer, such as silica, alumina, carbon black, fatty metal salt, etc., can be optionally contained in the coat layer.

Another electrophotographic toner of the present invention may be formed by formulating a polymer having a repeating unit represented by the general formula (1), inorganic fine particles, a colorant, an electric charge controlling material and, if necessary, other additives in the fixing resin. This toner may be produced by grinding a mixture obtained by dispersing the colorant in the above polymer, using the inorganic fine particle, and then dispersing the ground mixture in the fixing resin, together with the electric charge controlling material. More concretely, the above polymer may be ground by adding the inorganic fine particles to a mixture, wherein the colorant is uniformly dispersed in the polymer by mixing the polymer with the colorant using a dry blender, Henshel mixer, ball mill, etc., followed by mixing.

Next, a mixture obtained by preliminary mixing this ground product together with the fixing resin, electric charge controlling material, etc. using the above dry blender is melted and kneaded using a Banbury mixer, roll, single-screw or twin-screw extruder kneader, etc., and then the resulting kneaded product is cooled, grounded and optionally classified to obtain an electrophotographic toner of the present invention.

The kind and amount of the fixing resin, colorant, electric charge controlling material and other additives may be the same as those described above.

In the above polymer, examples of R^1 to R^5 and X^- include the same groups as those described above. The polymerization degree may be 2 or more, and the upper limit thereof is not specifically limited. When the polymerization degree is too high, the dispersion properties to the fixing resin deteriorate. Even if the polymer is ground with the inorganic fine particles, it cannot be dispersed uniformly in the fixing resin to agglomerate. Therefore, it is preferred that the polymerization degree n is about 2 to 100 within the above range.

The above polymer may be synthesized by reacting the imidazole derivative represented by the general formula (3) with the dihalide represented by the general formula (4) in a suitable molar ratio according to the same manner as that described above.

The amount of the above polymer to be blended is limited to 1 to 10 parts by weight, based on 100 parts by weight of the fixing resin. When the amount of the polymer is less than the above range, the effect of dispersing the colorant in the toner becomes insufficient to fracture the toner, and thereby to form a mass of the toner, which causes image failures such as toner scattering, image fog, etc. To the contrary, when the amount of the polymer to be blended exceeds the above range, the heat resistance of the toner is deteriorated to cause problems such as offset, blocking, fusing onto the photoconductor drum, etc.

The proportion (M:C) of the above polymer M to colorant C is not specifically limited, but the weight ratio thereof is preferably about 1:5 to 3:1. When the proportion (M:C) of the polymer M to colorant C deviates to the side where the amount of the polymer is less than the above range (M:C < 1:5), the effect of dispersing the colorant in the toner due to the polymer is likely to become insufficient to fracture the toner, and thereby to form a mass of the toner, which causes image failures such as toner scattering, image fog, etc. On the contrary, when the proportion (M:C) of the polymer M to colorant C deviates to the side where the amount of the polymer is more than the above range (M:C > 3:1), the amount of the colorant to be blended cannot be reduced drastically because the coloring properties of the toner are maintained. Therefore, the amount of the polymer is relatively increased and the heat resistance of the toner is likely to deteriorate to cause problems such as offset, blocking, fusing onto the photoconductor drum.

Examples of the inorganic fine particle include titanium oxide, silica, alumina, etc., as described above.

The particle size of the inorganic fine particles is not specifically limited, but is preferably about 0.005 to 1 μm. When the particle size of the inorganic fine particles is less than the above range, the dispersion properties of the polymer, wherein the colorant is dispersed, to the fixing resin are likely to become insufficient. On the contrary, when the particle size of the inorganic fine particles exceeds the above range, the charging properties of the toner are likely to be changed or the photoconductor is injured by the inorganic fine particle.

The amount of the inorganic fine particles to be formulated is 0.1 to 10 parts by weight, preferably 0.2 to 5 parts by weight, based on 100 parts by weight of the total amount of the polymer and colorant. When the amount of the inorganic fine particles to be blended is less than the above range, the effect of adding the inorganic fine particles cannot be obtained sufficiently and the dispersion properties of the polymer, wherein the colorant is dispersed, to the fixing resin becomes insufficient. Therefore, it is likely to become impossible to be dispersed uniformly. In addition, a large mass of the above polymer is likely to be formed and the toner is liable to be fractured. Otherwise, the above mass is exposed on the surface of the toner to cause blocking, offset, etc. On the contrary, when the amount of the inorganic fine particle to be formulated exceeds the above range, the charging properties of the toner are likely to be changed or the photoconductor is injured by the inorganic fine particles.

Others are the same as those of the above Examples.

EXAMPLES

The following Examples and Comparative Examples further illustrate the present invention in detail.

Synthesis 1 of graft polymer

100 Parts by weight of a styrene-butyl-methacrylate copolymer (styrene content: 90 molar %, glass transition temperature Tg: 40 °C, number-average molecular weight Mn: 5,000), 100 parts by weight of an imidazole derivative of the above general formula (2) wherein the group R^1 is an undecyl group; R^2 is a hydrogen atom; and R^3 is a methyl group, and 50 parts by weight of a dihalide of the general formula (3) wherein the group R^4 is a methyl group; R^5 is a hydrogen atom; and Y is a chlorine atom were dissolved in dimethylformamide, together with 10 parts by weight of sodium carbonate.

Then, the mixture was reacted under reflux with stirring at 80 °C for four hours and 4 parts by weight of benzyl chloride for terminal blocking was added, followed by additional reaction with stirring at 80 °C for two hours.

Then, the reaction product obtained by the above reaction was introduced into an aqueous solution prepared by dissolving 200 parts by weight of sodium hydroxynaphthosulfonate to 2,000 parts by weight of water with stirring, using a homomixer to obtain a precipitate. The precipitate was washed with water, filtered, and then dried to obtain a graft polymer I wherein a molar ratio (M:G) of the main chain M to graft chain G is 5:1.

Synthesis 2 of graft copolymer

According to the same manner as that described in the synthesis 1 of graft polymer except for using 40 parts by weight of a styrene-butyl-methacrylate copolymer (styrene content: 90 molar %, glass transition temperature Tg: 30 °C, number-average molecular weight Mn: 2,000), a graft polymer II having a molar ratio (M:G) of 5:1 was synthesized.

Synthesis 3 of graft copolymer

According to the same manner as that described in the synthesis 1 of graft polymer except for using 160 parts by weight of a styrene-butyl-methacrylate copolymer (styrene content: 90 molar %, glass transition temperature Tg: 50 °C, number-average molecular weight Mn: 8,000), a graft polymer III having a molar ratio (M:G) of 5:1 was synthesized.

Synthesis 4 of graft copolymer

According to the same manner as that described in the synthesis 1 of graft polymer except for using 20 parts by weight of a styrene-2-ethylhexyl methacrylate copolymer (styrene content: 90 molar %, glass transition temperature Tg: 10 °C, number-average molecular weight Mn: 1,000), a graft polymer IV having a molar ratio (M:G) of 5:1 was synthesized.

Synthesis 5 of graft copolymer

According to the same manner as that described in the synthesis 1 of graft polymer except for using 240 parts by weight of a styrene-butyl acrylate copolymer (styrene content: 90 molar %, glass transition temperature Tg: 60 °C, number-average molecular weight Mn: 12,000), a graft polymer V having a molar ratio (M:G) of 5:1 was synthesized.

Synthesis 6 of graft copolymer

According to the same manner as that described in the synthesis 1 of graft polymer except for using 80 parts by weight of a styrene-butyl methacrylate copolymer (styrene content: 90 molar %, glass transition temperature Tg: 40 °C, number-average molecular weight Mn: 1,000), a graft polymer VI having a molar ratio (M:G) of 20:1 was synthesized.

Synthesis 7 of graft copolymer

According to the same manner as that described in the synthesis 1 of graft polymer except for using 32 parts by weight of a styrene-butyl methacrylate copolymer (styrene content: 90 molar %, glass transition temperature Tg: 40 °C, number-average molecular weight Mn: 8,000), a graft polymer VII having a molar ratio (M:G) of 1:1 was synthesized.

Example 1

100 Parts by weight of a styrene-acrylic resin as the fixing resin was mixed with 8 parts by weight of a carbon black as the colorant, 4 parts by weight of the graft polymer produced in the above synthesis 1 of graft polymer, 3 parts by weight of a polypropylene wax as the release agent and 2 parts by weight of a low-molecular weight quaternary ammonium salt as the electric charge controlling material and, after melting and kneading, the mixture was pulverized and classified to produce a positive charging type electrophotographic toner having a particle size of 5 to 20 µm.

Comparative Example 1

According to the same manner as that described in Example 1 except for formulating no graft polymer I, an electrophotographic toner was produced.

Comparative Example 2

According to the same manner as that described in Example 1 except for changing the amount of the graft polymer I to be formulated to 0.5 parts by weight, an electrophotographic toner was produced.

Comparative Example 3

According to the same manner as that described in Example 1 except for changing the amount of the graft polymer I to be formulated to 12 parts by weight, an electrophotographic toner was produced.

Example 2

According to the same manner as that described in Example 1 except for using 4 parts by weight of the graft polymer II produced in the above synthesis 2 of graft polymer in place of the graft polymer I, an electrophotographic toner was produced.

Example 3

According to the same manner as that described in Example 1 except for using 4 parts by weight of the graft polymer III produced in the above synthesis 3 of graft polymer in place of the graft polymer I, an electrophotographic toner was produced.

Comparative Example 4

According to the same manner as that described in Example 1 except for using 4 parts by weight of the graft polymer IV produced in the above synthesis 4 of graft polymer in place of the graft polymer I, an electrophotographic toner was produced.

Comparative Example 5

According to the same manner as that described in Example 1 except for using 4 parts by weight of the graft polymer V produced in the above synthesis 5 of graft polymer in place of the graft polymer I, an electrophotographic toner was produced.

Comparative Example 6

According to the same manner as that described in Example 1 except for using 4 parts by weight of the graft polymer VI produced in the above synthesis 6 of graft polymer in place of the graft polymer I, an electrophotographic toner was produced.

Comparative Example 7

According to the same manner as that described in Example 1 except for using 4 parts by weight of the graft polymer VII produced in the above synthesis 7 of graft polymer in place of the graft polymer I, an electrophotographic toner was produced.

The electrophotographic toners of the above Examples and Comparative Examples were subjected to the following tests, and their characteristics were evaluated.

Evaluation of dispersion properties

A toner was cut with a microtome (MT6000, manufactured by DuPont Co.) and the fracture surface was observed by a transmission electron microscope (TEM) to evaluate the dispersion properties of the carbon black. Further, the dispersion properties were evaluated according to the following four-grade criteria.

Dispersion properties are particularly good (◎) when it is in a dispersion state where the carbon black is dispersed, nearly uniformly, as shown in Fig. **1** illustrating the fracture surface of the toner obtained in Example 4.

Dispersion properties are inferior (X) when it is in a dispersion state where a large mass due to the agglomeration the carbon black exists, as shown in Fig. **2** illustrating the fracture surface of the toner obtained in Comparative Example 1.

Dispersion properties are good (○) or slightly inferior (Δ) when it is in an intermediate state between the above states.

Heat resistance test

A toner (20 g) was charged in a glass cylinder (inner diameter: 26.5 mm) and a weight (100 g) was placed on the toner. After standing at a predetermined temperature for 30 minutes, a cylinder was removed and the toner was observed to record the temperature at which the toner does not go to pieces (B_1, °C).

Fixing properties test

100 Parts by weight of a toner was subjected to a surface treatment using 0.2 parts by weight of a hydrophobic silica (product No. RP130, manufactured by Nihon Aerogyl Co., Ltd.), and then mixed with a silicone-coated ferrite

carrier having an average particle size of 90 µm (manufactured by Powder Tec Co.) to produce a developer having a toner concentration of 3.0 % by weight.

The resulting developer was used for a reversal developing type plain paper facsimile apparatus having a positive charging type photoconductor (model No. AF-1000, manufactured by Mita Industrial Co., Ltd.), which was modified so that a fixing temperature of a heat fixing roller (circumferential velocity: 150 mm/second) can be adjusted, and a black solid image was printed while changing the fixing temperature.

Next, the image density of the printed image fixed on the paper surface by the above heat fixing roller was measured using a reflection densitometer (model No. TC-6D, manufactured by Tokyo Denshoku Co., Ltd.) and the surface was forced to rub five times with a weight (20 g/cm^2) obtained by coating the bottom of a column (26 mm in height x 50 mm in diameter) made of a mild steel with a cotton cloth. Then, the image density after rubbing was measured again using the above reflection densitometer to determine the fixing rate (%) according to the following equation:

$$\text{Fixing rate (\%)} = [(\text{Image density after rubbing})/(\text{Image density before rubbing})] \times 100$$

Thereafter, a minimum fixing temperature at which the fixing rate becomes 95 % or more (F_1, °C) was recorded.

Offset resistance test

The same developer as that used in the above fixing properties test was used for the same plain paper facsimile apparatus, and a black solid image was printed while changing the fixing temperature to record a maximum fixing temperature (F_2, °C) at which no offset is generated.

Practical machine test

The same developer as that used in the above fixing properties test was used for the same plain paper facsimile apparatus, and an image was continuously formed on 30,000 pieces of paper at a fixing temperature of 150 °C. At the point where the image has formed on 1, 5,000, 10,000, 20,000 or 30,000 pieces of papers, the formed image and interior of the apparatus were visually observed to record whether the image failure and abnormality of the toner in the interior of the apparatus are recognized or not, respectively. In addition, when the image failure and abnormality of the toner are not recognized, the symbol (○) was described in the table. When the image failure or abnormality of the toner is recognized, the symbol (X) was described in the table and, at the same time, the details of the failure or abnormality were described in the margin. In addition, when the image failure or abnormality of the toner is slightly recognized but it is enough to put to practical use, the symbol (Δ) was described.

The results are shown in Tables 1 to 3.

Table 1

	Example 1	Comparative Example 1	Comparative Example 2	Comparative Example 3
Dispersion properties	○	X	△	○
B_1 (℃)	65	70	65	45
F_1 (℃)	150	190	180	130
F_2 (℃)	220	230	220	170
Practical machine test**				
1	○	○	○	○
5,000	○	X*1	○	X*2
10,000	○	-	X*1	-
20,000	○	-	-	-
30,000	○	-	-	-

Table 2

	Example 2	Comparative Example 3	Comparative Example 4	Comparative Example 5
Dispersion properties	○	○	○	○
B_1 (℃)	60	70	45	70
F_1 (℃)	140	160	130	170
F_2 (℃)	200	230	160	240
Practical machine test**				
1	○	○	○	○
5,000	○	○	X*2	X*1
10,000	○	○	-	-
20,000	○	○	-	-
30,000	○	○	-	-

Table 3

	Comparative Example 6	Comparative Example 7
Dispersion properties	△	△
B_1 (°C)	50	65
F_1 (°C)	140	190
F_2 (°C)	170	220
Practical machine test**		
1	○	○
5,000	X*1	X*3
10,000	-	-
20,000	-	-
30,000	-	-

*1: Toner scattering and image fog due to inferior dispersion properties of carbon black were generated.

*2: Fusing of toner onto photoconductor drum was generated in apparatus.

*3: Decrease in image density due to over charging was generated.

**: Number of papers on which image was formed

Synthesis 8 of graft copolymer

According to the same manner as that described in the synthesis 1 of graft polymer except for using 120 parts by weight of a styrene-butyl methacrylate copolymer (styrene content: 90 molar %, glass transition temperature Tg: 40 °C, number-average molecular weight Mn: 6,000), a graft polymer VIII having a molar ratio (M:G) of 5:1 was synthesized.

Synthesis 9 of graft copolymer

According to the same manner as that described in the synthesis 1 of graft polymer except for using 200 parts by weight of a styrene-butyl methacrylate copolymer (styrene content: 90 molar %, glass transition temperature Tg: 50 °C, number-average molecular weight Mn: 10,000), a graft polymer IX having a molar ratio (M:G) of 5:1 was synthesized.

Example 4

2 Parts by weight of the graft polymer VIII produced in the above synthesis 8 of graft polymer was mixed with 8 parts by weight of a carbon black, and the mixture was molten and kneaded. Then, 100 parts by weight of a styrene-acrylic resin as the fixing resin, 3 parts by weight of a polypropylene wax as the release agent and 2 parts by weight of a nigrosine dye as the electric charge controlling material were added and, after melting and kneading, the mixture was pulverized and classified to produce a positive charging type electrophotographic toner having a particle size of 5 to 20 μm.

Comparative Example 8

According to the same manner as that described in Example 4 except for changing the amount of the graft polymer VIII to be formulated to 0.5 parts by weight, an electrophotographic toner was produced.

Comparative Example 9

According to the same manner as that described in Example 4 except for changing the amount of the graft polymer VIII to be formulated to 22 parts by weight, an electrophotographic toner was produced.

Example 5

According to the same manner as that described in Example 4 except for using 2 parts by weight of the graft polymer II produced in the above synthesis 2 of graft polymer in place of the graft polymer VIII, an electrophotographic toner was produced.

Example 6

According to the same manner as that described in Example 4 except for using 2 parts by weight of the graft polymer IX produced in the above synthesis 9 of graft polymer in place of the graft polymer VIII, an electrophotographic toner was produced.

Comparative Example 10

According to the same manner as that described in Example 4 except for using 2 parts by weight of the graft polymer IV produced in the above synthesis 4 of graft polymer in place of the graft polymer VIII, an electrophotographic toner was produced.

Comparative Example 11

According to the same manner as that described in Example 4 except for using 2 parts by weight of the graft polymer V produced in the above synthesis 5 of graft polymer in place of the graft polymer VIII, an electrophotographic toner was produced.

The electrophotographic toners of the above Examples and Comparative Examples were subjected to the same tests described above, and their characteristics were evaluated

The results are shown in Tables 4 and 5, together with those of Comparative Example 1.

Table 4

	Example 4	Comparative Example 1	Comparative Example 8	Comparative Example 9
Dispersion properties	◎	X	X	○
B_1 (℃)	65	70	70	40
F_1 (℃)	150	190	180	130
F_2 (℃)	220	230	220	160
Practical machine test**				
1	○	○	○	○
5,000	○	X*1	○	X*2
10,000	○	-	X*1	-
20,000	○	-	-	-
30,000	○	-	-	-

Table 5

	Example 5	Example 6	Comparative Example 10	Comparative Example 11
Dispersion properties	◎	○	◎	△
B_1 (℃)	60	70	45	70
F_1 (℃)	140	160	130	170
F_2 (℃)	210	240	170	240
Practical machine test**				
1	○	○	○	○
5,000	○	○	X*2	○
10,000	○	○	-	△
20,000	○	○	-	X*1
30,000	○	○	-	-

*1: Toner scattering and image fog due to inferior dispersion properties of carbon black were generated.

*2: Fusing of toner onto photoconductor drum was generated in apparatus.

**: Number of papers on which image was formed

Synthesis 10 of graft copolymer

100 Parts by weight of a styrene-butyl methacrylate copolymer (styrene content: 90 molar %, glass transition temperature Tg: 40 °C, number-average molecular weight Mn: 6,000), 90 parts by weight of an imidazole derivative of the above general formula (2) wherein the group R^1 is an undecyl group; R^2 is a hydrogen atom; and R^3 is a methyl group, and 50 parts by weight of a dihalide of the general formula (3) wherein the group R^4 is a methyl group; R^5 is a hydrogen atom; and Y is a chlorine atom were dissolved in dimethylformamide, together with 20 parts by weight of sodium carbonate.

Then, the mixture was reacted under reflux with stirring at 80 °C for four hours and 4 parts by weight of benzyl chloride for terminal blocking was added, followed by additional reaction with stirring at 80 °C for two hours.

Then, the reaction product obtained by the above reaction was introduced into an aqueous solution prepared by dissolving 200 parts by weight of sodium hydroxynaphthosulfonate to 2,000 parts by weight of water with stirring, using a homomixer to obtain a precipitate. The precipitate was washed with water, filtered, and then dried to obtain a graft polymer X wherein a molar ratio (M:G) of the main chain M to graft chain G is 5:1.

Synthesis 11 of graft copolymer

According to the same manner as that described in the synthesis 10 of graft polymer except for using 100 parts by weight of a styrene-butyl methacrylate copolymer (styrene content: 90 molar %, glass transition temperature Tg: 30 °C, number-average molecular weight Mn: 2,000), a graft polymer XI was synthesized.

Synthesis 12 of graft copolymer

According to the same manner as that described in the synthesis 10 of graft polymer except for using 100 parts by weight of a styrene-butyl methacrylate copolymer having a functional group (styrene content: 90 molar %, glass transition temperature Tg: 60 °C, number-average molecular weight Mn: 10,000), a graft polymer XII was synthesized.

Synthesis 13 of graft copolymer

According to the same manner as that described in the synthesis 10 of graft polymer except for using 100 parts by weight of a styrene-butyl methacrylate copolymer (styrene content: 90 molar %, glass transition temperature Tg: 10 °C, number-average molecular weight Mn: 1,000), a graft polymer XIII was synthesized.

Synthesis 14 of graft copolymer

According to the same manner as that described in the synthesis 10 of graft polymer except for using 100 parts by weight of a styrene-butyl methacrylate copolymer (styrene content: 90 molar %, glass transition temperature Tg: 70 °C, number-average molecular weight Mn: 12,000), a graft polymer XIV was synthesized.

Example 7

(1) Production of toner

100 Parts by weight of a styrene-acrylic resin as the fixing resin was mixed with 8 parts by weight of a carbon black, 4 parts by weight of the graft polymer X produced in the above synthesis 10 of graft polymer and 3 parts by weight of a polypropylene wax and, after melting and kneading, the mixture was pulverized and classified to produce

a positive charging type electrophotographic toner having a particle size of 5 to 20 µm.

Then, 100 parts by weight of this toner was subjected to a surface treatment using 0.2 parts by weight of a hydrophobic silica (product No. RP130, manufactured by Nihon Aerogyl Co., Ltd.).

(2) Production of magnetic carrier

A coating material prepared by dissolving a silicone resin (product No. SR2400, manufactured by Toray Dow Corning Co., Ltd.) in toluene was applied on the surface of ferrite particles having a particle size of 80 µm using a fluidized bed method, followed by subjecting to a heat treatment at 300 °C for one hour, to produce a magnetic carrier wherein the surface of the above magnetic particles are coated with a coat layer of 1.0 % by weight of a silicone resin.

(3) Production of electrophotographic developer

The above toner and magnetic carrier were mixed so that a toner concentration became 3 % by weight to produce an electrophotographic developer.

Comparative Example 12

According to the same manner as that described in Example 7 except for changing the amount of the graft polymer X to be formulated into the toner to 0.5 parts by weight, a toner was prepared. Then, this toner was mixed with the same magnetic carrier as that produced in Example 7 in the same proportion to produce an electrophotographic developer.

Comparative Example 13

According to the same manner as that described in Example 7 except for changing the amount of the graft polymer X to be formulated into the toner to 12 parts by weight, a toner was prepared. Then, this toner was mixed with the same magnetic carrier as that produced in Example 7 in the same proportion to produce an electrophotographic developer.

Comparative Example 14

According to the same manner as that described in Example 1 except for using 2 parts by weight of a nigrosine dye in place of the graft polymer X, a toner was prepared. Then, this toner was mixed with the same magnetic carrier as that produced in Example 1 in the same proportion to produce an electrophotographic developer.

Comparative Example 15

According to the same manner as that described in Example 7 except for using 2 parts by weight of a low-molecular weight quaternary ammonium salt in place of the graft polymer X, a toner was prepared. Then, this toner was mixed with the same magnetic carrier as that produced in Example 7 in the same proportion to produce an electrophotographic developer.

The electrophotographic developers of the above Examples and Comparative Examples were subjected to the evaluation of dispersion properties, heat resistance test, fixing properties test, offset resistance test and practical machine test according to the same manner as that described above, and their characteristics were evaluated.

The test results are shown in Table 6.

Table 6

	Example 7	Comparative Example 12	Comparative Example 13	Comparative Example 14	Comparative Example 15
Dispersion properties	○	○	○	X	X
B_1 (℃)	65	65	50	65	65
F_1 (℃)	150	160	140	190	190
F_2 (℃)	220	220	200	200	210
Practical machine test**					
1	○	X*4	○	○	○
5,000	○	-	X*5	X*3	X*3
10,000	○	-	-	-	-
20,000	○	-	-	-	-
30,000	○	-	-	-	-

*4: Toner scattering and image fog due to lack of charged amount were generated.

*5: Blocking of toner was generated in apparatus.

*3: Deterioration of image density due to over charging was generated.

**: Number of papers on which image was formed

Example 8

According to the same manner as that described in Example 7 except for using 4 parts by weight of the graft polymer XI produced in the above synthesis 11 of graft polymer in place of the graft polymer X, a toner was prepared. Then, this toner was mixed with the same magnetic carrier as that produced in Example 7 in the same proportion to produce an electrophotographic developer.

Example 9

According to the same manner as that described in Example 7 except for using 4 parts by weight of the graft polymer XII produced in the above synthesis 12 of graft polymer in place of the graft polymer X, a toner was prepared. Then, this toner was mixed with the same magnetic carrier as that produced in Example 7 in the same proportion to produce an electrophotographic developer.

Comparative Example 16

According to the same manner as that described in Example 7 except for using 4 parts by weight of the graft polymer XIII produced in the above synthesis 13 of graft polymer in place of the graft polymer X, a toner was prepared. Then, this toner was mixed with the same magnetic carrier as that produced in Example 7 in the same proportion to produce an electrophotographic developer.

Comparative Example 17

According to the same manner as that described in Example 7 except for using 4 parts by weight of the graft polymer XIV produced in the above synthesis 14 of graft polymer in place of the graft polymer X, a toner was prepared. Then, this toner was mixed with the same magnetic carrier as that produced in Example 7 in the same proportion to produce an electrophotographic developer.

The electrophotographic developers of the above Examples and Comparative Examples were subjected to the above respective tests, and their characteristics were evaluated. The results are shown in Table 7, together with those of Example 7.

Table 7

	Example 7	Example 8	Example 9	Comparative Example 16	Comparative Example 17
Dispersion properties	○	○	○	○	X
B_1 (℃)	65	65	55	55	70
F_1 (℃)	150	140	160	130	170
F_2 (℃)	220	210	240	170	240
Practical machine test**					
1	○	○	○	○	○
5,000	○	○	○	X*2	○
10,000	○	○	○	-	△
20,000	○	○	○	-	X*4
30,000	○	○	○	-	-

*2: Fusing of toner onto photoconductor was generated.

*4: Toner scattering and image fog due to lack of charged amount were generated.

**: Number of papers on which image was formed

Example 10

The same toner as that produced in Example 7 was mixed with the following magnetic carrier in the same proportion to produce an electrophotographic developer.

Production of magnetic carrier

A coating material prepared by dissolving a fluororesin (trade name of Teflon S594-100, manufactured by Du Pont Co.) in tetrahydrofuran was applied on the surface of ferrite particles having a particle size of 80 µm using a fluidized bed method, followed by subjecting to a heat treatment at 200 °C for 0.5 hours, to produce a magnetic carrier wherein the surface of the above magnetic particles are coated with a coat layer of 0.5 % by weight of a fluororesin.

Comparative Example 18

The same toner as that produced in Example 7 was mixed with an iron powder carrier (particle size: 80 µm) of which surface is not coated with a coat layer in the same proportion to produce an electrophotographic developer.

The electrophotographic developers of the above Examples and Comparative Examples were subjected to the above practical machine test and the following build-up charging properties test, and their characteristics were evaluated.

Build-up charging characteristics test

An electrophotographic developer was charged in a plurality of polypropylene containers (polyethylene container, content: 3 ml) and subjected to moisture conditioning by standing one day under an operating environment, respectively.

Then, one polyethylene container of each Example was put in a miniature bottle (content: 300 ml) and the miniature bottle was revolved at 100 r.p.m. After the miniature bottle was revolved 10 times, the charged amount (µC/g) was measured using the total amount of the developer in the sample according to blow-off method.

The above test was conducted repeatedly by setting the number of revolutions of the miniature bottle to 50, 100, 500, 1,000 or 3,000. Then, the build-up charging characteristics of the electrophotographic developers of the respective Examples and Comparative Examples were evaluated by a change in charged amount due to the number of revolutions of the miniature bottle.

The results are shown in Table 8, together with those of Example 7.

Table 8

	Example 7	Example 10	Comparative Example 18
Charged amount $\mu C/g$			
10 Times	4.46	4.61	2.12
50 Times	8.53	8.19	5.04
100 Times	10.5	10.6	7.18
500 Times	13.3	12.7	7.94
1000 Times	13.7	12.7	7.74
3000 Times	12.2	11.8	6.98
Practical machine test**			
1	○	○	X*4
5,000	○	○	-
10,000	○	○	-
20,000	○	○	-
30,000	○	○	-

*4: Toner scattering and image fog due to lack of charged amount were generated.

**: The number of papers on which the image was formed.

Synthesis of polymer

100 Parts by weight of an imidazole derivative of the above general formula (2) wherein the group R^1 is an undecyl group; R^2 is a hydrogen atom; and R^3 is a methyl group, and 50 parts by weight of a dihalide of the above general formula (3) wherein the group R^4 is a methyl group; R^5 is a hydrogen atom; and Y is a chlorine atom were dissolved in dimethylformamide, together with 15 parts by weight of sodium carbonate.

Then, the mixture was reacted under reflux with stirring at 80 °C for four hours and 4 parts by weight of benzyl chloride as a monohalide for terminal blocking was added to the reaction system, followed by additional reaction with stirring at 80 °C for two hours.

Then, the reaction product obtained by the above reaction was introduced into an aqueous solution prepared by dissolving 200 parts by weight of sodium hydroxynaphthosulfonate to 2,000 parts by weight of water with stirring, using a homomixer to obtain a precipitate. The precipitate was washed with water, filtered, and then dried to obtain a polymer.

Example 11

4 Parts by weight of the polymer obtained in the above synthesis of polymer was mixed with 8 parts by weight of a carbon black using a Henshel mixer and 0.1 parts by weight of titanium oxide having a particle size of 0.05µm was added, followed by additional stirring, to obtain a ground product.

Then, 12.1 parts by weight of this ground product was mixed with 100 parts by weight of a styrene-acrylic resin as the fixing resin, 3 parts by weight of a polypropylene wax and 2 parts by weight of a nigrosine dye using a Henshel mixer. The mixture was molten and kneaded using a twin-screw extruder, pulverized using a jet mill, and then subjected to air classification to produce a positive charging type electrophotographic toner having a particle size of 5 to 20 µm.

Comparative Example 19

According to the same manner as that described in Example 11 except for using 8.1 parts by weight of a mixture containing no polymer, obtained by mixing 8 parts by weight of a carbon black and 0.1 parts by weight of titanium oxide having a particle size of 0.05 µm using a Henshel mixer, in place of the ground product, an electrophotographic toner was produced.

Comparative Example 20

According to the same manner as that described in Example 11 except for using 12.0 parts by weight of a mixture containing no inorganic fine particles, obtained by mixing 4 parts by weight of a polymer and 8 parts by weight of a carbon black using a Henshel mixer, in place of the ground product, an electrophotographic toner was produced.

Example 12

According to the same manner as that described in Example 11 except for using 11.08 parts by weight of a ground product, obtained by mixing 3 parts by weight of a polymer, 11 parts by weight of a carbon black and 0.1 parts by weight of alumina having a particle size of 0.02 µm using a Henshel mixer, an electrophotographic toner was produced.

Example 13

According to the same manner as that described in Example 11 except for using 14.1 parts by weight of a ground product, obtained by mixing 10 parts by weight of a polymer, 4 parts by weight of a carbon black and 0.1 parts by weight of alumina having a particle size of 0.02 µm using a Henshel mixer, an electrophotographic toner was produced.

Comparative Example 21

According to the same manner as that described in Example 11 except for using 11.08 parts by weight of a ground product, obtained by mixing 2 parts by weight of a polymer, 11 parts by weight of a carbon black and 0.1 parts by weight of alumina having a particle size of 0.02 µm using a Henshel mixer, an electrophotographic toner was produced.

Comparative Example 22

According to the same manner as that described in Example 11 except for using 14.09 parts by weight of a ground product, obtained by mixing 12 parts by weight of a polymer, 3 parts by weight of a carbon black and 0.1 parts by weight of alumina having a particle size of 0.02 µm using a Henshel mixer, an electrophotographic toner was produced.

The electrophotographic toners of the above Examples and Comparative Examples were subjected to the evaluation of dispersion properties, heat resistance test, fixing properties test, offset resistance test and practical machine test according to the same manner as that described above, and their characteristics were evaluated. The results are shown in Tables 9 and 10.

Further, the dispersion properties were evaluated according to the following four-grade criteria.

Dispersion properties are particularly good (◎) when it is in a dispersed state of Example 11 shown in Fig. **3**.

Dispersion properties are inferior (X) when it is in a dispersion state where a large mass due to the agglomeration of the carbon black exists, as Comparative Example 19 shown in Fig.**4**.

Dispersion properties are good (○) or slightly inferior (△) when it is in an intermediate state between the above states.

Table 9

	Example 11	Comparative Example 19	Comparative Example 20
Dispersion properties	◎	X	△
B_1 (℃)	65	70	65
F_1 (℃)	140	190	140
F_2 (℃)	220	230	220
Practical machine test**			
1	○	○	○
5,000	○	X*1	○
10,000	○	-	X*1
20,000	○	-	-
30,000	○	-	-

Table 10

	Example 12	Example 13	Comparative Example 21	Comparative Example 22
Dispersion properties	○	◎	△	◎
B_1 (℃)	65	60	70	50
F_1 (℃)	160	140	170	130
F_2 (℃)	230	180	230	160
Practical machine test**				
1	○	○	○	○
5,000	○	○	○	X*2
10,000	○	○	X*1	-
20,000	○	○	-	-
30,000	○	○	-	-

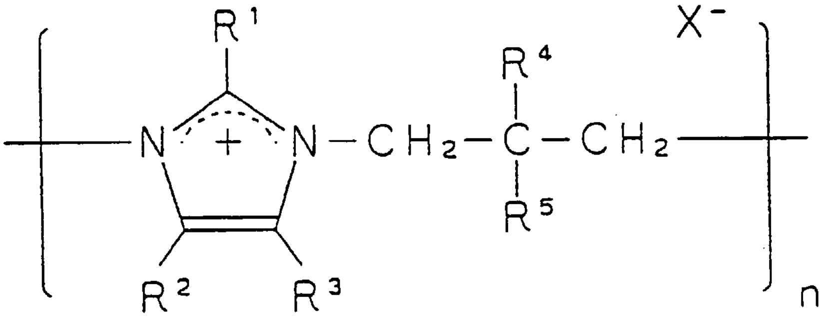
*1: Toner scattering and image fog due to inferior dispersion properties of carbon black were generated.

*2: Fusing of toner onto photoconductor drum was degenerated in apparatus.

**: Number of papers on which image was formed

Claims

1. An electrophotographic toner comprising (i) a fixing resin, (ii) a colorant contained in the fixing resin and (iii) a graft polymer comprising a main chain of a styrene polymer having a glass transition temperature Tg of 30 to 60 °C and a number-average molecular weight of 2,000 to 10,000, and a graft chain represented by the general formula (1):



(1)

wherein R^1 is a hydrogen atom, an alkyl group having 11 to 17 carbon atoms or aryl group; R^2 and R^3 are the same or different and indicate a hydrogen atom or an alkyl group having 1 to 17 carbon atoms; R^4 is an alkyl group having 1 to 12 carbon atoms; R^5 is a hydrogen atom, a hydroxyl group or a methyl group; X^- is an anion; and n is an integer of not less than 2,

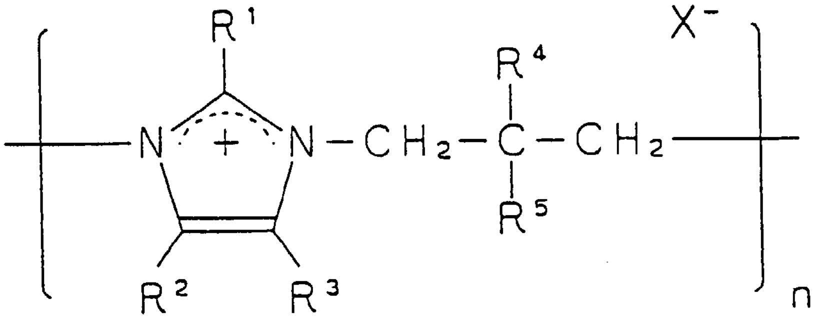
the graft polymer being present in a proportion of 1 to 10 parts by weight, based on 100 parts by weight of the fixing resin.

2. The electrophotographic toner according to claim 1, wherein a molar ratio of the main chain to graft chain is 2:1 to 18:1.

3. An electrophotographic toner comprising (i) a fixing resin, (ii) a colorant contained in the fixing resin and (iii) the graft polymer defined in claim 1, which is contained in the fixing resin, the graft polymer being contained at a particulately dispersed state in the proportion of 1 to 20 parts by weight, based on 100 parts by weight of the fixing resin, the colorant being retained in or on particle of the graft polymer.

4. An electrophotographic developer comprising the toner defined in claim 1, and a magnetic carrier wherein the surface of a magnetic particle is coated with a coat layer of a silicone resin or a fluororesin.

5. An electrophotographic toner comprising (i) a fixing resin, (ii) a colorant contained in the fixing resin, (iii) a polymer represented by the general formula (1):



(1)

wherein R^1 is a hydrogen atom, an alkyl group having 11 to 17 carbon atoms or aryl group; R^2 and R^3 are the same or different and indicate a hydrogen atom or an alkyl group having 1 to 17 carbon atoms; R^4 is an alkyl group having 1 to 12 carbon atoms; R^5 is a hydrogen atom, a hydroxyl group or a methyl group; X^- is an anion; and n is an integer of not less than 2, and (iv) an inorganic particle,

the polymer being present in a proportion of 1 to 10 parts by weight, based on 100 parts by weight of the fixing resin, and the inorganic particle being present in a proportion of 0.1 to 10 parts by weight, based on 100 parts by weight of the fixing resin.

Fig. 1

Fig. 2

Fig. 3

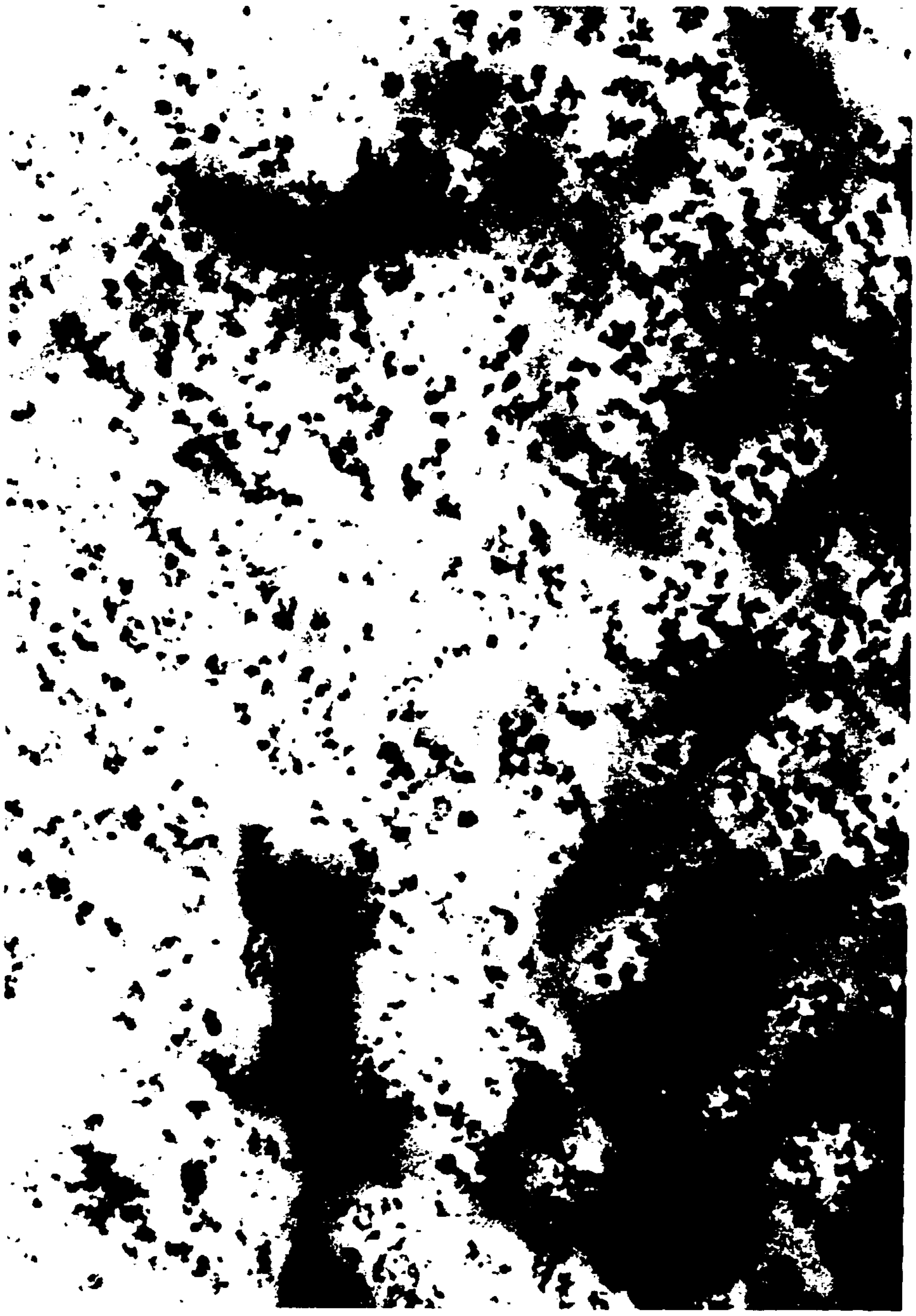


Fig. 4

European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 95 30 8608

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	DE-A-40 18 986 (SANYO) * examples 1,2 * ---	1-5	G03G9/087
D,A	DATABASE WPI Week 9331 Derwent Publications Ltd., London, GB; AN 93-245563 & JP-A-05 165 259 (SANYO) * abstract * ---	1-5	
A	DATABASE WPI Week 9236 Derwent Publications Ltd., London, GB; AN 92-295472 & JP-A-04 202 305 (SANYO) * abstract * ---	1-5	
A	DATABASE WPI Week 8731 Derwent Publications Ltd., London, GB; AN 87-360336 & JP-A-62 264 066 (MINOLTA CAMERA) * abstract * -----	1-5	TECHNICAL FIELDS SEARCHED (Int.Cl.6) G03G

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	2 April 1996	Heywood, C

CATEGORY OF CITED DOCUMENTS

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