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㊿ TONER FOR ELECTROPHOTOGRAPHY.

(57) A toner for electrophotography, which contains as a major component a vinyl polymer having a number-average molecular weight (Mn) of 1,000 to 5,000 and a ratio of the weight-average molecular weight to the number-average molecular weight, Mw/Mn, of 1 to 3. This toner exhibits excellent fixability at a high speed or at low temperatures.

Croydon Printing Company Ltd

TITLE MODIFIED
see front page

SPECIFICATION

Electrophotographic Toner

Field of the Invention

The present invention relates to an electrophotographic toner powder for use in the development of an electrostatic image in electrophotography, and more particularly relates to an electrophotographic toner which exerts excellent lower temperature fixing ability in a hot-roll copying method.

Backgroud of the Technic

The electrophotographic dry toner is conventionally composed of a resin composition, coloring agent which contains pigments or dyestuffs, charge control agent, wax and the like. Synthetic or natural resin is used for the resin composition singly or as a suitable mixture. A relatively high molecular weight styrene containing polymer is generally used in admixture with a relatively low molecular weight styrene containing polymer in a suitable proportion. The composition and thermal properties of the styrene containing polymer employed are important factors deciding the toner characteristics, and currently their improvement is strongly required.

Many kinds of fixation method which called hot-roll process are employed in the electrophotographic copying machines and printers. In these methods, toner particles which were electrostatically transferred on copying papers are passed through heated press rolls, thereby the particles are melted and fixed on the paper. Copying machine have recently been developed for conducting duplication at a high speed and a low energy fixation. Conventional toner, however, is not always satisfactory for the performance of these machines and printers by the following reasons. The heat quantity transferred from the hot rolls to the toner particles at high duplication speed is less than at low duplication speed. A remarkable decrease in the surface temperature of hot rolls is also caused by the increase in heat removal to the copying papers, which leads to insufficient fusion and deteriorated fixation of the toner particles. Besides the copying machines fitted with various auxiliary devices are required to operate all of these devices within a limited consumption of electricity. Since the proportion of electrical consumption for heating the rolls is very high in the total consumption, it is strongly required to lower the temperature of hot rolls.

The conventional toner, however, cannot perform satisfactory melting and adhesion to the copying papers at lower surface temperatures of the hot rolls. Therefore it has been strongly desired to develop the toner which exhibits sufficient fixing ability by supplying a smaller quantity of heat.

As a countermeasure to this problem, there is a method for satisfactorily conducting the fixation under conditions of high speed and lower temperature conditions by lowering the softening temperature or melt viscosity of the resin constituting the toner particles. That is, the toner melting at the lower temperatures can be prepared by adjusting the mixing ratio of the resin. This method, however, increases the proportion of low molecular weight styrene containing resin and remarkably decreases the melt viscosity of resin at high temperatures. As a result, the toner particles which were melted and pressed on a copying paper by the hot rolls at the fixation stage are transferred and left on the hot roll surface when the paper was removed from the rolls. The attached toner on the roll surface is pressed again on the next paper, which is so-called "offset phenomenon". The offset phenomenon causes a serious disadvantage that the copying papers are contaminated and good images cannot be obtained.

The resin which is free from the blocking phenomenon and moreover has a low softening temperature can be prepared by similary reducing molecular weight of the low molecular weight styrene containing polymer which constitutes the resin. A polymerization initiator, however, is uneconomically required in a relatively large amount in order to obtain such low molecular weight styrene containing polymer. Furthermore, a large amount of relatively high-polar impurities such as residue of the polymerization initiator is supposed to contaminate in the toner. Thus frictional charge of the toner is extremely labilized and it becomes difficult to obtain sharp, clear and good quality images over a long period.

Besides the low molecular weight styrene containing polymer can also be obtained by using a small amount of polymerization initiator in combination with a chain transfer agent such as mercaptan. The toner containing a low molecular weight polypropylene (Japanese Patent Publication No. 3,304/1977) and the toner obtained by using α,β-unsaturated ethylene polymer having a broad molecular weight distribution, e.g. weight average molecular weight (Mw)/number average molecular weight (Mn) = 3.5 - 40, as the resin (Japanese Patent Publication No. 6,895/1980) are also known. These toners can improve offset resistance to some extent, but cannot improve fixing ability. Besides as a method for improving the fixing ability, the toner added with plasticizers such as phthalic acid esters etc. (Japanese Patent Publication (12,679/1971) is known. The added plasticizers, however, migrate with the passage of time, deteriorate stability and cause problems in actual use.

Besides the toner containing the resin composed of a vinyl polymer or its mixture which has at least one peak value respectively in the molecular weight regions of 10^3 - 8 x 10^4 and 10^5 - 2 x 10^6 (Japanese Patent Laid-open No. 16,144/1981, relevant to U.S.P. 4,499,168) is known. Furthermore, the toner containing a low molecular weight polymer which has a number average molecular weight of 3,000 - 50,000 and Mw/Mn of less than 3.5, and a polymer which is insoluble and infusible (Japanese Patent Publication No. 86558/1983) has also been proposed recently.

The toner obtained from such polymer, however, is still unsatisfactory in charge stability, cannot provide a good image under high relative humidity in particular and leads to serious problems in actual use. In addition, the toner is apt to cause blocking in high relative humidity, and is difficult to employ in practical application.

Disclosure of the Invention

The object of this invention is to provide an electrophotographic toner which is excellent in the fixing ability at a high duplication speed and low temperature, capable of obtaining a sharp, clean and good image, and also outstanding in the resistance against blocking and offset.

The aforesaid object of this invention can be achieved by providing an electrophotographic toner containing a vinyl polymer as a primary component. The vinyl polymer has 1,000 - 5,000 in a number average molecular weight (Mn) and 1 - 3 in a ratio (Mw/Mn) of a weight average molecular weight (Mw) to the number average molecular weight.

The toner of this invention is excellent as a one component toner containing magnetic powder or a two component toner employed after mixing with a carrier. The toner is also excellent in the fixing ability at the high duplication speed and under low heat supply, outstanding in the blocking resistance and always capable of providing stable and good quality images. Therefore, the toner is suitable for the electrophotographic duplication operating, for example, at a high speed of 40 - 100 sheets/min. and a lower temperature of 130 - 140°C.

Preferred Embodiments of the Invention

The vinyl monomer having carboxyl groups which is used in this invention includes, for example, acrylic acid, methacrylic acid, crotonic acid, itaconic acid, cinnamic acid, maleic anhydride, fumaric acid, maleic acid and their methyl, ethyl and 2-ethylhexyl monoesters. These monomers are used singly or a combination of two and more. In consideration of hygroscopic property of the polymer, methacrylic acid, maleic anhydride and cinnamic acid are particularly preferable. Besides the ratio of vinyl monomer to styrene is determined so as to obtain an acid value in the range of preferably 0 - 50 KOHmg/g, and more preferably 0 - 30 KOHmg/g.

The acid value exceeding 50 KOHmg/g is undesirable because the hygroscopic property increases and charge stability is eliminated.

The vinyl polymer used in this invention can be prepared by any of conventionally known methods such as solution polymerization, suspension polymerization, emulsion polymerization, bulk polymerization. The solution polymerization is preferred in consideration of quality stabilization. The polymerization initiator or the chain transfer agent is frequently used in a large amount particularly in the case of preparing the low molecular weight polymer. In the solution polymerization, solvent is always distilled off at high temperatures and under high vacuum in the final step of preparation. The residue of polymerization initiator, unreacted monomer and low boiling fractions are simultaneously removed in this step to obtain a high quality polymer containing very small amount of impurities. Therefore the toner obtained from the polymer has a good humidity resistance and an excellent stability of quality even in the copying test for many days, for example, for the duplication of 50,000 sheets of paper.

The polymerization initiator for use in this invention is at least one of known radical polymerization initiator which belongs to perester, hydroperoxide, dialkyl peroxide, ketone peroxide, diacyl peroxide, percarbonate, azobis derivative. The initiator includes, for example, t-butyl peroctoate, t-butyl perbenzoate, t-butyl perisobutyrate, t-butyl hydroperoxide, cumene hydroperoxide, di-t-butyl peroxide, t-butyl cumyl peroxide, dicumyl peroxide, methyl ethyl ketone peroxide, methyl isobutyl ketone peroxide, cyclohexanone peroxide, acetyl peroxide, lauryl peroxide, benzoyl peroxide, diisopropyl peroxydicarbonate, bis(4-t-butylcyclohexyl) peroxydicarbonate, 2,2'-azobisisobutyronitrile, 2-phenylazo-2,4-dimethyl-4-methoxyvaleronitrile, and 2,2'-azobis(2-methylpropane).

The dialkyl peroxide polymerization initiators such as di-t-butyl peroxide, t-butyl cumyl peroxide and di-cumyl peroxide are particularly preferred for use among these initiators.

The initiator is used in an amount of 0.05 - 15.0 parts by weight per 100 parts by weight of the vinyl monomer.

The solvent which is used in this invention is a compound having sufficient solubility for the vinyl monomer and its polymer. The solvent includes, for example, aliphatic hydrocarbons, aromatic hydrocarbons, esters, ethers, ketones, alcohols, cellosolves, carbitols, formamides and sulfamides. These known solvent can be used singly or in combination. Particularly preferable solvent for this invention is xylene, ethylbenzene, benzene, toluene, ethyl acetate and Solvesso^{TM} #100 and #150 (products of Esso Petroleum Co.).

The vinyl polymer which is used in this invention is obtained by polymerizing the aforesaid vinyl monomer and preferably contains styrene as the major ingredient. The number average molecular weight of the polymer is required to be 1,000 - 5,000 and preferred to be 1,500 - 2,800. Mw/Mn is required to be 1 - 3. The number average molecular weight of less than 1,000 is undesirable because the toner decreases the blocking resistance. That of more than 5,000 or also Mw/Mn of more than 3 deteriorate the fixing ability and render the toner useless.

Generally in the number average molecular weight of 5,000 and less, copolymer of styrene with acrylic acid ester such as butyl acrylate which is conventionally used for the toner resin lowers Tg to less than 50°C, causes blocking and renders the toner useless. On the other hand, vinyl polymer of this invention derived from styrene alone or styrene and vinyl monomer containing carboxyl group can maintain Tg at not lower than 50°C and satisfy both fixing ability and blocking resistance.

Tg of the vinyl polymer is preferably 50 - 75°C in this invention. Tg of not higher than 50°C is undesirable because of blocking generation, while Tg exceeding 75°C causes lack of fixing ability.

The vinyl polymer of this invention is used as an ingredient of the electrophotographic toner in combination with below described other polymers. The amount is normally 30 - 80% by weight, preferably 35 - 70% by weight of the resin in the toner.

Besides the most general method for preparing the electrophotographic toner of this invention is, for example, as follows. The aforesaid resin is ground to a size of about 0.5 - 2 mm and mixed with carbon black. The resulting mixture is optionally added with other polymer such as acrylic resin, coloring agent, magnetic powder, a small amount of charge control agent and wax. The mixture thus obtained is subjected to dispersion mixing with a Henshel mixer and then to melt kneading at a temperature of 130 - 180°C with a kneader. The resulting mass is crushed to coarse particles, and successively ground and classified in air to obtain particles having a size of 5 - 25 µm.

In the presence of magnetic powder, the above-mentioned toner contains the resin normally in an amount of 10 - 99% by weight and more generally contains 40% by weight of the magnetic powder and 60% by weight of the resin. In the absence of magnetic powder, the toner contains 50 - 99% by weight of the resin and more generally contains, for example, 5 - 10% by weight of carbon black and 95 - 90% by weight of the resin.

Other polymers which may be used in the preparation of aforesaid electrophotographic toner include, for example, acrylic resin, styrene-acrylic resin, styrene-butadien resin, styrene-maleic acid resin, polyamide resin, polyester resin, polyurethane resin, epoxy resin and cellulosic resin. In order to maintain the toner strength,high molecular weight polymer having

Mw of not less than 100,000 is preferred in particular. The toner deteriorates the fixing ability when the content of aforementioned polymers other than the vinyl polymer is less than 30% by weight. The toner cannot maintain its strength and deteriorates apparent fixing ability when the content exceeds 80%. The use of crosslinked polymers which are insoluble and infusible is undesirable because of fixing ability deterioration.

In addition, the coloring agent employed is pigments and dyestuffs, and includes, for example, carbon black, aniline blue, alcoyl blue, chrome yellow, ultramarine blue, quinoline yellow, methylene blue, phthalocyanine blue, malachite green, rose bengal and magnetite.

The charge control agent which may be used includes, for example, nigrosine, triphenylmethane dyestuffs, chrome complex of 3,5-di-t-butylsalicylic acid. Furthermore, conventionally known additives such as colloidal silica, zinc stearate, low molecular weight polypropylene, polyethylene wax, polytetrafluoroethylene etc. may also be added if required.

Besides in this invention, Mw and Mn are determined by separating in accordance with gel permeation chromatography (hereinafter abbreviated as GPC) using tetrahydrofuran (THF) as solvent, detecting with a differential refractometer (SHODEX SE-RII) and calculating on the basis of the analytical curve of standard polystyrene. Mw and Mn are expressed as reduced values of weight average molecular weight and number average molecular weight.

Example 1

A 5 ℓ four necked flask fitted with a reflux condenser, thermometer and stirrer was charged with 2,000 parts of xylene and fed under reflux over 10 hours with a mixture composed of 1,000 parts of xylene, 1,000 parts of styrene and azobisisobutyronitrile (hereinafter referred to as AIBN) in an amount illustrated in Table 1. The reaction was continued for an hour under reflux to complete the polymerization. Finally 1,000 parts of the resulting polymer solution was heated at 200°C under reduced pressure of 10 mmHg to remove the solvent. The molecular weight and Tg of the polymer (A) thus obtained are illustrated in Table 1.

In the next step, 2,000 parts of the resulting polymer solution was mixed with 500 parts of styrene n-butyl acrylate copolymer (styrene:n-butyl acrylate = 70:30 by weight, Mw = 280,000, Mn = 96,000, Tg = 58°C, ratio to polymer A = 1:1) and finally heated at 200°C under reduced pressure of 10 mmHg to obtain polymer (B).

To 1,000 parts of polymer (B), 70 parts of carbon black (MA-100, a product of Mitsubishi Chemical Co.) were added and kneaded with a bumbury mixer in a molten state. The resulting mass was crushed to coarse particles, finely ground with a jet mill and classified to obtain the toner having an average particle size of 12 μm.

Developing agents were prepared by mixing each 3 parts of these toners with 100 parts of ferrite carrier (F-95-100, a product of Japan Iron Powder Co.).

In order to evaluate the fixing ability, a commercially available copying machine (DC-313Z, a product of Mita Industry Co.) was reformed to freely prescribe the temperature of hot rolls.

Ten sheets of paper were continuously duplicated and subjected to a cellophane tape separation test. The minimum fixation temperature was defined as the lowest temperature at which no transfer of the toner was found on the cellophane tape at all. The temperature was further raised to check the temperature at which offset phenomenon was initiated.

Furthermore blocking was examined by standing 10 parts of the toner in a polyethylene vessel at 50°C for a week. Results were illustrated by the following three classes.

◎ ... No blocking was found at all.

Δ ... Aggregation was found partially, but easily unfastened.

X ... Coagulate was found.

Example 2

The same procedures as in Example 1 were carried out to obtain the polymer except 970 parts of styrene and 30 parts of methacrylic acid were used in place of 1,000 parts of styrene and the amount of AIBN was changed to 80 parts. The resulting polymer had Mn of 2,600, Mw/Mn of 2.0, Tg of 69°C and an acid value of 19 KOHmg/g. The toner was prepared and evaluated by the same procedures as in Example 1. As a result, the minimum fixation temperature was 145°C and the offset initiation temperature was 240°C. No blocking was found at all.

Comparative Example 1

The polymer was obtained by carrying out the same procedure as in Example 2 except n-butyl acrylate was used in place of methacrylic acid. The polymer obtained had Mn of 2,500, Mw/Mn of 1.9 and Tg of 46°C. The toner was prepared and evaluated by the same procedures as in Example 1. The toner had a minimum fixation temperature of 145°C and an offset initiation temperature of 240°C. The toner, however, was perfectly coagulated after the blocking test at 50°C for a week.

Comparative Example 2

In Run-3 of Example 1, the polymer was obtained by the same procedures as in Example 1 except the first half of the mixture composed of xylene, styrene and AIBN was fed over 2 hours and the other half of the mixture was fed over 8 hours. The resulting polymer had Mn of 1900, Mw/Mn of 4.2 and Tg of 48°C.

In addition, the toner was prepared and evaluated by the same procedures as in Example 1. The toner had a minimum fixation temperature of 145°C and an offset initiation temperature of 240°C. The toner, however, was almost coagulated after the blocking test at 50°C for a week and could not be applied for actual use.

Table 1

Run - No.	1	2	3	4	5	6	7
Styrene (part by weight)	1000	1000	1000	1000	1000	1000	1000
AIBN (part by weight)	200	150	110	80	60	40	30
<u>Polymer (A)</u>							
Tg (°C)	28	51	59	66	70	75	82
Mn	950	1700	2300	2800	3200	4200	6100
Mw/Mn	1.8	1.9	2.0	2.0	2.0	2.1	2.3
Minimum fixation temp. (°C)	140	145	145	145	150	150	160
Offset initiation temp. (°C)	220	230	240	240	240	240	240
Blocking resistance	X	◎	◎	◎	◎	◎	◎
Remarks	Comparative Example	Examples of this invention					Comparative Examples

CLAIMS

What is claimed is:

(1) An electrophotographic toner containing a vinyl polymer having 1,000 - 5,000 in a number average molecular weight (Mn) and 1 - 3 in a ratio (Mw/Mn) of a weight average molecular weight (Mw) to the number average molecular weight.

(2) The toner as claimed in claim 1 wherein the vinyl polymer is prepared from styrene alone or from styrene and carboxyl group containing monomer.

(3) The toner as claimed in claim 1 wherein the polymer has a number average molecular weight of 1,500 - 2,800.

(4) The toner as claimed in claim 1 wherein the polymer has a glass transition temperature of 50 - 75°C.

(5) The toner as claimed in claim 2 wherein the vinyl monomer is a combination of styrene with at least one of carboxyl group containing vinyl monomer selected from the group consisting of acrylic acid, methacrylic acid, crotonic acid, itaconic acid, cinnamic acid, maleic acid anhydride, fumaric acid, maleic acid and methyl, ethyl, butyl and 2-ethylhexyl

monoester of same.

(6) The toner as claimed in claim 5 wherein the vinyl monomer is styrene alone or a mixture of styrene with methyl methacrylate and/or methacrylic acid.

(7) The toner as claimed in claim 1 wherein the vinyl polymer is in an amount of 30 - 80% by weight of the resin in the toner.

(8) The toner as claimed in claim 6 wherein the vinyl polymer is in an amount of 35 - 70% by weight of the resin in the toner.

INTERNATIONAL SEARCH REPORT

International Application No PCT/JP87/00722

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [3]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl^4 G03G9/08, 9/14

II. FIELDS SEARCHED

Minimum Documentation Searched [4]

Classification System	Classification Symbols
IPC	G03G9/00, 9/08, 9/10, 9/14

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [5]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [14]

Category *	Citation of Document, [16] with indication, where appropriate, of the relevant passages [17]	Relevant to Claim No. [18]
Y	JP, A, 59-188657 (Canon Inc.) 26 October 1984 (26. 10. 84) Page 3 (Family: none)	1-8
Y	JP, A, 56-083749 (Canon Inc.) 8 July 1981 (08. 07. 81) Page 7 & DE, Al, 3045983	1-8
Y	JP, A, 56-113143 (Konishiroku Photo Ind. Co., Ltd.) 5 September 1981 (05. 09. 81) (Family: none)	1-8

* Special categories of cited documents: [15]

"A" document defining the general state of the art which is not considered to be of particular relevance

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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search [2] November 25, 1987 (25.11.87)	Date of Mailing of this International Search Report [2] December 7, 1987 (07.12.87)
International Searching Authority [1] Japanese Patent Office	Signature of Authorized Officer [20]