(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number : **0 640 882 A1**

(12) # EUROPEAN PATENT APPLICATION

(21) Application number : **94306341.2**

(51) Int. Cl.[6] : **G03G 9/087**

(22) Date of filing : **30.08.94**

(30) Priority : **30.08.93 JP 235939/93**
02.08.94 JP 200250/94

(43) Date of publication of application :
01.03.95 Bulletin 95/09

(84) Designated Contracting States :
DE FR GB

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(54) **Toner for electrophotography and process for the production thereof.**

(57) A biodegradable or hydrolyzable toner for electrophotography, which permits the easy reclaiming and recycling of used copying paper comprises as a binder resin, a lactic acid-based resin of the formula (1),

$$H\text{-}[\text{-}O\text{-}CH(CH_3)\text{-}CO\text{-}]_n\text{-}OR \quad (1)$$

wherein R is hydrogen, alkyl, an alkali metal or an alkaline earth metal, and n is an integer of 10 to 20,000, and may further comprise at least one of a colourant, a charge control agent or an offset preventer.

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Field of the Invention

The present invention relates to a toner for electrophotography. More specifically, it relates to a toner for electrophotography, which has hydrolyzability and biodegradability and permits facile deinking (removal of ink) with an existing deinking system, and which can be easily waste-treated.

Prior Art of the Invention

In recent years, with a view to both environmental protection and waste treatment, i.e., the protection of forest resources and the prevention of global warming, it is actively promoted worldwide to use waste paper. For promoting the use of waster paper, there are methods in which the content of a deinked pulp in reclaimed paper is increased and the process of incorporating a deinked pulp into woodfree paper and paper for information industry is developed. For this purpose, it is required to improve the quality of a deinked pulp obtained from waster paper from printed matter such as newspaper, magazines, and the like, by increasing the deinking ratio and dustproof ratio of the deinked pulp.

Meanwhile, copying machines and printers using electrophotographic systems are now widely used, and the waste of used copying paper is increasing in amount. It has been therefore proposed to attempt to obtain a deinked pulp from used copying paper. In copying paper, however, a toner composed mainly of a colorant and a binder resin is strongly adhering to a paper surface, and it is difficult to regenerate a high-quality deinked pulp by a conventional deinking treatment method.

In view of the protection of global environment, the safety of waste is also an important issue. In Italy, a tax on non-decomposable shipping bags has been enforced since 1987 for overcoming the problem of plastic waste, and a law has been issued which provides that shopping bags and bottles are to be produced from biodegradable materials from 1991 onward. Further, regulations against the use of plastics or bills for the conversion of materials to decomposable polymers are studied in other European countries and some States of the U.S.A.

Under the circumstances, developments of biodegradable resins are now under way, and biodegradable resins for medical materials have been put to practical use to a considerable extent. In the field of agriculture, biodegradable materials are practically used as multifiles, sustained-releasable agrochemicals, fertilizers and gardening tools. In leisure industry, some of fishing lines, fishing tackle and tees for golfing are practically produced from biodegradable materials. Further, some of packaging materials for daily necessities such as containers are practically produced from biodegradable materials.

A toner waste from used copying paper or an electrophotographic process is also required to be free of problems when disposed of. JP-A-4-179967 discloses a toner containing a specific polyester-based biodegradable binder resin. However, this toner is with high humidity absorption properties and unstable in chargeability, and it further has a problem in that it has insufficient deinking properties due to its insolubility in an alkali solution.

A conventional toner for electrophotography is generally produced as follows. A binder resin, a colorant, an offset preventer and other optional additives as components for the toner are mixed in advance. The resultant mixture is kneaded while the binder resin is melted by heating the mixture, to obtain a mass, and the mass is pulverized to obtain a toner having a desired particle diameter. However, in the above conventional production method, the dispersibility of the additives in the binder resin is poor when the mixture is kneaded while the binder resin is melted. It is therefore required to employ very severe conditions for the melt-kneading. Further, the toner sometimes has a problem in properties for practical use such as uniform chargeability and offset prevention properties.

Summary of the Invention

It is an object of the present invention to provide a toner for electrophotography, which permits the easy reclaiming and recycling of used copying paper, and a process for the production of said toner.

It is another object of the present invention to provide a toner for electrophotography, which permits the easy deinking by an existing deinking system, and a process for the production thereof.

It is further another object of the present invention to provide a toner for electrophotography, which can decrease environmental pollution caused by a toner waste, and a process for the production thereof.

It is still further another object of the present invention to provide a toner for electrophotography, which has excellent toner properties owing to the uniform dispersion of additives, and a process for the production thereof.

According to the present invention, there is provided a toner for electrophotography, which contains, as a

binder resin, a lactic acid-based resin of the formula (1),

$$H\text{-}[\text{-}O\text{-}CH(CH_3)\text{-}CO\text{-}]_n\text{-}OR \qquad (1)$$

wherein R is hydrogen, alkyl, an alkali metal or an alkaline earth metal, and n is an integer of 10 to 20,000.

Further, according to the present invention, there is provided a process for the production of a toner for electrophotography, which comprises the step of polymerizing a monomer which is to form a lactic acid-based resin of the formula (1),

$$H\text{-}[\text{-}O\text{-}CH(CH_3)\text{-}CO\text{-}]_n\text{-}OR \qquad (1)$$

wherein R is hydrogen, alkyl, an alkali metal or an alkaline earth metal, and n is an integer of 10 to 20,000, as a component for the toner for electrophotography, in the presence of at least one additive selected from the group consisting of a colorant, a charge control agent and an offset preventer.

Detailed Description of the Invention

The present inventors have made diligent studies to accomplish the facile disposal or reclaiming of used copying paper and as a result found the following. A lactic acid obtained by the lactic acid fermentation of glucose is directly dehydratively condensed, or a cyclic dimer of lactic acid (lactide) is ring-opening polymerized, to prepare a lactic acid-based resin, and this lactic acid-based resin is incorporated into a toner as a binder, whereby the toner can be imparted with hydrolyzability and biodegradability. The so-obtained hydrolyzable and biodegradable toner can achieve the above objects.

The cyclic dimer of lactic acid (lactide) is obtained by concentrating a lactic acid aqueous solution to obtain a lactic acid polycondensate and allowing the lactic acid polycondensate to react under heat (140 to 200°C) in the presence of a catalyst. The reaction product is distilled, recrystallized and dried, and the resultant cyclic dimer of lactic acid (lactide) is used as a monomer for the ring-opening polymerization. The ring-opening polymerization of the lactide is preferably carried out in the presence of a tin compound. The lactic acid-based resin is produced with an apparatus such as an extruder, a pressure kneader or a Banbury mixer.

The lactic acid-based resin is available, for example, as a product supplied by SHIMADZU CORPORATION in the trade name of "Lacty". A lactic acid-based resin is easily hydrolyzable in the presence of an alkali solution, and it has an advantage in that a toner containing a colorant such as carbon black can be effectively removed from used copying paper.

The colorant used in the present invention includes carbon black, a monoazo red pigment, a diazo yellow pigment, a quinacridone magenta pigment and an anthraquinone pigment. The charge control agent includes a Nigrosine dye, a quaternary ammonium salt and a monoazo metal complex dye. As the offset preventer, preferred is an polyolefin having a weight average molecular weight of approximately 1,000 to 45,000. The polyolefin is required to have high dispersibility in lactic acid monomer or dimer or the lactic acid-based resin, and it increases the fusion temperature of the toner if it has too high a melting point. In view of these points, it is preferred to use a polyolefin having a proper molecular weight. The weight average molecular weight of the polyolefin is particularly preferably about 2,000 to 6,000. Further, the softening point of the polyolefin is preferably 100 to 180°C, particularly preferably 130 to 160°C.

Specific examples of the above polyolefin include polyethylene, polypropylene and polybutylene. Of these polyolefins, polypropylene is particularly preferred.

The offset preventer which can be used effectively can be further selected from fatty acid metal salts such as zinc salt, barium salt, lead salt, cobalt salt, calcium salt and magnesium salt of stearic acid, zinc salt, manganese salt, iron salt and lead salt of olefinic acid and zinc acid, cobalt salt and magnesium salt of palmitic acid; higher fatty acids having at least 16 carbon atoms; higher alcohols having at least 16 carbon atoms, esters of polyhydric or monohydric alcohols; natural or synthetic paraffins; fatty acid esters or partial saponification products thereof; and ethylene-bisstearoylamides.

The above offset preventers may be used alone or in combination. The amount of the offset preventer per 100 parts by weight of the binder resin or the monomer to constitute the binder resin is generally 0.1 to 10 parts by weight, preferably 0.5 to 5 parts by weight.

The toner for electrophotography, provided by the present invention, may contain other thermoplastic resin as a binder resin in combination with the lactic acid-based resin. The "other" thermoplastic resin includes polystyrene, polyacrylic acid ester, a styrene-acrylate copolymer, polyvinyl chloride, polyvinyl acetate, polyvinylidene chloride, a phenolic resin, an epoxy resin and a polyester resin.

When the "other" thermoplastic resin is used in combination with the lactic acid-based resin, the amount of the "other" thermoplastic resin based on the total weight of the binder reins is preferably 80 % by weight or less, particularly preferably 50 % by weight or less. When the amount of the "other" thermoplastic resin exceeds 80 % by weight, the bonding strength thereof to a paper surface is too high, and the toner shows decreased deinking properties. When the toner of the present invention is used as a biodegradable toner, it is preferred

not to incorporate the "other" thermoplastic resin.

The toner for electrophotography, provided by the present invention, is obtained by a method in which the lactic acid-based resin as a binder, the colorant, the charge control agent, the offset preventer and other additive are mixed, the mixture is melt-kneaded, the kneaded mixture is cooled to solidify it and the solidified mixture is pulverized and classified. More preferably, the toner of the present invention is obtained by a method in which the additives such as the colorant, the charge control agent, the offset preventer, etc., are added, as required, to the lactic acid-based resin prepared by the polymerization in the presence of at least one additive selected from the colorant, the charge control agent and the offset preventer, the mixture is melt-kneaded, the kneaded mixture is cooled to solidify it and the solidified mixture is pulverized and classified.

Of the above two methods, the latter method has an advantage in that the additives such as the colorant, the charge control agent, the offset preventer, etc., can be contained in the binder resin in a state where these additives are remarkably uniformly dispersed in the binder resin. That is because, by polymerizing the monomer which is to give the binder resin in a state where the additives are mixed with the monomer, the additives are mixed with the monomer in a liquid state before the completion of the polymerization of the monomer. That is, when the monomer itself is in a liquid state (or it may be in a solution state), the additives can be fully uniformly dispersed in the monomer. As a result, the additives are fully uniformly dispersed among molecular chains of the resin.

When the colorant, carbon black in particular, is uniformly dispersed in the binder resin, the toner shows a decreased intrinsic volume resistance, and the toner for electrophotography exhibits stable chargeability. This is also the case with the charge control agent. When the offset preventer is uniformly dispersed in the binder resin, there can be obtained a toner for electrophotography which has non-offset properties effective for practical use and which can be fixed with a hot roller.

A fluidization agent such as hydrophobic silica or colloidal silica and a magnetic powder may be incorporated into the toner for electrophotography, provided by the present invention, in order to impart the toner with fluidity. These additives may be used in a state where the toner particle surfaces are covered with particles of these additives.

The toner for electrophotography, provided by the present invention, may be mixed with a carrier comprising an iron powder, ferrite or granulated magnetite for the use of the mixture as a two-component developer. Further, when a magnetic material is incorporated into the toner, the toner can be used as a one-component developer without mixing it with any carrier.

The present invention will be detailed hereinafter with reference to Examples, in which "part" stands for "part by weight" and "%" stands for "% by weight" unless otherwise specified.

Synthesis Example 1

L-lactide (supplied by SHIMADZU CORPORATION) 100 parts
Lauryl alcohol 0.05 part
Tin octylate ("Cosmos 29" supplied by TH. GOLDSCHMIDT AG., catalyst for ring-opening polymerization) 0.2 part

A raw material having the above composition was fed to the raw material feeding port of a twin-screw kneading extruder. The cylinder temperature was set at 190°C, and the screw rotation was set at 60 rpm in one direction. A nitrogen gas was introduced through a feeding port. The average residence time in the twin-screw kneading extruder was 15 minutes. The resultant polymer was extruded through a nozzle having an opening diameter of 2 mm, and the extrudate was cooled to solidify it, and the solidified polymer was cut to give chips of a lactic acid-based resin. The so-obtained chips had a weight average molecular weight of 100,000. This resin had the formula (1) in which n was 1,400 and R was dodecyl.

Example 1

Lactic acid-based resin obtained in Synthesis Example 1 100 parts
Polyolefin wax ("NP-105", supplied by MITSUI PETROCHEMICAL INDUSTRIES, LTD.) 2 parts
Charge control agent ("NXVP 434", supplied by Hoechst) 2 parts
Carbon black ("MA-100", supplied by MITSUBISHI KASEI CORPORATION) 6 parts

A raw material having the above composition was mixed with a super mixer and melt-kneaded under heat with a twin-screw kneader, and the kneaded mixture was pulverized with a jet mill. Then, the pulverized product was classified with a dry-method flush classifier to give negatively chargeable toner particles having an average particle diameter of 12 μm. 100 Parts of the so-obtained toner particles and 0.3 part of hydrophobic silica ("R972", supplied by Nippon Aerosil Co., Ltd.) were stirred with a Henschel mixer for 1 minute to allow the hy-

drophobic silica to adhere to the toner particles, whereby a toner (A) for electrophotography was obtained.

Example 2

A toner (B) for electrophotography was obtained in the same manner as in Example 1 except that the amount of the lactic acid-based resin was changed to 50 parts and that 50 parts of a styrene/acrylate copolymer resin ("NC-6550" supplied by Nippon Carbide Industries Co., Inc.) was added.

Comparative Example 1

A toner (C) for electrophotography was obtained in the same manner as in Example 1 except that the lactic acid-based resin was replaced with 100 parts of the same styrene/acrylate copolymer resin as that used in Example 2.

Example 3

Lactic acid-based resin obtained in Synthesis Example 1 100 parts
Polyolefin wax ("NP-105", supplied by MITSUI PETROCHEMICAL INDUSTRIES, LTD.) 2 parts
Charge control agent ("Bontron S-34", supplied by Orient Chemical Industries, Co., Ltd.) 2 parts
Tri-iron tetroxide (average particle diameter: 0.2 μm) 40 parts

A toner (D) for electrophotography was obtained from a raw material having the above composition in the same manner as in Example 1.

Comparative Example 2

A toner (E) for electrophotography was obtained in the same manner as in Example 3 except that the lactic acid-based resin was replaced with 100 parts of the same styrene/acrylate copolymer resin as that used in Example 2.

Synthesis Example 2

L-lactide (supplied by SHIMADZU CORPORATION) 100 parts
Lauryl alcohol 0.05 part
Tin octylate ("Cosmos 29" supplied by TH. GOLDSCHMIDT AG., catalyst for ring-opening polymerization) 0.2 part
Carbon black ("MA-100" supplied by MITSUBISHI KASEI CORPORATION) 6 parts

A raw material having the above composition was fed to the raw material feeding port of a twin-screw kneading extruder. The cylinder temperature was set at 190°C, and the screw rotation was set at 60 rpm in one direction. A nitrogen gas was introduced through a feeding port. The average residence time in the twin-screw kneading extruder was 15 minutes. The resultant polymer was extruded through a nozzle having an opening diameter of 2 mm, and the extrudate was cooled to solidify it, and the solidified polymer was cut to give chips of a lactic acid-based resin. The so-obtained chips had a weight average molecular weight of 110,000. This resin had the formula (1) in which n was 1,500 and R was dodecyl.

Example 4

Lactic acid-based resin obtained in Synthesis Example 2 106 parts
Polyolefin wax ("NP-105", supplied by MITSUI PETROCHEMICAL INDUSTRIES, LTD.) 2 parts
Charge control agent ("NXVP 434", supplied by Hoechst) 2 parts

A raw material having the above composition was mixed with a super mixer and melt-kneaded under heat with a twin-screw kneader, and the kneaded mixture was pulverized with a jet mill. Then, the pulverized product was classified with a dry-method flush classifier to give negatively chargeable toner particles having an average particle diameter of 12 μm. 100 Parts of the so-obtained toner particles and 0.3 part of hydrophobic silica ("R972", supplied by Nippon Aerosil Co., Ltd.) were stirred with a Henschel mixer for 1 minute to allow the hydrophobic silica to adhere to the toner particles, whereby a toner (F) for electrophotography was obtained.

Synthesis Example 3

L-lactide (supplied by SHIMADZU CORPORATION) 100 parts
Lauryl alcohol 0.05 part
Tin octylate ("Cosmos 29" supplied by TH. GOLDSCHMIDT AG., catalyst for ring-opening polymerization) 0.2 part
Charge control agent ("NXVP 434", supplied by Hoechst) 2 parts

A raw material having the above composition was fed to the raw material feeding port of a twin-screw kneading extruder. The cylinder temperature was set at 190°C, and the screw rotation was set at 60 rpm in one direction. A nitrogen gas was introduced through a feeding port. The average residence time in the twin-screw kneading extruder was 15 minutes. The resultant polymer was extruded through a nozzle having an opening diameter of 2 mm, and the extrudate was cooled to solidify it, and the solidified polymer was cut to give chips of a lactic acid-based resin. The so-obtained chips had a weight average molecular weight of 110,000. This resin had the formula (1) in which n was 1,500 and R was dodecyl.

Example 5

Lactic acid-based resin obtained in Synthesis Example 3 102 parts
Carbon black ("MA-100", supplied by MITSUBISHI KASEI CORPORATION) 6 parts
Polyolefin wax ("NP-105", supplied by MITSUI PETROCHEMICAL INDUSTRIES, LTD.) 2 parts

A raw material having the above composition was mixed with a super mixer and melt-kneaded under heat with a twin-screw kneader, and the kneaded mixture was pulverized with a jet mill. Then, the pulverized product was classified with a dry-method flush classifier to give negatively chargeable toner particles having an average particle diameter of 12 μm. 100 Parts of the so-obtained toner particles and 0.3 part of hydrophobic silica ("R972", supplied by Nippon Aerosil Co., Ltd.) were stirred with a Henschel mixer for 1 minute to allow the hydrophobic silica to adhere to the toner particles, whereby a toner (G) for electrophotography was obtained.

Synthesis Example 4

L-lactide (supplied by SHIMADZU CORPORATION) 100 parts
Lauryl alcohol 0.05 part
Tin octylate ("Cosmos 29" supplied by TH. GOLDSCHMIDT AG., catalyst for ring-opening polymerization) 0.2 part
Polyolefin wax ("NP-105", supplied by MITSUI PETROCHEMICAL INDUSTRIES, LTD.) 2 parts

A raw material having the above composition was fed to the raw material feeding port of a twin-screw kneading extruder. The cylinder temperature was set at 190°C, and the screw rotation was set at 60 rpm in one direction. A nitrogen gas was introduced through a feeding port. The average residence time in the twin-screw kneading extruder was 15 minutes. The resultant polymer was extruded through a nozzle having an opening diameter of 2 mm, and the extrudate was cooled to solidify it, and the solidified polymer was cut to give chips of a lactic acid-based resin. The so-obtained chips had a weight average molecular weight of 100,000. This resin had the formula (1) in which n was 1,400 and R was dodecyl.

Example 6

Lactic acid-based resin obtained in Synthesis Example 4 102 parts
Carbon black ("MA-100", supplied by MITSUBISHI KASEI CORPORATION) 6 parts
Charge control agent ("NXVP 434", supplied by Hoechst) 2 parts

A raw material having the above composition was mixed with a super mixer and melt-kneaded under heat with a twin-screw kneader, and the kneaded mixture was pulverized with a jet mill. Then, the pulverized product was classified with a dry-method flush classifier to give negatively chargeable toner particles having an average particle diameter of 12 μm. 100 Parts of the so-obtained toner particles and 0.3 part of hydrophobic silica ("R972", supplied by Nippon Aerosil Co., Ltd.) were stirred with a Henschel mixer for I minute to allow the hydrophobic silica to adhere to the toner particles, whereby a toner (H) for electrophotography was obtained.

Synthesis Example 5

L-lactide (supplied by SHIMADZU CORPORATION) 100 parts
Lauryl alcohol 0.05 part

Tin octylate ("Cosmos 29" supplied by TH. GOLDSCHMIDT AG., catalyst for ring-opening polymerization) 0.2 part
Carbon black ("MA-100", supplied by MITSUBISHI KASEI CORPORATION) 6 parts
Polyolefin wax ("NP-105", supplied by MITSUI PETROCHEMICAL INDUSTRIES, LTD.) 2 parts
Charge control agent ("NXVP 434", supplied by Hoechst) 2 parts

A raw material having the above composition was fed to the raw material feeding port of a twin-screw kneading extruder. The cylinder temperature was set at 190°C, and the screw rotation was set at 60 rpm in one direction. A nitrogen gas was introduced through a feeding port. The average residence time in the twin-screw kneading extruder was 15 minutes. The resultant polymer was extruded through a nozzle having an opening diameter of 2 mm, and the extrudate was cooled to solidify it, and the solidified polymer was cut to give chips of a lactic acid-based resin. The so-obtained chips had a weight average molecular weight of 120,000. This resin had the formula (1) in which n was 1,650 and R was dodecyl.

Example 7

A raw material composed of the lactic acid-based resin obtained in Synthesis Example 5 was mixed with a super mixer and melt-kneaded under heat with a twin-screw kneader, and the kneaded mixture was pulverized with a jet mill. Then, the pulverized product was classified with a dry-method flush classifier to give negatively chargeable toner particles having an average particle diameter of 12 μm. 100 Parts of the so-obtained toner particles and 0.3 part of hydrophobic silica ("R972", supplied by Nippon Aerosil Co., Ltd.) were stirred with a Henschel mixer for 1 minute to allow the hydrophobic silica to adhere to the toner particles, whereby a toner (I) for electrophotography was obtained.

Example 8

Lactic acid-based resin obtained in Synthesis Example 1 100 parts
Natural wax ("Rice Wax, supplied by Noda Wax Co., Ltd.) 2 parts
Charge control agent ("NXVP 434", supplied by Hoechst) 2 parts

A white toner (J) having an average particle diameter of 12 μm was obtained from a raw material having the above composition in the same manner as in Example 1.

Comparative Example 3

A white toner (K) having an average particle diameter of 12 μm was obtained in the same manner as in Comparative Example 1 except that no carbon black was used.

The toners for electrophotography obtained in the above Examples and Comparative Examples were tested as follows.

(1) Deinking properties

The toners for electronphotography, obtained in Examples 1 to 7 and Comparative Examples 1 and 2 were used for forming test images having a black and white ratio of 6 % on surfaces of paper sheets having a weight of 75 g/m^2 to pare test sheets. Then, hand-made paper sheets were prepared from these test sheets under the following conditions.

Defibering: An aqueous dispersion containing 5.0 % of the test sheet, 0.7 % of NaOH, 3.0 % of sodium silicate, 3.0 % of H_2O_2 and 0.2 % of a deinking agent ("Liptol" S2800, supplied by LION CORPORATION) was stirred in a beaker at 50°C for 20 minutes.

Dilution-Dehydration-Kneader treatment: Water was added to the aqueous dispersion such that the aqueous dispersion had a solid content of 5 %, and the mixture was centrifugally dehydrated. Further, pulp, sodium silicate, etc., were added such that the mixture had a pulp content of 20 %, a sodium silicate content of 3.0 % and an NaOH content of 0.5 %, and these components were disaggregated with a kneader.

Aging: The disaggregation mixture was aged at 50°C for 2 hours.

Floatation: Water was added to the aged product to prepare a dispersion having a pulp concentration of 1 %, and fine air bubbles were introduced into the dispersion for 7 minutes to allow the bubbles to adsorb the toner. The bubbles adsorbing the toner went upward and floated on the water surface, whereby the toner and the water were separated.

Washing: 2.4 Grams of the deinked pulp was washed with 1 liter of water twice.

Preparation of hand-made sheet: A hand-made sheet having a basis weight of 100 g.m^2 was prepared with

a TAPPI sheet machine.

Evaluation of deinking properties: The numbers of toner spots having a diameter of more than 100 μm (visually detectable size) and a diameter of 60 to 100 μm present on the hand-made sheet having an area of 9 cm^2 were counted visually and through a microscope.

Table 1 shows the above test results. Each value in Table 1 shows the number of remaining toner spots.

Table 1

	60 - 100 μm Number	More than 100 μm Number	Total Number
Example 1	9	6	15
Example 2	10	10	20
Example 3	9	4	13
Example 4	8	6	14
Example 5	10	5	15
Example 6	10	4	14
Example 7	8	5	13
Comparative Example 1	34	28	62
Comparative Example 2	28	25	53

Table 1 clearly shows that the toner for electrophotography, provided by the present invention, shows excellent deinking properties.

(2) Biodegradability

Each of the test toners (A), (B), (D), (F), (G), (H), (I) and (J) and the comparative toners (C), (E) and (K) was separately melt-molded into a film having a thickness of about 50 μm, and allowed to remain in soil for 6 months.

The films from the toners (A), (D), (F), (G), (H), (I) and (J) completely disappeared in form, and the film from the toner (B) also mostly disappeared in form, while the films from the comparative toners (C), (E) and (K) remained intact in form. The white toners (J) and (K) were allowed themselves to remain in soil for 3 months. The white toner (J) was completely decomposed, while the white toner (K) was not decomposed.

(3) Observation of Colorant dispersion state

The kneaded mixture (not pulverized) obtained in Examples 1, 2, 4 and 7 were cut to a thickness of 0.5 μm, and their cross sections were observed through an optical microscope (400 times). Table 2 shows the number of dispersed carbon black particles in the field of microscopic vision. Headings in Table 2 show the diameters of the carbon black particles and numbers of carbon black particles having these diameters.

Table 2

	Over 10 μm	10 - 5 μm	Below 5 μm
Example 1	7	21	Abundant
Example 2	6	13	Abundant
Example 4	0	4	Abundant
Example 7	0	3	Abundant

Table 2 shows that the dispersion state of the colorant in each of Examples 1, 2, 4 and 7 had no problem in practical use, and that the dispersion states in Examples 4 and 7 were excellent.

(4) Image Quality and Utilization

4 Parts of each of the toners obtained in Examples 1, 2, 4, 5, 6 and 7 was separately mixed with 96 parts of a ferrite carrier ("F1530", supplied by POWDERTECH CO., LTD.) to prepare two-component developers for image evaluation. The so-obtained developers were evaluated with an electronic copying machine ("BD-3810", supplied by TOSHIBA CORPORATION) to give excellent bakcground-free images having a high image density.

Table 3 shows the image quality of the initial copy and 5,000th copy.

The properties were evaluated as follows.

Triboelectric charge: Measured with a blow-off frictional charge measuring apparatus supplied by Toshiba Chemical Co., Ltd.

Image density: Measured with a reflection densitometer "RD-914" supplied by Macbeth.

Background: Measured with a color difference meter "Z-1001DP" supplied by NIPPON DENSHOKU KOGYO CO., LTD.

Table 3

	Toner density in developer		Triboelectric charge (μc/g)		Image density		Background	
	Initial	5,000th	Initial	5,000th	Initial	5,000th	Initial	5,000th
Ex. 1	4.0	4.4	-21.8	-18.6	1.42	1.45	0.68	0.82
Ex. 2	4.0	4.2	-22.4	-21.2	1.41	1.42	0.62	0.75
Ex. 4	4.0	4.1	-22.3	-21.5	1.42	1.43	0.41	0.52
Ex. 5	4.0	3.9	-23.5	-24.2	1.41	1.42	0.48	0.60
Ex. 6	4.0	4.2	-22.5	-21.2	1.42	1.44	0.52	0.65
Ex. 7	4.0	3.9	-23.4	-24.0	1.42	1.42	0.33	0.45

Table 3 shows that the toners obtained in Examples 1, 2, 4, 5, 6 and 7 had no problem in practical use, and the toners obtained in Examples 4 and 7 gave excellent images free of background.

25 Parts of the toner obtained in Example 3 was mixed with 75 parts of magnetite carrier having an average particle diameter of 60 μm to prepare a two-component developer. The so-obtained developer was evaluated with a printer ("KX-P4430", supplied by Matsushita Electric Industrial Co., Ltd.) to give excellent images free of density nonuniformity or background.

Table 4 shows the image properties of the initial print and the 5,000th print.

Table 4

	Toner density in developer		Frictional charge (μc/g)		Image density		Background	
	Initial	5,000th	Initial	5,000th	Initial	5,000th	Initial	5,000th
Ex. 3	25.0	27.9	-18.4	-17.6	1.42	1.43	0.64	0.76

Ex. = Example, CEx. = Comparative Example

The toner for electrophotography composed mainly of a lactic acid-based resin, provided by the present invention, reacts with water in an alkaline aqueous solution, and the resin molecules are hydrolyzed to decrease the bonding strength. Therefore, it can permit the facile deinking with an existing deinking system. As a result, the recycling of used copying paper is advantageously advanced. Further, the toner of the present invention is biodegradable, and has advantages in that a recovered toner can be disposed of without any problem and that waste paper can be disposed of without any problem.

In the binder resin used in the toner according to the invention R may be alkyl, suitably C_{2-20}, preferably C_{6-16}, more preferably C_{10-14}, for example dodecyl. The value of n is from 10 to 20,000, preferably from 500 to 10,000, more preferably from 800 to 5,000, most preferably from 1,000 to 2,500.

The toner of the invention comprises, as binder resin, a lactic acid-based resin of the formula (1) above, and may further comprise at least one of a colourant, a charge control agent or an offset preventer. Preferably, the toner comprises a colourant, a charge control agent and an offset preventer.

Claims

1. A toner for electrophotography, which comprises, as a binder resin, a lactic acid-based resin of the formula (1),

$$H\text{-}[\text{-}0\text{-}CH(CH_3)\text{-}CO\text{-}]_n\text{-}OR \qquad (1)$$

wherein R is hydrogen, alkyl, an alkali metal or an alkaline earth metal, and n is an integer of 10 to 20,000.

2. A toner according to claim 1, wherein the toner further contains at least one of a colourant, a charge control agent or an offset preventer.

3. A toner according to claim 2, wherein the colourant is at least one of carbon black, a monoazo red pigment, a disazo yellow pigment, a quinacridone magenta pigment and an anthraquinone pigment.

4. A toner according to claim 2, wherein the charge control agent is at least one of a Nigrosine dye, a quaternary ammonium salt and a monoazo metal complex dye.

5. A toner according to claim 2, wherein the offset preventer is a polyolefin having a weight average molecular weight of 1,000 to 45,000.

6. A toner according to claim 2, wherein the offset preventer is at least one of fatty acid metal salts, higher fatty acids, higher alcohols, esters of polyhydric or monohydric alcohols, natural or synthetic paraffins, fatty acid esters or partial saponification products thereof and ethylene-bisstearoylamides.

7. A toner according to any preceding claim, wherein the binder resin further comprises a thermoplastic resin other than the lactic acid-based resin in an amount of 80 % by weight or less based on the binder resin.

8. A toner according to any preceding claim, wherein the lactic acid-based resin is a resin produced by polymerizing lactic acid in the presence of at least one additive selected from a colourant, a charge control agent and an offset preventer.

9. A process for the production of a toner for electrophotography, which comprises the step of polymerizing a monomer which is to form a lactic acid-based resin of the formula (1),

$$H\text{-}[\text{-}0\text{-}CH(CH_3)\text{-}CO\text{-}]_n\text{-}OR \qquad (1)$$

wherein R is hydrogen, alkyl, an alkali metal or an alkaline earth metal, and n is an integer of 10 to 20,000, as a component for the toner for electrophotography, in the presence of at least one additive selected from a colourant, a charge control agent and an offset preventer.

10. A process for the production of a toner for electrophotography, which process comprises mixing a lactic acid-based resin of the formula (1),

$$H\text{-}[\text{-}0\text{-}CH(CH_3)\text{-}CO\text{-}]_n\text{-}OR \qquad (1)$$

wherein R is hydrogen, alkyl, an alkali metal or an alkaline earth metal, and n is an integer of 10 to 20,000, with at least one additive selected from a colourant, a charge control agent and an offset preventer.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 94 30 6341

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)
X	WO-A-92 01245 (DU PONT DE NEMOURS) * page 3, line 26 - line 28; claims 1,3,4; example 1 *	1-7,10	G03G9/087
Y	* page 4, line 12 - page 5, line 6 *	8,9	
Y	EP-A-0 203 818 (MITA) * page 25, line 30 - page 26, line 5; claim 1 *	8,9	
Y	XEROX DISCLOSURE JOURNAL, vol.4, no.6, 1 November 1979, STAMFORD, CONN. USA page 733 C.AUCLAIR 'Dispersion of carbon black in polyester during polymerisation'	8,9	
			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	7 December 1994	VANHECKE, H

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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E : earlier patent document, but published on, or after the filing date
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