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(54) **TONER FOR ELECTROSTATIC IMAGE DEVELOPMENT**

(57) A toner for electrostatic image development containing a resin binder and a colorant, wherein the resin binder contains an amorphous polyester resin A which is a polycondensate of a polyethylene terephthalate, an alcohol component and a carboxylic acid component, and the colorant contains an organic yellow pigment having an NH group amount of 4.0 mmol/g or more and 15.0 mmol/g or less, when a value of a total

number of -NH-group and -NH₂ group present in a molecule divided by a molecular weight is defined as the NH group amount, and a method of producing the same. The toner for electrostatic image development of the present invention is suitably used in the development and the like of latent images formed in electrophotography, electrostatic recording method, electrostatic printing method and the like

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DescriptionTECHNICAL FIELD

5 **[0001]** The present invention relates to a toner for electrostatic image development used in development of latent images formed in electrophotography, electrostatic recording method, electrostatic printing method and the like, and a method of producing the same.

BACKGROUND ART

10 **[0002]** Recently, as a yellow pigment used in a toner for electrostatic image development, C.I. pigment yellow 74 is widely known, but a switch to other yellow pigments has been studied from the viewpoints of weather resistance and safety.

[0003] For example, Patent Publication 1 has proposed a yellow pigment having three or more aromatic rings in a molecule and having a molecular weight of 600 or more and 1500 or less.

[0004] Patent Publication 1: Japanese Patent Laid-Open No. 2020-154154

SUMMARY OF THE INVENTION

20 **[0005]** The present invention relates to:

- [1] A toner for electrostatic image development containing a resin binder and a colorant, wherein the resin binder contains an amorphous polyester resin A which is a polycondensate of a polyethylene terephthalate, an alcohol component and a carboxylic acid component, and the colorant contains an organic yellow pigment having an NH group amount of 4.0 mmol/g or more and 15.0 mmol/g or less, when a value of a total number of -NH- group and -NH₂ group present in a molecule divided by a molecular weight is defined as the NH group amount; and
- [2] A method of producing a toner for electrostatic image development as defined by the above [1] including melt-kneading at least a resin binder and a colorant, and pulverizing the resulting kneaded product.

DETAILED DESCRIPTION OF THE INVENTION

[0006] A toner containing an organic yellow pigment has a problem that smearing property of images after printing is not sufficient.

[0007] The present invention relates to a toner for electrostatic image development having excellent smearing property, and a method of producing the same.

[0008] The toner for electrostatic image development of the present invention exhibits excellent effects in smearing property.

[0009] The toner for electrostatic image development of the present invention (hereinafter, merely also referred to as "toner") is characterized by a combination of an amorphous polyester resin (amorphous polyester resin A) using a polyethylene terephthalate (PET) and an organic yellow pigment having large NH group amounts. Although the reason why the toner for electrostatic image development of the present invention has excellent smearing property is not clear, the reason is assumed as follows.

[0010] The amorphous polyester resin A obtained by using the PET is incorporated into a polyester resin chain by a transesterification reaction in a polycondensation reaction of an alcohol component, a carboxylic acid component and the PET while the PET being subjected to depolymerization. However, the amorphous polyester resin A is not completely randomized, and a unit called as a PET segment is present in the resulting resin. This PET segment has a high ester group concentration and is likely to interact with an organic yellow pigment containing a large amount of NH group. Therefore, it is considered that since the amorphous polyester resin A forms a pseudo-bridged structure via the organic yellow pigment upon fusing, impact resistance of a printout is improved, and the toner has excellent smearing property.

[0011] The amorphous polyester resin A is a polycondensate of a PET, an alcohol component and a carboxylic acid component.

[0012] A PET is incorporated into a polyester resin by polycondensation reaction of the alcohol component and the carboxylic acid component, and/or by subjecting ethylene glycol and terephthalic acid generated by depolymerization of a part of a PET to polycondensation reaction as a raw material monomer. A PET is an equimolar polycondensate of ethylene glycol and terephthalic acid, and the amount of the alcohol component and the carboxylic acid component mentioned later contains the ethylene glycol and the terephthalic acid constituting a PET, respectively.

[0013] The PET may be a new Virgin PET or a recycled PET.

[0014] The recycled PET is obtained by collecting a used PET, pulverizing the collected PET optionally after washing or selection from other materials, degrading the pulverized PET into a monomer unit by depolymerization, and subjecting the degraded PET to resynthesis as a raw material.

[0015] In the present invention, the PET is preferably a PET having a relatively lower IV value as compared to a conventionally used PET, i.e. a PET having a low molecular weight. Depolymerization of the PET more evenly proceeds by introducing the PET having a low IV value (low molecular weight) into a polyester resin.

[0016] The IV value of the PET is preferably 0.40 or more, more preferably 0.45 or more, even more preferably 0.50 or more, and even more preferably 0.55 or more from the above viewpoint, and the IV value is preferably 0.85 or less, more preferably 0.80 or less, even more preferably 0.75 or less, even more preferably 0.70 or less, and even more preferably 0.65 or less, from the viewpoints of low-temperature fusing ability and evenness of depolymerization. An IV value is an intrinsic viscosity, which is used as an index of a molecular weight. The IV value of the PET can be adjusted by polycondensation time and the like.

[0017] Commercially available products of the PET having an IV value of 0.40 or more and 0.85 or less include RAMAPET L1 (manufactured by Indorama Ventures, IV value: 0.60), RAMAPET BF3067 (manufactured by Indorama Ventures, IV value: 0.65), RAMAPET N2G (manufactured by Indorama Ventures, IV value: 0.75), TRN-NTJ (manufactured by TEIJIN LIMITED, IV value: 0.53), TRN-RTJC (manufactured by TEIJIN LIMITED, IV value: 0.64), RAMAPET S1 (manufactured by Indorama Ventures, IV value: 0.84), UK-31 (manufactured by Utsumi Recycle Systems Inc, IV value: 0.67) and the like.

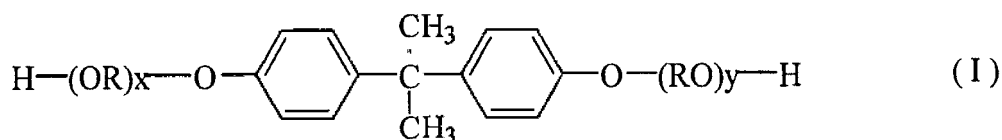
[0018] The content of the PET having a low IV value is preferably 90% by mass or more, more preferably 95% by mass or more, even more preferably 98% by mass or more, and even more preferably 100% by mass in a total amount of the PET subjected to the polycondensation.

[0019] The content of the PET in the amorphous polyester resin A is preferably 5% by mol or more, more preferably 10% by mol or more, and even more preferably 20% by mol or more, and the content is preferably 75% by mol or less, more preferably 70% by mol or less, even more preferably 65% by mol or less, even more preferably 50% by mol or less, even more preferably 40% by mol or less, and even more preferably 30% by mol or less in a total amount of the alcohol component, the carboxylic acid component and the PET, from the viewpoint of smearing property. In a case where the amorphous polyester resin A is composed of two or more kinds of resins, a weighted average of the PET content of each resin is defined as a PET content of an amorphous polyester resin A.

[0020] Here, since the PET is a polycondensate of ethylene glycol and terephthalic acid, dimethyl terephthalate or the like, a unit of terephthalic acid-ethylene glycol (Mw: 192) is converted as one mole. Accordingly, the number of moles of the PET equals the number of moles of ethylene glycol unit equals the number of moles of terephthalic acid unit.

[0021] The alcohol component preferably contains an alkylene oxide adduct of bisphenol A, from the viewpoint of smearing property.

[0022] The alkylene oxide adduct of bisphenol A is preferably a compound represented by Formula (I):



[0023] wherein, OR and RO are an oxyalkylene group, wherein R is an ethylene group and/or a propylene group; and each of x and y is a positive number showing an average number of moles of alkylene oxide added, wherein the number of the sum of x and y is 1 or more and preferably 1.5 or more, and 16 or less, preferably 8 or less, more preferably 6 or less and even more preferably 4 or less.

[0024] The content of the alkylene oxide adduct of bisphenol A in the alcohol component is preferably 25% by mol or more, more preferably 40% by mol or more, and even more preferably 55% by mol or more, and the content is preferably 95% by mol or less, more preferably 90% by mol or less, and even more preferably 85% by mol or less, from the viewpoint of low-temperature fusing ability. The alcohol component, as used herein, contains an ethylene glycol unit in the PET.

[0025] Other alcohol components include an aliphatic diol, an alicyclic diol, a bisphenol A and the like.

[0026] As the aliphatic diol, an aliphatic diol other than ethylene glycol is preferred, and the aliphatic diol includes 1,2-propanediol, 1,3-propanediol, 1,4-butanediol, 2,3-butanediol, 1,5-pentanediol, 1,6-hexanediol, 1,7-heptanediol, 1,8-octanediol, neopentyl glycol, 1,9-nonanediol, 1,10-decanediol, 1,11-undecanediol, 1,12-dodecanediol and the like.

[0027] The alicyclic diol includes a hydrogenated bisphenol A and the like.

[0028] The carboxylic acid component includes an aromatic dicarboxylic acid compound, an aliphatic dicarboxylic acid compound and the like.

[0029] The aromatic dicarboxylic acid compound includes phthalic acid, isophthalic acid, terephthalic acid, anhydride of these acids, alkyl esters of which alkyl has 1 or more carbon atoms and 3 or less carbon atoms of these acids, and the like.

[0030] The aliphatic dicarboxylic acid compound includes fumaric acid, maleic acid, succinic acid, a succinate derivative substituted with a hydrocarbon group, glutaric acid, adipic acid, and sebacic acid, anhydrides of these acids, alkyl esters of which alkyl has 1 or more carbon atoms and 3 or less carbon atoms of these acids, and the like.

[0031] The trivalent or higher polyvalent raw material monomer may be used in the alcohol component and/or the carboxylic acid component of the amorphous polyester resin A, from the viewpoint of adjustment of softening point.

[0032] The trihydric or higher polyhydric alcohol includes sorbitol, pentaerythritol, glycerol, trimethylolpropane, and the like.

[0033] The tricarboxylic or higher polycarboxylic acid compound includes trimellitic acid, pyromellitic acid, anhydrides of these acids, alkyl esters of which alkyl has 1 or more carbon atoms and 3 or less carbon atoms of these acids, and the like.

[0034] The content of the trivalent or higher polyvalent raw material monomer is preferably 2% by mol or more, and more preferably 4% by mol or more, and the content is preferably 25% by mol or less, and more preferably 20% by mol or less in a total amount of the alcohol component, the carboxylic acid component and the PET.

[0035] The alcohol component may properly contain monohydric alcohol, and the carboxylic acid component may properly contain monocarboxylic acid compound.

[0036] Here, in the present specification, a macromonomer or a hydroxy carboxylic acid is not included in the alcohol component and the carboxylic acid component.

[0037] Equivalent ratio of the carboxylic acid component (including a terephthalic acid unit in PET) to the alcohol component (including an ethylene glycol unit in PET), COOH group or groups / OH group or groups is preferably 0.6 or more, more preferably 0.7 or more, and even more preferably 0.8 or more, and the equivalent molar ratio is preferably 1.3 or less, and more preferably 1.2 or less.

[0038] The amorphous polyester resin A can be produced by, for example, polycondensing the alcohol component, the carboxylic acid component and the PET in an atmosphere of inert gas, preferably in the presence of an esterification catalyst, and further optionally in the presence of a promoter, a polymerization inhibitor and the like, at a temperature of preferably 130°C or higher, and more preferably 170°C or higher, and the temperature of preferably 250°C or lower, and more preferably 240°C or lower.

[0039] The esterification catalyst includes tin compounds such as dibutyltin oxide and tin(II) 2-ethylhexanoate; titanium compounds such as titanium diisopropoxy bis(triethanolamine) and titanium dihydroxy bis(triethanolamine); and the like. The amount of the esterification catalyst used is preferably 0.01 parts by mass or more, and more preferably 0.1 parts by mass or more, and the amount is preferably 1.5 parts by mass or less, and more preferably 1 part by mass or less, based on 100 parts by mass of a total amount of the alcohol component, the carboxylic acid component and the PET. The promoter of the esterification catalyst includes gallic acid and the like. The amount of the promoter used is preferably 0.001 parts by mass or more, and more preferably 0.01 parts by mass or more, and the amount is preferably 0.5 parts by mass or less, and more preferably 0.1 parts by mass or less, based on 100 parts by mass of a total amount of the alcohol component, the carboxylic acid component and the PET. The polymerization inhibitor includes tert-butyl catechol and the like. The amount of the polymerization inhibitor used is preferably 0.001 parts by mass or more, and more preferably 0.01 parts by mass or more, and the amount is preferably 0.5 parts by mass or less, and more preferably 0.1 parts by mass or less, based on 100 parts by mass of a total amount of the alcohol component, the carboxylic acid component and the PET.

[0040] Here, in the present invention, the polyester resin may be a polyester resin that is modified to an extent that the properties thereof are not substantially impaired. The modified polyester resin includes, for example, a polyester resin grafted or blocked with a phenol, an urethane, an epoxy or the like according to a method described in Japanese Patent Laid-Open No. Hei-11-133668, Japanese Patent Laid-Open Hei-10-239903, Japanese Patent Laid-Open Hei-8-20636, or the like. Among the modified polyester resins, urethane-modified polyester resins in which polyester resins are urethane-extended with a polyisocyanate compound are preferred.

[0041] The ester group concentration of the amorphous polyester resin A is preferably 3.5 mmol/g or more, more preferably 3.7 mmol/g or more, and even more preferably 4.0 mmol/g or more, and the ester group concentration is preferably 12.0 mmol/g or less, more preferably 10.0 mmol/g or less, and even more preferably 6.0 mmol/g or less. Here, in the case where two or more kinds of amorphous polyester resin A are used, a weighed average of the ester group concentration of each amorphous polyester resin A is defined as an ester group concentration of the amorphous polyester resin A.

[0042] In the present invention, the ester group concentration of the polyester resin is calculated according to the following formula:

$$\text{Ester Group Concentration} \frac{(\text{mmol/g})}{(\text{mmol/g})} = \frac{A (\text{mol})}{B (\text{g}) - A (\text{mol}) \times 18} \times 10^3$$

wherein, A is a binding amount (mol) of a total ester generated when all raw materials of a polyester resin react, and B is a total mass (g) of raw material monomers constituting a polyester resin. Incidentally, the insides of the parentheses in the formula mean a unit of each numeral value.

[0043] The softening point of the amorphous polyester resin A is preferably 70°C or higher, more preferably 90°C or higher, and even more preferably 100°C or higher, from the viewpoint of charge stability, and the softening point is preferably 170°C or lower, more preferably 160°C or lower, and even more preferably 150°C or lower, from the viewpoint of low-temperature fusing ability.

[0044] Here, the crystallinity of the resin is expressed by a crystallinity index, which is defined by a ratio of a softening point to a temperature of the maximum endothermic peak as determined by a differential scanning calorimeter, i.e. a value of [softening point / temperature of the maximum endothermic peak].

[0045] The amorphous resin is a resin in which no endothermic peak is observed, or if the endothermic peak is observed, the amorphous resin is a resin having a crystallinity index exceeding 1.4, or a resin having a crystallinity index of less than 0.6.

[0046] On the other hand, the crystalline resin is a resin having a crystallinity index of 0.6 or more and 1.4 or less.

[0047] Crystallinity of the resin can be adjusted by the kinds and the ratios of the raw material monomers, the production conditions (for example, reaction temperatures, reaction time, cooling rate) and the like. Here, the temperature of the maximum endothermic peak refers to a temperature of the peak having the largest peak area, among the observed endothermic peaks. In a crystalline resin, the temperature of the maximum endothermic peak is defined as a melting point.

[0048] The amorphous polyester resin A may be composed of resins having different softening points, from the viewpoints of low-temperature fusing ability and fusing range. The difference of the softening points of two resins is preferably 10°C or more, and more preferably 20°C or more, and the difference is preferably 60°C or less, and more preferably 40°C or less.

[0049] The softening point of the amorphous resin having a higher softening point, Resin AH, is preferably 100°C or higher, more preferably 110°C or higher, and even more preferably 120°C or higher, from the viewpoint of fusing range, and the softening point is preferably 170°C or lower, more preferably 160°C or lower, and even more preferably 150°C or lower, from the viewpoint of low-temperature fusing ability.

[0050] In addition, the softening point of the amorphous resin having lower softening point, Resin AL, is preferably 70°C or higher, more preferably 90°C or higher, and even more preferably 100°C or higher, from the viewpoint of charge stability, and the softening point is preferably 130°C or lower, more preferably 125°C or lower, even more preferably 120°C or lower, and even more preferably 110°C or lower, from the viewpoint of low-temperature fusing ability.

[0051] The mass ratio of the Resin AH to the Resin AL, i.e. Resin AH / Resin AL is preferably 10/90 or more, more preferably 20/80 or more, and even more preferably 30/70 or more, and the mass ratio is preferably 90/10 or less, more preferably 80/20 or less, and even more preferably 75/25 or less.

[0052] The glass transition temperature of the amorphous polyester resin A is preferably 40°C or higher, and more preferably 50°C or higher, from the viewpoint of storage property, and the glass transition temperature is preferably 80°C or lower, and more preferably 70°C or lower, from the viewpoint of low-temperature fusing ability.

[0053] The acid value of the amorphous polyester resin A is preferably 1 mgKOH/g or more, and more preferably 3 mgKOH/g or more, from the viewpoint of charge stability, and the acid value is preferably 20 mgKOH/g or less, and more preferably 18 mgKOH/g or less, from the viewpoint of durability.

[0054] The content of the amorphous polyester resin A in the resin binder is preferably 70% by mass or more, more preferably 75% by mass or more, and even more preferably 80% by mass or more, from the viewpoint of durability, and the content is preferably 100% by mass or less, more preferably 99% by mass or less, even more preferably 97% by mass or less, and even more preferably 95% by mass or less, from the viewpoint of low-temperature fusing ability.

[0055] Further, the resin binder preferably contains a crystalline polyester resin C from the viewpoint of low-temperature fusing ability.

[0056] The crystalline polyester resin C is a polycondensate of an alcohol component containing an aliphatic diol and a carboxylic acid component containing an aliphatic dicarboxylic acid compound.

[0057] The aliphatic diol includes ethylene glycol, 1,2-propanediol, 1,3-propanediol, 1,4-butanediol, 2,3-butanediol, 1,5-pentanediol, 1,6-hexanediol, 1,4-butanediol, 1,7-heptanediol, 1,8-octanediol, neopentyl glycol, 1,9-nonanediol, 1,10-decanediol, 1,11-undecanediol, 1,12-dodecanediol and the like.

[0058] The number of carbon atoms of the aliphatic diol is 2 or more, and preferably 6 or more, and the number of carbon atoms is preferably 14 or less, and more preferably 12 or less, from the viewpoint of adjusting the ester group

concentration.

[0059] The aliphatic diol preferably has a hydroxide group at the terminus of a carbon chain from the viewpoint of improving low-temperature fusing ability of the toner, and the aliphatic diol is more preferably α,ω -linear alkane diol.

[0060] The content of the aliphatic diol in the alcohol component is preferably 80% by mol or more, more preferably 90% by mol or more, and even more preferably 95% by mol or more, and the content is 100% by mol or less.

[0061] The alcohol component other than the aliphatic diol includes an aromatic diol such as an alkylene oxide adduct of bisphenol A and bisphenol A, a hydrogenated bisphenol A, trihydric or higher polyhydric alcohol such as a sorbitol, a pentaerythritol, glycerol, and trimethylolpropane, and the like.

[0062] The aliphatic dicarboxylic acid compound includes succinic acid (number of carbon atoms: 4), fumaric acid (number of carbon atoms: 4), adipic acid (number of carbon atoms: 6), suberic acid (number of carbon atoms: 8), azelaic acid (number of carbon atoms: 9), sebacic acid (number of carbon atoms: 10), dodecanedioic acid (number of carbon atoms: 12), tetradecanedioic acid (number of carbon atoms: 14), anhydrides of these acids, alkyl esters of which alkyl has 1 or more carbon atoms and 3 or less carbon atoms of these acids, and the like. Here, when the aliphatic dicarboxylic acid compound is an alkyl ester, the number of carbon atoms of the alkyl group is not included in the above-mentioned number of carbon atoms.

[0063] The number of carbon atoms of the aliphatic dicarboxylic acid compound is preferably 4 or more, more preferably 6 or more, and even more preferably 8 or more, and the number of carbon atom is preferably 14 or less, and more preferably 12 or less, from the viewpoint of adjusting the ester group concentration.

[0064] The content of the aliphatic dicarboxylic acid compound in the carboxylic acid component is preferably 50% by mol or more, more preferably 60% by mol or more, even more preferably 70% by mol or more, and even more preferably 80% by mol or more, from the viewpoint of hydrophobicity, and the content is 100% by mol or less.

[0065] Other carboxylic acid components include an aromatic dicarboxylic acid compound such as phthalic acid, isophthalic acid and terephthalic acid, tricarboxylic or higher polycarboxylic acid compound such as trimellitic acid and pyromellitic acid, and the like.

[0066] The alcohol component may properly contain monohydric alcohol, and the carboxylic acid component may properly contain monocarboxylic acid compound.

[0067] Equivalent ratio of a carboxylic group of the carboxylic acid component to a hydroxylic group of the alcohol component, COOH group or groups / OH group or groups is preferably 0.8 or more, and more preferably 0.9 or more, from the viewpoint of charge stability, and the equivalent molar ratio is preferably 1.2 or less, and more preferably 1.1 or less, from the viewpoint of low-temperature fusing ability.

[0068] The polycondensation reaction condition for the alcohol component and the carboxylic acid component of the crystalline polyester resin C is similar to that of the amorphous polyester resin A, except that the suitable reaction temperature is 120°C or higher, and more preferably 180°C or higher and 230°C or lower, and more preferably 220°C or lower.

[0069] The softening point of the crystalline polyester resin C is preferably 50°C or higher, more preferably 65°C or higher, and even more preferably 70°C or higher, from the viewpoint of durability, and the softening point is preferably 140°C or lower, more preferably 120°C or lower, and even more preferably 100°C or lower, from the viewpoint of low-temperature fusing ability.

[0070] The melting point of the crystalline polyester resin C is preferably 50°C or higher, more preferably 65°C or higher, and even more preferably 70°C or higher, from the viewpoint of durability, and the melting point is preferably 130°C or lower, more preferably 120°C or lower, and even more preferably 100°C or lower, from the viewpoint of low-temperature fusing ability.

[0071] The acid value of the crystalline polyester resin C is preferably 1 mgKOH/g or more, and more preferably 3 mgKOH/g or more, from the viewpoint of low-temperature fusing ability, and the acid value is preferably 30 mgKOH/g or less, and more preferably 25 mgKOH/g or less, from the viewpoint of durability.

[0072] The content of the crystalline polyester resin C in the resin binder is preferably 1% by mass or more, more preferably 3% by mass or more, and even more preferably 5% by mass or more, from the viewpoint of low-temperature fusing ability, and the content is preferably 30% by mass or less, more preferably 25% by mass or less, and even more preferably 20% by mass or less, from the viewpoint of durability.

[0073] The mass ratio of the crystalline polyester resin C to the amorphous polyester resin A, i.e. crystalline polyester resin C / amorphous polyester resin A is preferably 1/99 or more, more preferably 3/97 or more, and even more preferably 5/95 or more, and the mass ratio is preferably 30/70 or less, more preferably 25/75 or less, and even more preferably 20/80 or less, from the viewpoint of charge stability.

[0074] Other resin binders include a vinyl-based resin such as a styrene-acrylic resin, an epoxy resin, a polycarbonate, a polyurethane, a composite resin containing two or more kinds of these resins, and the like.

[0075] The total content of the amorphous polyester resin A and the crystalline polyester resin C in the resin binder is preferably 70% by mass or more, more preferably 80% by mass or more, even more preferably 90% by mass or more, even more preferably 95% by mass or more, and even more preferably 100% by mass.

[0076] In addition, the content of the resin binder in the toner is preferably 60% by mass or more, more preferably 70% by mass or more, and even more preferably 80% by mass or more, and the content is preferably less than 100% by mass, more preferably 98% by mass or less, and even more preferably 95% by mass or less.

[0077] The colorant contains an organic yellow pigment having the specified NH group amount from the viewpoint of interaction with the amorphous polyester resin A.

[0078] The NH group amount of the organic yellow pigment is 4.0 mmol/g or more, preferably 5.0 mmol/g or more, and more preferably 6.0 mmol/g or more, and the NH group amount is 15.0 mmol/g or less, preferably 12.5 mmol/g or less, and more preferably 10.0 mmol/g or less. Here, the NH group amount is a value of the total number of -NH-group and -NH₂ group present in a molecule divided by molecular weight.

[0079] As the organic yellow pigment, at least one selected from the group consisting of a benzimidazolone pigment, an isoindoline pigment and a condensed disazo pigment, from the viewpoint of desired NH group amount.

[0080] The benzimidazolone pigment includes C.I. pigment yellow 180 (a total number of -NH-group and -NH₂ group present in a molecule = 6, molecular weight = 733, NH group amount = 8.2 mmol/g) and the like.

[0081] The isoindoline pigment includes C.I. pigment yellow 185 (a total number of -NH-group and -NH₂ group present in a molecule = 4, molecular weight = 337, NH group amount = 11.9 mmol/g) and the like.

[0082] The condensed disazo pigment includes C.I. pigment yellow 93 (a total number of -NH-group and -NH₂ group present in a molecule = 4, molecular weight = 937, NH group amount = 4.3 mmol/g), C.I. pigment yellow 95 (a total number of -NH-group and -NH₂ group present in a molecule = 4, molecular weight = 917, NH group amount = 4.4 mmol/g) and the like.

[0083] The organic yellow pigment used in the present invention is preferably at least one selected from benzimidazolone pigment and isoindoline pigment, and more preferably at least one selected from C.I. pigment yellow 180 (PY180) and C.I. pigment yellow 185 (PY185), from the viewpoint of smearing property of the toner.

[0084] The content of the organic yellow pigment is preferably 1 part by mass or more, more preferably 2 parts by mass or more, and even more preferably 3 parts by mass or more, and the content is preferably 20 parts by mass or less, more preferably 18 parts by mass or less, and even more preferably 15 parts by mass or less, based on 100 parts by mass of the amorphous polyester resin A.

[0085] The colorant may contain other colorants within the range not impairing the effects of the present invention, and the content of the organic yellow pigment in the colorant is preferably 80% by mass or more, more preferably 90% by mass or more, even more preferably 95% by mass or more, and even more preferably 100% by mass. Other colorants include carbon blacks, Phthalocyanine Blue, Permanent Brown FG, Brilliant Fast Scarlet, Pigment Green B, Rhodamine-B Base, Solvent Red 49, Solvent Red 146, Solvent Blue 35, quinacridone, carmine 6B, disazo yellow, and the like.

[0086] The content of the colorant is preferably 1 part by mass or more, more preferably 2 parts by mass or more, and even more preferably 3 parts by mass or more, and the content is preferably 20 parts by mass or less, more preferably 18 parts by mass or less, and even more preferably 15 parts by mass or less, based on 100 parts by mass of the resin binder.

[0087] The toner for electrostatic image development of the present invention may contain, besides the resin binder and the colorant, an additive such as a releasing agent, a charge control agent, a magnetic powder, a flowability improver, an electric conductivity modifier, a reinforcing filler such as a fibrous material, an antioxidant, or a cleanability improver.

[0088] The releasing agent includes hydrocarbon waxes such as polypropylene wax, polyethylene wax, ethylene-propylene copolymer wax, microcrystalline wax, paraffin wax, Fischer-Tropsch wax, and oxides thereof; ester-based waxes such as carnauba wax, montan wax and deacidified waxes thereof, and fatty acid ester waxes; fatty acid amides, fatty acids, higher alcohols, metal salts of fatty acids, and the like. These releasing agents can be used alone or in a mixture of two or more kinds.

[0089] The melting point of the releasing agent is preferably 60°C or higher, and more preferably 70°C or higher from the viewpoint of transferring ability of a toner, and the melting point is preferably 160°C or lower, more preferably 140°C or lower, even more preferably 120°C or lower, and even more preferably 110°C or lower, from the viewpoint of low-temperature fusing ability.

[0090] The content of the releasing agent is preferably 0.5 parts by mass or more, more preferably 1 part by mass or more, and even more preferably 1.5 parts by mass or more, and the content is preferably 10 parts by mass or less, more preferably 8 parts by mass or less, and even more preferably 7 parts by mass or less, based on 100 parts by mass of the resin binder, from the viewpoints of low-temperature fusing ability and offset resistance of the toner and the viewpoint of dispersibility into a resin binder.

[0091] The charge control agent may contain, without being particularly limited to, any of positively chargeable charge control agents and negatively chargeable charge control agents.

[0092] The positively chargeable charge control agent includes Nigrosine dyes, for example, "Nigrosine Base EX," "OIL BLACK BS," "OIL BLACK SO," "BONTRON N-01," "BONTRON N-04," "BONTRON N-07," "BONTRON N-09,"

"BONTRON N-11" (hereinafter manufactured by Orient Chemical Industries Co., Ltd.), and the like; triphenylmethane-based dyes containing a tertiary amine as a side chain; quaternary ammonium salt compounds, for example, "BONTRON P-51" (manufactured by Orient Chemical Industries Co., Ltd.), cetyltrimethylammonium bromide, "COPY CHARGE PX VP435" (manufactured by Clariant), and the like; polyamine resins, for example, "AFP-B" (manufactured by Orient Chemical Industries Co., Ltd.), and the like; imidazole derivatives, for example, "PLZ-2001," "PLZ-8001" (hereinafter manufactured by SHIKOKU CHEMICALS CORPORATION), and the like; styrene-acrylic resins, for example, "FCA-701PT," "FCA-201-PS" (manufactured by Fujikura Kasei Co., Ltd.), and the like.

[0093] In addition, the negatively chargeable charge control agent includes metal-containing azo dyes, for example, "VARIFAST BLACK 3804," "BONTRON S-31," "BONTRON S-32," "BONTRON S-34," "BONTRON S-36" (hereinafter manufactured by Orient Chemical Industries Co., Ltd.), "AIZEN SPILON BLACK TRH," "T-77" (manufactured by Hodogaya Chemical Co., Ltd.), and the like; metal compounds of benzoic acid compounds, for example, "LR-147," "LR-297" (hereinafter manufactured by Japan Carlit Co., Ltd.), and the like; metal compounds of salicylic acid compounds, for example, "BONTRON E-81," "BONTRON E-84," "BONTRON E-88," "BONTRON E-304" (hereinafter manufactured by Orient Chemical Industries Co., Ltd.), "TN-105" (manufactured by Hodogaya Chemical Co., Ltd.), and the like; copper phthalocyanine dyes; quaternary ammonium salts, for example, "COPY CHARGE NX VP434" (manufactured by Clariant), nitroimidazole derivatives, and the like; organometallic compounds and the like.

[0094] The content of the charge control agent is preferably 0.01 parts by mass or more, and more preferably 0.2 parts by mass or more, and the content is preferably 10 parts by mass or less, more preferably 5 parts by mass or less, even more preferably 3 parts by mass or less, and even more preferably 2 parts by mass or less, from the viewpoint of charge stability of the toner, based on 100 parts by mass of the resin binder.

[0095] The toner may be a toner obtained by any of the conventionally known methods such as a melt-kneading method, an emulsion aggregation method, and a suspension polymerization method, or a toner having a core-shell structure, and a pulverized toner produced by the melt-kneading method is preferred, from the viewpoint of smearing property. In the case of a pulverized toner produced by a melt-kneading method, the toner is preferably produced by a method including melt-kneading at least the resin binder and the colorant, and pulverizing the obtained kneaded product, and for example, the toner can be produced by homogeneously mixing the amorphous polyester resin A and the colorant optionally together with a raw material such as a crystalline polyester resin, a releasing agent, and a charge control agent with a mixer such as a Henschel mixer, thereafter melt-kneading the mixture with a closed kneader, a single-screw or twin-screw extruder, an open-roller type kneader or the like, cooling, pulverizing, and classifying the product.

[0096] In the toner of the present invention, an external additive is preferably used, for the purpose of improving transferability. The external additive includes fine inorganic particles of silica, alumina, titania, zirconia, tin oxide, zinc oxide, and the like, and fine organic particles of resin particles such as fine melamine resin particles and fine polytetrafluoroethylene resin particles. Two or more kinds of the external additives may be used in combination. Among them, silica is preferred, and a hydrophobic silica that is hydrophobically treated is more preferred, from the viewpoint of transferability of the toner.

[0097] The hydrophobically treating agent for hydrophobically treating the surface of silica particles includes hexamethyldisilazane (HMDS), dimethyldichlorosilane (DMDS), a cyclic silazane, a silicone oil, an aminosilane, octyltriethoxysilane (OTES), methyltriethoxysilane, and the like.

[0098] The average particle size of the external additive is preferably 5 nm or more, more preferably 10 nm or more, and even more preferably 15 nm or more, and the average particle size is preferably 250 nm or less, more preferably 200 nm or less, and even more preferably 90 nm or less, from the viewpoints of chargeability, flowability, and transferability of the toner.

[0099] The externally adding treatment by mixing the toner particle and the external additive can be carried out according to a conventional method, and the treatment can use a mixer such as a Henschel mixer.

[0100] The content of the external additive is preferably 0.05 parts by mass or more, more preferably 0.1 parts by mass or more, and even more preferably 0.3 parts by mass or more, and the content is preferably 5 parts by mass or less, and more preferably 3 parts by mass or less, based on 100 parts by mass of the toner particle before treatment with the external additive, from the viewpoints of chargeability, flowability, and transferability of the toner.

[0101] The volume-median particle size D_{50} of the toner of the present invention is preferably 3 μm or more, and more preferably 4 μm or more, and the volume-median particle size D_{50} is preferably 15 μm or less, and more preferably 10 μm or less. Here, the volume-median particle size D_{50} as used herein means a particle size of which cumulative volume frequency calculated on a volume percentage is 50% counted from the smaller particle sizes. Also, in a case where the toner is treated with the external additive, the volume-median particle size of the toner particles before the treatment with the external additive is defined as a volume-median particle size of the toner.

[0102] The toner of the present invention can be directly used as a toner for monocomponent development, or mixed with a carrier to be used as a toner for two-component development, and the toner can be used in an image-forming device in a monocomponent development manner or a two-component development manner, respectively.

[0103] With respect to the embodiments described above, the present invention further discloses the following toners for electrostatic image development and the method of producing the same.

<1> A toner for electrostatic image development containing a resin binder and a colorant, wherein the resin binder contains an amorphous polyester resin A which is a polycondensate of a polyethylene terephthalate, an alcohol component and a carboxylic acid component, and the colorant contains an organic yellow pigment having an NH group amount of 4.0 mmol/g or more and 15.0 mmol/g or less, when a value of a total number of -NH-group and -NH₂ group present in a molecule divided by a molecular weight is defined as the NH group amount.

<2> The toner for electrostatic image development according to the above <1>, wherein the polyethylene terephthalate contains a polyethylene terephthalate having a low IV value of 0.40 or more, preferably 0.45 or more, more preferably 0.50 or more, and even more preferably 0.55 or more, and 0.85 or less, preferably 0.80 or less, more preferably 0.75 or less, even more preferably 0.70 or less, and even more preferably 0.65 or less.

<3> The toner for electrostatic image development according to the above <2>, wherein the content of the polyethylene terephthalate having a low IV value is 90% by mass or more, preferably 95% by mass or more, more preferably 98% by mass or more, and even more preferably 100% by mass in a total amount of the polyethylene terephthalate subjected to a polycondensation.

<4> The toner for electrostatic image development according to any one of the above <1> to <3>, wherein the content of the polyethylene terephthalate is 5% by mol or more, preferably 10% by mol or more, and more preferably 20% by mol or more, and 75% by mol or less, preferably 70% by mol or less, more preferably 65% by mol or less, even more preferably 50% by mol or less, even more preferably 40% by mol or less, and even more preferably 30% by mol or less, in a total amount of the alcohol component, the carboxylic acid component and the polyethylene terephthalate.

<5> The toner for electrostatic image development according to any one of the above <1> to <4>, wherein the alcohol component contains an alkylene oxide adduct of bisphenol A represented by the formula (I).

<6> The toner for electrostatic image development according to the above <5>, wherein the content of the alkylene oxide adduct of bisphenol A is 25% by mol or more, preferably 40% by mol or more, and more preferably 55% by mol or more, and 95% by mol or less, preferably 90% by mol or less, and more preferably 85% by mol or less in the alcohol component (including ethylene glycol unit in the polyethylene terephthalate).

<7> The toner for electrostatic image development according to any one of the above <1> to <6>, wherein the amorphous polyester resin A has an ester group concentration of 3.5 mmol/g or more, preferably 3.7 mmol/g or more, and more preferably 4.0 mmol/g or more, and 12.0 mmol/g or less, preferably 10.0 mmol/g or less, and more preferably 6.0 mmol/g or less.

<8> The toner for electrostatic image development according to any one of the above <1> to <7>, wherein the amorphous polyester resin A has a softening point of 70°C or higher, preferably 90°C or higher, and more preferably 100°C or higher, and 170°C or lower, preferably 160°C or lower, and more preferably 150°C or lower.

<9> The toner for electrostatic image development according to any one of the above <1> to <8>, wherein the amorphous polyester resin A contains resins having different softening points, and the difference of the softening points is 10°C or more, and preferably 20°C or more, and 60°C or less, and preferably 40°C or less.

<10> The toner for electrostatic image development according to the above <9>, wherein the amorphous resin having a higher softening point, Resin AH, has a softening point of 100°C or higher, preferably 110°C or higher, and more preferably 120°C or higher, and 170°C or lower, preferably 160°C or lower, and more preferably 150°C or lower.

<11> The toner for electrostatic image development according to the above <9> or <10>, wherein the amorphous resin having lower softening point, Resin AL, has a softening point of 70°C or higher, preferably 90°C or higher, and more preferably 100°C or higher, and 130°C or lower, preferably 125°C or lower, more preferably 120°C or lower, and even more preferably 110°C or lower.

<12> The toner for electrostatic image development according to any one of the above <9> to <11>, wherein the mass ratio of the amorphous resin having a higher softening point, Resin AH, to the amorphous resin having lower softening point, Resin AL, i.e. Resin AH / Resin AL is 10/90 or more, preferably 20/80 or more, and more preferably 30/70 or more, and 90/10 or less, preferably 80/20 or less, and more preferably 75/25 or less.

<13> The toner for electrostatic image development according to any one of the above <1> to <12>, wherein the amorphous polyester resin A has a glass transition temperature of 40°C or higher, and preferably 50°C or higher, and 80°C or lower, and preferably 70°C or lower.

<14> The toner for electrostatic image development according to any one of the above <1> to <13>, wherein the content of the amorphous polyester resin A in the resin binder is 70% by mass or more, preferably 75% by mass or more, and more preferably 80% by mass or more, and 100% by mass or less, preferably 99% by mass or less, more preferably 97% by mass or less, and even more preferably 95% by mass or less.

<15> The toner for electrostatic image development according to any one of the above <1> to <14>, wherein the

resin binder contains a crystalline polyester resin C.

<16> The toner for electrostatic image development according to the above <15>, wherein the crystalline polyester resin C is a polycondensate of an alcohol component containing an aliphatic diol and a carboxylic acid component containing an aliphatic dicarboxylic acid compound.

<17> The toner for electrostatic image development according to the above <16>, wherein the aliphatic diol has a hydroxide group at the terminus of a carbon chain, and the aliphatic diol is preferably α,ω -linear alkane diol.

<18> The toner for electrostatic image development according to the above <16> or <17>, wherein the content of the aliphatic diol in the alcohol component is 80% by mol or more, preferably 90% by mol or more, and more preferably 95% by mol or more, and 100% by mol or less.

<19> The toner for electrostatic image development according to any one of the above <16> to <18>, wherein the content of the aliphatic dicarboxylic acid compound in the carboxylic acid component is 50% by mol or more, preferably 60% by mol or more, more preferably 70% by mol or more, and even more preferably 80% by mol or more, and 100% by mol or less.

<20> The toner for electrostatic image development according to any one of the above <15> to <19>, wherein the crystalline polyester resin C has a softening point of 50°C or higher, preferably 65°C or higher, and more preferably 70°C or higher, and 140°C or lower, preferably 120°C or lower, and more preferably 100°C or lower.

<21> The toner for electrostatic image development according to any one of the above <15> to <20>, wherein the crystalline polyester resin C has a melting point of 50°C or higher, preferably 65°C or higher, and more preferably 70°C or higher, and 130°C or lower, preferably 120°C or lower, and more preferably 100°C or lower.

<22> The toner for electrostatic image development according to any one of the above <15> to <21>, wherein the content of the crystalline polyester resin C in the resin binder is 1% by mass or more, preferably 3% by mass or more, and more preferably 5% by mass or more, and 30% by mass or less, preferably 25% by mass or less, and more preferably 20% by mass or less.

<23> The toner for electrostatic image development according to any one of the above <15> to <22>, wherein the mass ratio of the crystalline polyester resin C to the amorphous polyester resin A, i.e. crystalline polyester resin C / amorphous polyester resin A is 1/99 or more, preferably 3/97 or more, and more preferably 5/95 or more, and 30/70 or less, preferably 25/75 or less, and more preferably 20/80 or less.

<24> The toner for electrostatic image development according to any one of the above <15> to <23>, wherein the total content of the amorphous polyester resin A and the crystalline polyester resin C in the resin binder is 70% by mass or more, preferably 80% by mass or more, more preferably 90% by mass or more, even more preferably 95% by mass or more, and even more preferably 100% by mass.

<25> The toner for electrostatic image development according to any one of the above <1> to <24>, wherein the organic yellow pigment has the NH group amount of preferably 5.0 mmol/g or more, and more preferably 6.0 mmol/g or more, and preferably 12.5 mmol/g or less, and more preferably 10.0 mmol/g or less.

<26> The toner for electrostatic image development according to any one of the above <1> to <25>, wherein the organic yellow pigment is at least one selected from the group consisting of a benzimidazolone pigment, an isoindoline pigment and a condensed disazo pigment.

<27> The toner for electrostatic image development according to any one of the above <1> to <25>, wherein the organic yellow pigment is at least one selected from benzimidazolone pigment and isoindoline pigment, and the organic yellow pigment is at least one selected from preferably C.I. pigment yellow 180 (PY180) and C. I. pigment yellow 185 (PY185).

<28> The toner for electrostatic image development according to any one of the above <1> to <27>, wherein the content of the organic yellow pigment is 1 part by mass or more, preferably 2 parts by mass or more, and more preferably 3 parts by mass or more, and 20 parts by mass or less, preferably 18 parts by mass or less, and more preferably 15 parts by mass or less, based on 100 parts by mass of the amorphous polyester resin A.

<29> The toner for electrostatic image development according to any one of the above <1> to <28>, wherein the content of the colorant is 1 part by mass or more, preferably 2 parts by mass or more, and more preferably 3 parts by mass or more, and 20 parts by mass or less, preferably 18 parts by mass or less, and more preferably 15 parts by mass or less, based on 100 parts by mass of the resin binder.

<30> A method of producing a toner for electrostatic image development as defined in any one of the above <1> to <29>, including melt-kneading at least a resin binder and a colorant, and pulverizing the resulted kneaded product.

[0104] Hereinafter, the present invention will be described more specifically by showing Examples, without intending to limit the scope of the present invention to the following Examples. The physical properties of resins and the like can be measured according to the following methods.

[IV Value of PET]

[0105] A sample is dissolved in a 60/40 mass ratio mixed solvent of phenol/tetrachloroethane at a concentration of 4 g/L, and the solution is subjected to a measurement with Ubbelohde viscometer, and the value can be obtained by the following formula.

$$IV = (-1 + \sqrt{1 + 4k\eta}) / (2kC),$$

wherein, $k = 0.33$, and $C = 0.004$ g/mL, and $\eta = (t_1/t_0) - 1$, wherein t_0 is the number of seconds of dropping only the solvent, and t_1 is the number of seconds of dropping sample solution.

[Softening Point of Resin]

[0106] Using a flow tester "CFT-500D," manufactured by Shimadzu Corporation, a 1 g of sample is extruded through a nozzle having a diameter of 1 mm and a length of 1 mm with applying a load of 1.96 MPa thereto with a plunger, while heating the sample at a heating rate of 6°C/min. The softening point refers to a temperature at which half of the sample flows out, when plotting a downward movement of the plunger of the flow tester against temperature.

[Temperature of Maximum Endothermic Peak of Resin]

[0107] Using a differential scanning calorimeter "Q-100," manufactured by TA Instruments Japan Inc., 0.01 to 0.02 g of sample is weighed out in an aluminum pan, and cooled from room temperature (25°C) to 0°C at a cooling rate of 10°C/min, and kept at 0°C for one minute. Thereafter, the temperature of the sample is raised at a heating rate of 10°C/min to take measurements. Of the endothermic peaks observed, a temperature of the peak having the largest peak area is defined as a temperature of the maximum endothermic peak. In a crystalline resin, the temperature of the maximum endothermic peak is defined as a melting point.

[Glass Transition Temperature of Resin]

[0108] Using a differential scanning calorimeter "Q-100," manufactured by TA Instruments Japan Inc., 0.01 to 0.02 g of sample is weighed out in an aluminum pan, heated to 200°C, and cooled from that temperature to 0°C at a cooling rate of 10°C/min. Next, the sample is heated at a heating rate of 10°C/min to take measurements of endothermic peaks. A temperature at an intersection of the extension of the baseline of equal to or lower than the temperature of the maximum endothermic peak and the tangential line showing the maximum inclination between the kick-off of the peak and the top of the peak in the above measurement is defined as a glass transition temperature.

[Acid Value of Resin]

[0109] The acid value is determined by a method according to JIS K0070:1992 except that only a determination solvent is changed from a mixed solvent of ethanol and ether as prescribed in JIS K0070 to a mixed solvent of acetone and toluene in a volume ratio of acetone : toluene = 1:1 in an amorphous resin, and to a mixed solvent of chloroform and dimethyl formamide in a volume ratio of chloroform : dimethyl formamide = 7:3 in a crystalline resin, respectively.

[Melting Point of Releasing Agent]

[0110] Using a differential scanning calorimeter "Q-100," manufactured by TA Instruments Japan Inc., 0.02 g of sample is weighed out in an aluminum pan, heated to 200°C, and cooled from 200°C to 0°C at a cooling rate of 10°C/min. Next, the temperature of the sample is raised at a heating rate of 10°C/min to measure calory. A temperature of the maximum endothermic peak is defined as a melting point.

[Volume-Median Particle Size and CV Value of Resin Particles, Colorant Particles and Releasing Agent Particles]

[0111]

- (1) Measuring Apparatus: Laser Diffraction Particle Size Analyzer, LA-920, manufactured by HORIBA, Ltd.
- (2) Measurement Conditions: Sample dispersion is taken in a cell for measurement, distilled water is added thereto, and volume-median particle size D_{50} and volume-mean particle size are measured at a temperature in

which an absorbance is within a proper range. In addition, the CV value is calculated according to the following formula.

$$\text{CV Value (\%)} = (\text{Standard Deviation of Particle Size Distribution} / \text{Volume-Mean Particle Size}) \times 100$$

[Solid Content Concentration of Resin Dispersion, Colorant Dispersion and Releasing Agent Dispersion]

[0112] Five grams of measurement sample is dried at 150°C of a dry-temperature, under a condition of measurement mode 96 (monitoring time: 2.5 minutes, fluctuation range: 0.05%) using Infrared Moisture Tester, "FD-230," manufactured by Kett Electric Laboratory Co. Ltd., and the water content (% by mass) of a dispersion is measured. The solid content concentration is calculated according to the following formula.

Solid Content Concentration (% by mass) = 100 - Water Content (% by mass)

[Volume-Median Particle Size of Aggregated Particles]

[0113]

- Measuring Apparatus: "Coulter Multisizer (registered trademark) III," manufactured by Beckman Coulter, Inc.
- Aperture Diameter: 50 μm
- Analyzing Software: "Multisizer (registered trademark) III Ver. 3.51," manufactured by Beckman Coulter, Inc.
- Electrolytic Solution: "Isotone (registered trademark) II," manufactured by Beckman Coulter, Inc.
- Measurement Conditions: The sample dispersion is added to 100 mL of the above electrolytic solution to adjust to a concentration at which particle sizes of 30,000 particles can be measured in 20 seconds, and thereafter the 30,000 particles are measured, and a volume-median particle size D_{50} is obtained from the particle size distribution.

[Average Particle Size of External Additive]

[0114] The average particle size refers to a number-average particle size, which is defined as a number-average of particle sizes (average of length and breadth) determined for 500 particles from a photograph taken with a scanning electron microscope (SEM).

[Volume-Median Particle Size D_{50} of Toner]

[0115]

- Measuring Apparatus: "Coulter Multisizer (registered trademark) III," manufactured by Beckman Coulter, Inc.
- Aperture Diameter: 50 μm
- Analyzing Software: "Multisizer (registered trademark) III Ver. 3.51," manufactured by Beckman Coulter, Inc.
- Electrolytic Solution: "Isotone (registered trademark) II," manufactured by Beckman Coulter, Inc.
- Dispersion: polyoxyethylene lauryl ether, "EMULGEN (registered trademark) 109P," manufactured by Kao Corporation, HLB (Griffin) = 13.6, is dissolved in the electrolytic solution to adjust to a concentration of 5% by mass to provide a dispersion.
- Dispersion Conditions: Ten milligrams of a measurement sample is added to 5 mL of the above dispersion, and the mixture is dispersed for 1 minute with an ultrasonic disperser (name of machine: US-1, manufactured by SND Co., Ltd., output: 80 W). Thereafter, 25 mL of the above electrolytic solution is added to the dispersion, and further dispersed with the ultrasonic disperser for 1 minute, to prepare a sample dispersion.
- Measurement Conditions: The above sample dispersion is added to 100 mL of the above electrolytic solution to adjust to a concentration at which particle sizes of 30,000 particles can be measured in 20 seconds, and thereafter the 30,000 particles are measured, and a volume-median particle size D_{50} is obtained from the particle size distribution.

[Circularity of Toner]

[0116] A circularity of toner particles is measured according to the following condition.

- Measuring Apparatus: Flow Particle Image Analyzer "FPIA-3000," manufactured by SYSMEX CORPORATION
- Preparation of Dispersion: A dispersion of toner particles is diluted with deionized water to have a solid content concentration of from 0.001 to 0.05% by mass, to prepare a dispersion.
- Measuring Mode: HPF measuring mode

Resin Production Example 1

[0117] An alcohol component, a carboxylic acid component other than trimellitic anhydride, a PET, an esterification catalyst and a promoter shown in Tables 1 to 3 were charged into a 10-L four-necked flask equipped with a nitrogen inlet tube, a flow condenser with a dehydration tube, a stirrer and a thermocouple, the content was heated to 235°C under the nitrogen atmosphere, and then the content was subjected to polycondensation at 235°C for 6 hours. Thereafter, the content was cooled to 210°C, trimellitic anhydride shown in Tables 1 to 3 was added thereto, the mixture was reacted for one hour at 210°C, and then the mixture was further reacted at 210°C under a reduced pressure of 10 kPa until softening points described in Tables were reached, to provide amorphous polyester resins (Resins AH1 to AH8, AH13 to AH16). Physical properties are shown in Tables 1 to 3.

Resin Production Example 2

[0118] An alcohol component, a carboxylic acid component, a PET, an esterification catalyst and a promoter shown in Tables 2 and 5 were charged into a 10-L four-necked flask equipped with a nitrogen inlet tube, a flow condenser with a dehydration tube, a stirrer and a thermocouple, temperature of the content was kept at 180°C for one hour under the nitrogen atmosphere, then the content was heated from 180°C to 235°C at a rate of 10°C/h, and the content was further subjected to polycondensation at 235°C for 5 hours. Thereafter, the content was cooled to 210°C to carry out reaction under a reduced pressure of 10 kPa until softening points described in Tables were reached, to provide amorphous polyester resins (Resin AH9, Resin AL9). Physical properties are shown in Tables 2 and 5.

Resin Production Example 3

[0119] An alcohol component, a carboxylic acid component other than trimellitic anhydride, a PET, an esterification catalyst and a promoter shown in Table 2 were charged into a 10-L four-necked flask equipped with a nitrogen inlet tube, a flow condenser with a dehydration tube, a stirrer and a thermocouple, the content was heated to 235°C under the nitrogen atmosphere, and then the content was subjected to polycondensation at 235°C for 10 hours. Thereafter, the content was cooled to 210°C, trimellitic anhydride shown in Table 2 was added thereto, the mixture was reacted for one hour at 210°C, and then the mixture was further reacted at 210°C under a reduced pressure of 10 kPa until softening point described in Table 2 was reached, to provide an amorphous polyester resin (Resin AH10). Physical properties are shown in Table 2.

Resin Production Example 4

[0120] An alcohol component, a carboxylic acid component other than trimellitic anhydride, an esterification catalyst and a promoter shown in Table 2 were charged into a 5-L four-necked flask equipped with a nitrogen inlet tube, a dehydration tube provided with a fractionating column through which water heated at 98°C was flowed, a stirrer and a thermocouple, temperature of the content was kept at 180°C for one hour under the nitrogen atmosphere, then the content was heated from 180°C to 235°C at a rate of 10°C/h, and the content was subjected to polycondensation at 235°C for 5 hours. Thereafter, the content was cooled to 210°C, trimellitic anhydride shown in Table 2 was added thereto, and the mixture was reacted at 210°C for one hour, and then the mixture was further reacted at 210°C under a reduced pressure of 10 kPa until softening point described in Table 2 was reached, to provide an amorphous polyester resin (Resin AH11). Physical properties are shown in Table 2.

Resin Production Example 5

[0121] An alcohol component, a carboxylic acid component other than trimellitic anhydride, an esterification catalyst and a promoter shown in Table 2 were charged into a 10-L four-necked flask equipped with a nitrogen inlet tube, a flow condenser with a dehydration tube, a stirrer and a thermocouple, the content was heated to 235°C under the nitrogen

atmosphere, and then the content was subjected to polycondensation at 235°C for 6 hours. Thereafter, the content was cooled to 210°C, trimellitic anhydride shown in Table 2 was added thereto, the mixture was reacted at 210°C for one hour, and the mixture was further reacted at 210°C under a reduced pressure of 10 kPa until softening point described in Table 2 was reached, to provide an amorphous polyester resin (Resin AH12). Physical properties are shown in Table 2.

Resin Production Example 6

[0122] An alcohol component, a carboxylic acid component, a PET, an esterification catalyst and a promoter shown in Tables 4 to 6 were charged into a 10-L four-necked flask equipped with a nitrogen inlet tube, a flow condenser with a dehydration tube, a stirrer and a thermocouple, the content was heated to 235°C under the nitrogen atmosphere, and then the content was subjected to polycondensation at 235°C for 6 hours. Thereafter, the content was cooled to 210°C and reacted under a reduced pressure of 10 kPa until softening points described in Tables 4 to 6 were reached, to provide amorphous polyester resins (Resins AL1 to AL8, AL13 to AL16). Physical properties are shown in Tables 4 to 6.

Resin Production Example 7

[0123] An alcohol component, a carboxylic acid component, a PET, an esterification catalyst and a promoter shown in Table 5 were charged into a 10-L four-necked flask equipped with a nitrogen inlet tube, a flow condenser with a dehydration tube, a stirrer and a thermocouple, the content was heated to 235°C under the nitrogen atmosphere, and then the content was subjected to polycondensation at 235°C for 10 hours. Thereafter, the content was cooled to 210°C and reacted under a reduced pressure of 10 kPa until softening point described in Table 5 was reached, to provide an amorphous polyester resin (Resin AL10). Physical properties are shown in Table 5.

Resin Production Example 8

[0124] An alcohol component, a carboxylic acid component, an esterification catalyst and a promoter shown in Table 5 were charged into a 5-L four-necked flask equipped with a nitrogen inlet tube, a dehydration tube provided with a fractionating column through which water heated at 98°C was flowed, a stirrer and a thermocouple, the content was kept at 180°C for one hour under the nitrogen atmosphere, then heated from 180°C to 235°C at a rate of 10°C/h, and the content was subjected to polycondensation at 235°C for 5 hours. Thereafter, the content was cooled to 210°C and reacted under a reduced pressure of 10 kPa until softening point described in Table 5 was reached, to provide an amorphous polyester resin (Resin AL11). Physical properties are shown in Table 5.

Resin Production Example 9

[0125] An alcohol component, a carboxylic acid component, an esterification catalyst and a promoter shown in Table 5 were charged into a 10-L four-necked flask equipped with a nitrogen inlet tube, a flow condenser with a dehydration tube, a stirrer and a thermocouple, the content was heated to 235°C under the nitrogen atmosphere, and then the content was subjected to polycondensation at 235°C for 6 hours. Thereafter, the content was cooled to 210°C and reacted under a reduced pressure of 10 kPa until softening point described in Table 5 was reached, to provide an amorphous polyester resin (Resin AL12). Physical properties are shown in Table 5.

[Table 1]

[0126]

Table 1

		Resin AH1		Resin AH2		Resin AH3		Resin AH4		Resin AH5		Resin AH6	
		ratio	g	ratio	g	ratio	g	ratio	g	ratio	g	ratio	g
Alcohol component [A]	BPA-PO(2.2) ¹⁾	65	3757	65	3757	80	4148	90	4367	45	3070	32.5	1915
	BPA-EO ²⁾	--	--	--	--	--	--	--	--	--	--	32.5	1779
Carboxylic acid component [C]	Terephthalic acid	20	548	20	548	35	861	45	1036	--	--	20	559
	Dodecenylsuccinic anhydride	30	1268	30	1268	30	1138	30	1065	30	1497	30	1293
	Trimellitic anhydride	10	317	10	317	10	284	10	266	10	374	10	323
PET [P]	PET1 ³⁾	35	1110	--	--	20	569	10	266	55	2059	35	1131
	PET2 ⁴⁾	--	--	35	1110	--	--	--	--	--	--	--	--
Esterification catalyst	Tin(II) 2-ethylhexanoate	0.5	35	0.5	35	0.5	35	0.5	35	0.5	35	0.5	35
Promoter	Gallic acid	0.05	3.5	0.05	3.5	0.05	3.5	0.05	3.5	0.05	3.5	0.05	3.5
PET content in [A+C+P] (% by mol)		22	22	22	22	11	11	5	5	39	39	22	22
	Softening point (°C)	129	129	130	130	128	128	129	129	132	132	130	130
	Temperature of the maximum endothermic peak (°C)	59	59	59	59	59	59	60	60	57	57	58	58
Physical properties	Crystallinity index	2.2	2.2	2.2	2.2	2.2	2.2	2.2	2.2	2.3	2.3	2.2	2.2
	Glass transition temperature (°C)	56	56	56	56	57	57	58	58	56	56	55	55
	Acid value (mgKOH/g)	13	13	13	13	14	14	14	14	11	11	12	12
	Ester group concentration (mmol/g)	4.7	4.7	4.7	4.7	4.3	4.3	4.0	4.0	5.5	5.5	4.8	4.8
Note 1) The ratio of the alcohol component, the carboxylic acid component and the PET shows a molar ratio based on 100 moles of the alcohol component (including the ethylene glycol unit contained in the PET). Provided that for the PET, (ethylene glycol-terephthalic acid) unit is defined as 1 mol. Note 2) The ratio of the esterification catalyst and the promoter shows a mass ratio based on 100 parts by mass of a total of the alcohol component, the carboxylic acid component and the PET. 1) Polyoxypropylene(2.2)-2,2-bis(4-hydroxyphenyl)propane 2) Polyoxyethylene(2.2)-2,2-bis(4-hydroxyphenyl)propane 3) Virgin PET: RAMAPET L1, manufactured by Indorama Ventures, IV value: 0.60 4) Recycled PET: UK-31, manufactured by Utsumi Recycle Systems Inc, IV value: 0.67													

[Table 2]

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[0127]

Table 2

		Resin AH7		Resin AH8		Resin AH9		Resin AH10		Resin AH11		Resin AH12	
		ratio	g	ratio	g	ratio	g	ratio	g	ratio	g	ratio	g
Alcohol com- ponent [A]	BPA-PO(2.2) ¹⁾	65	4043	70	4152	--	--	65	3757	65	3648	100	4560
	Glycerol	--	--	--	--	5	153	--	--	--	--	--	--
	Neopentyl glycol	--	--	--	--	20	690	--	--	--	--	--	--
	Ethylene glycol	--	--	--	--	--	--	--	--	35	348	--	--
Carboxylic acid compo- nent [C]	Terephthalic acid	35	1033	55	1547	25	1377	20	548	55	1464	55	1190
	Dodecenylsuccinic anhydride	--	--	--	--	--	--	30	1268	30	1232	30	1000
	Adipic acid	15	389	--	--	--	--	--	--	--	--	--	--
	Trimellitic anhydride	10	341	10	325	--	--	10	317	10	308	10	250
PET [P]	PET1 ²⁾	35	1194	30	976	75	4780	35	1110	--	--	--	--
Esterification catalyst	Tin(II) 2-ethylhexanoate	0.5	35	0.5	35	0.5	35	0.5	35	0.5	35	0.5	35
Promoter	Gallic acid	0.05	3.5	0.05	3.5	0.05	3.5	0.05	3.5	0.05	3.5	0.05	3.5
PET content in [A+C+P] (% by mol)		22		18		60		22		0		0	
Physical prop- erties	Softening point (°C)	129		130		127		130		129		130	
	Temperature of the maximum endothermic peak (°C)	56		62		56		60		60		61	
	Crystallinity Index	2.3		2.1		2.3		2.2		2.2		2.1	
	Glass transition temperature (°C)	53		60		53		57		57		58	
	Acid value (mgKOH/g)	10		16		9		14		12		15	
	Ester group concentration (mmol/g)	5.1		4.9		9.4		4.7		4.7		3.8	
Note 1) The ratio of the alcohol component, the carboxylic acid component and the PET shows a molar ratio based on 100 moles of the alcohol component (including the ethylene glycol unit contained in the PET). Provided that for the PET, (ethylene glycol-terephthalic acid) unit is defined as 1 mol.													
Note 2) The ratio of the esterification catalyst and the promoter shows a mass ratio based on 100 parts by mass of a total of the alcohol component, the carboxylic acid component and the PET.													
1) Polyoxypropylene(2.2)-2,2-bis(4-hydroxyphenyl)propane 2) Virgin PET: RAMAPET L1, manufactured by Indorama Ventures, IV value: 0.60													

[Table 3]

[0128]

Table 3

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		Resin AH13		Resin AH14		Resin AH15		Resin AH16	
		ratio	g	ratio	g	ratio	g	ratio	g
Alcohol component [A]	BPA-PO(2.2) ¹⁾	--	--	32.5	1915	32.5	1915	--	--
	BPA-PO(3.0) ²⁾	65	4118	--	--	--	--	65	4118
	BPA-EO ³⁾	--	--	32.5	1779	32.5	1779	--	--
Carboxylic acid component [C]	Terephthalic acid	35	916	20	559	20	559	35	916
	Dodecenylsuccinic anhydride	15	605	30	1293	30	1293	15	605
	Trimellitic anhydride	10	302	10	323	10	323	10	302
PET [P]	PET1 ⁴⁾	35	1059	35	1131	35	1131	--	--
	PET2 ⁵⁾	--	--	--	--	--	--	35	1059
Esterification catalyst	Tin(II) 2-ethylhexanoate	0.5	35	--	--	--	--	--	--
	Titanium diisopropoxy bis(triethanolamine)	--	--	0.5	35	--	--	0.5	35
	Titanium dihydroxy bis(triethanolamine)	--	--	--	--	0.5	35	--	--
Promoter	Gallic acid	0.05	3.5	0.05	3.5	0.05	3.5	0.05	3.5
PET content in [A+C+P] (% by mol)		22		22		22		22	
Physical properties	Softening point (°C)	133		131		129		132	
	Temperature of the maximum endothermic peak (°C)	58		58		57		57	
	Crystallinity Index	2.3		2.3		2.3		2.3	
	Glass transition temperature (°C)	55		55		54		54	
	Acid value (mgKOH/g)	10		11		13		11	
	Ester group concentration (mmol/g)	4.5		4.8		4.8		4.5	

Note 1) The ratio of the alcohol component, the carboxylic acid component and the PET shows a molar ratio based on 100 moles of the alcohol component (including the ethylene glycol unit contained in the PET). Provided that for the PET, (ethylene glycol-terephthalic acid) unit is defined as 1 mol.

Note 2) The ratio of the esterification catalyst and the promoter shows a mass ratio based on 100 parts by mass of a total of the alcohol component, the carboxylic acid component and the PET.

1) Polyoxypropylene(2.2)-2,2-bis(4-hydroxyphenyl)propane 2) Polyoxypropylene (3.0)-2,2-bis(4-hydroxyphenyl)propane

3) Polyoxyethylene(2.2)-2,2-bis(4-hydroxyphenyl)propane

4) Virgin PET: RAMAPET L1, manufactured by Indorama Ventures, IV value: 0.60

5) Recycled PET: UK-31, manufactured by Utsumi Recycle Systems Inc, IV value: 0.67

[Table 4]

[0129]

Table 4

	Resin AL1	Resin AL2		Resin AL3		Resin AL4		Resin AL5		Resin AL6	
	ratio	g	ratio	g	ratio	g	ratio	g	ratio	g	ratio
Alcohol component [A]	65	3780	65	3780	80	4171	90	4390	45	3093	32.5
	--	--	--	--	--	--	--	--	--	--	1790
Carboxylic acid component [C]	30	827	30	827	45	1113	55	1272	10	326	30
	30	1276	30	1276	30	1144	30	1070	30	1508	30
PET [P]	35	1117	--	--	20	572	10	268	55	2073	35
	--	--	35	1117	--	--	--	--	--	--	--
Esterification catalyst	0.5	35	0.5	35	0.5	35	0.5	35	0.5	35	0.5
Promoter	0.05	3.5	0.05	3.5	0.05	3.5	0.05	3.5	0.05	3.5	0.05
PET content in [A+C+P] (% by mol)	22	22	22	22	11	11	5	39	22	22	22
Softening point (°C)	104	105	105	105	105	105	106	103	105	105	105
Temperature of the maximum endothermic peak (°C)	58	58	58	58	58	58	59	56	57	57	57
Crystallinity Index	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8
Glass transition temperature (°C)	55	55	55	55	55	55	56	53	54	54	54
Acid value (mgKOH/g)	9	9	9	9	10	10	10	8	9	9	9
Ester group concentration (mmol/g)	4.7	4.7	4.7	4.7	4.2	4.2	4.0	5.5	4.9	4.9	4.9

Note 1) The ratio of the alcohol component, the carboxylic acid component and the PET shows a molar ratio based on 100 moles of the alcohol component (including the ethylene glycol unit contained in the PET). Provided that for the PET, (ethylene glycol-terephthalic acid) unit is defined as 1 mol.

Note 2) The ratio of the esterification catalyst and the promoter shows a mass ratio based on 100 parts by mass of a total of the alcohol component, the carboxylic acid component and the PET.

1) Polyoxypolypropylene(2,2)-2,2-bis(4-hydroxyphenyl)propane 2) Polyoxypolypropylene(2,2)-2,2-bis(4-hydroxyphenyl)propane

3) Virgin PET: RAMAPET L1, manufactured by Indorama Ventures. IV value: 0.60

4) Recycled PET: UK-31, manufactured by Utsumi Recycle Systems Inc, IV value: 0.67

[Table 5]

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[0130]

Table 5

	Resin AL7		Resin AL8		Resin AL9		Resin AL10		Resin AL11		Resin AL12	
	ratio	g	ratio	g	ratio	g	ratio	g	ratio	g	ratio	g
Alcohol component [A]	BPA-PO(2.2) ¹⁾											
	--	--	--	4039	--	--	65	3780	65	3670	100	4582
	--	--	--	--	25	934	--	--	--	--	--	--
Carboxylic acid com- ponent [C]	Ethylene glycol											
	--	--	--	--	--	--	--	--	35	350	--	--
	Terephthalic acid											
	45	1336	60	1768	15	894	30	827	65	1741	65	1413
PET [P]	Dodecenylsuccinic anhydride											
	--	--	--	--	--	--	30	1276	30	1239	30	1005
Esterification catalyst	Adipic acid											
	15	392	--	--	--	--	--	--	--	--	--	--
	35	1202	35	1193	75	5172	35	1117	--	--	--	--
Promoter	Tin(II) 2-ethylhexanoate											
	0.5	35	0.5	35	0.5	35	0.5	35	0.5	35	0.5	35
PET content in [A+C+P] (% by mol)	Gallic acid											
	0.05	3.5	0.05	3.5	0.05	3.5	0.05	3.5	0.05	3.5	0.05	3.5
Physical properties	Softening point (°C)											
	Temperature of the maximum endothermic peak (°C)											
	Crystallinity Index											
	Glass transition temperature (°C)											
	Acid value (mgKOH/g)											
	Ester group concentration (mmol/g)											

Note 1) The ratio of the alcohol component, the carboxylic acid component and the PET shows a molar ratio based on 100 moles of the alcohol component (including the ethylene glycol unit contained in the PET). Provided that for the PET, (ethylene glycol-terephthalic acid) unit is defined as 1 mol.

Note 2) The ratio of the esterification catalyst and the promoter shows a mass ratio based on 100 parts by mass of a total of the alcohol component, the carboxylic acid component and the PET.

1) Polyoxypropylene(2.2)-2,2-bis(4-hydroxyphenyl)propane 2) Virgin PET: RAMAPET L1, manufactured by Indorama Ventures, IV value: 0.60

[0131] [Table 6]

Table 6

		Resin AL13		Resin AL14		Resin AL15		Resin AL16	
		ratio	g	ratio	g	ratio	g	ratio	g
Alcohol component [A]	BPA-PO(2.2) ¹⁾	--	--	32.5	1927	32.5	1927	--	--
	BPA-PO(3.0) ²⁾	65	4185	--	--	--	--	65	4185
	BPA-EO ³⁾	--	--	32.5	1790	32.5	1790	--	--
Carboxylic acid component [C]	Terephthalic acid	50	1329	30	844	30	844	50	1329
	Dodecenylsuccinic anhydride	10	410	30	1301	30	1301	10	410
PET [P]	PET1 ⁴⁾	35	1076	35	1138	35	1138	--	--
	PET2 ⁵⁾	--	--	--	--	--	--	35	1076
Esterification catalyst	Tin(II) 2-ethylhexanoate	0.5	35	--	--	--	--	--	--
	Titanium diisopropoxy bis(triethanolamine)	--	--	0.5	35	--	--	0.5	35
	Titanium dihydroxy bis(triethanolamine)	--	--	--	--	0.5	35	--	--
Promoter	Gallic acid	0.05	3.5	0.05	3.5	0.05	3.5	0.05	3.5
PET content in [A+C+P] (% by mol)		22		22		22		22	
Physical properties	Softening point (°C)	108		106		104		107	
	Temperature of the maximum endothermic peak (°C)	56		57		56		56	
	Crystallinity Index	1.9		1.9		1.9		1.9	
	Glass transition temperature (°C)	53		54		53		53	
	Acid value (mgKOH/g)	7		8		10		8	
	Ester group concentration (mmol/g)	4.6		4.9		4.9		4.6	
Note 1) The ratio of the alcohol component, the carboxylic acid component and the PET shows a molar ratio based on 100 moles of the alcohol component (including the ethylene glycol unit contained in the PET). Provided that for the PET, (ethylene glycol-terephthalic acid) unit is defined as 1 mol.									
Note 2) The ratio of the esterification catalyst and the promoter shows a mass ratio based on 100 parts by mass of a total of the alcohol component, the carboxylic acid component and the PET.									
1) Polyoxypropylene(2.2)-2,2-bis(4-hydroxyphenyl)propane 2) Polyoxypropylene (3.0)-2,2-bis(4-hydroxyphenyl)propane									
3) Polyoxyethylene(2.2)-2,2-bis(4-hydroxyphenyl)propane									
4) Virgin PET: RAMAPET L1, manufactured by Indorama Ventures, IV value: 0.60									
5) Recycled PET: UK-31, manufactured by Utsumi Recycle Systems Inc, IV value: 0.67									

Resin Production Example 10

[0132] An alcohol component and a carboxylic acid component shown in Table 7 were charged into a 10-L four-necked flask equipped with a thermometer, a stainless-stirrer bar, a flow condenser with a dehydration tube and a nitrogen inlet tube, and the content was heated to 200°C over 8 hours in a mantle heater under a nitrogen atmosphere. Thereafter, an esterification catalyst shown in Table 7 was added thereto and the mixture was reacted at 8.0 kPa until softening point shown in Table 7 was reached, to provide a crystalline polyester resin (Resin C1). Physical properties are shown in Table 7.

[Table 7]

[0133]

Table 7

		Resin C1	
		Molar ratio	g
Alcohol component	1,10-Decanediol	100	3188
Carboxylic acid component	Sebacic acid	103	3812
Esterification catalyst	Tin(II) 2-ethylhexanoate	14 g	
Physical properties	Softening point (°C)	89	
	Melting point (°C)	77	
	Crystallinity Index	1.1	
	Acid value (mgKOH/g)	15	
Note) The molar ratio shows a molar ratio based on 100 mol of the alcohol component.			

Examples 1 to 6, 8 to 11 and 14 to 18, and Comparative Examples 2 and 3 [Melt-Kneading Method]

[0134] One hundred parts by mass of a resin binder as listed in Table 8, 5 parts by mass of a colorant "Toner Yellow HG," manufactured by Clariant, C.I. pigment yellow 180, 3 parts by mass of releasing agent "Carnauba Wax C1," manufactured by S. KATO & CO., melting point: 83°C, and 0.5 parts by mass of a negatively chargeable charge control agent "BONTRON E-304," manufactured by Orient Chemical Industries Co., Ltd. were mixed with a Henschel mixer.

[0135] The resulting mixture was melt-kneaded at a screw rotational speed of 200 r/min, at a barrel setting temperature of 100°C with a same direction revolution twin-screw extruder having a full length of kneading portion of 1560 mm, a screw diameter of 42 mm and a barrel inner diameter of 43 mm, to provide a melt-kneaded product. The feeding rate of the mixture was 20 kg/h, and the average residence time was about 18 seconds.

[0136] The resulting melt-kneaded product was cooled and roughly pulverized, then pulverized with a jet mill, and classified with an air flow type classifier, manufactured by Nippon Pneumatic Mfg. Co., Ltd., to provide toner particles having a volume-median particle size D_{50} of 7.0 μm .

[0137] One hundred parts by mass of the resulting toner particles were mixed with 1.0 parts by mass of a hydrophobic silica "R972," manufactured by NIPPON AEROSIL CO., LTD., hydrophobically treating agent: DMDS, average particle size: 16 nm, and 1.0 parts by mass of a hydrophobic silica "RY-50," manufactured by NIPPON AEROSIL CO., LTD., hydrophobically treating agent: silicone oil, average particle size: 40 nm as external additives with a Henschel mixer at a rotational speed of 3000 r/min (peripheral speed of 32 m/sec) for 3 minutes, to provide yellow toners.

Example 7

[0138] The same manner as that of Example 1 was carried out except that "Paliotol Yellow D1155," manufactured by Sun Chemical Corporation, C.I. pigment yellow 185 was used in place of the colorant "Toner Yellow HG," manufactured by Clariant, C.I. pigment yellow 180 in Example 1, to provide a yellow toner.

Comparative Example 1

[0139] The same manner as that of Example 1 was carried out except that "Toner Yellow 3GP-CT," manufactured by Clariant, C.I. pigment yellow 155 (a total number of -NH-group and -NH₂ group present in a molecule = 2, molecular weight = 717, NH group amount = 2.8 mmol/g) was used in place of the colorant "Toner Yellow HG," manufactured by Clariant, C.I. pigment yellow 180 in Example 1, to provide a yellow toner.

Comparative Example 4

[0140] The same manner as that of Example 1 was carried out except that "HANSA Yellow 5GX01," manufactured by Clariant, C.I. pigment yellow 74 (a total number of -NH-group and -NH₂ group present in a molecule = 1, molecular

weight = 386, NH group amount = 2.6 mmol/g) was used in place of the colorant "Toner Yellow HG," manufactured by Clariant, C.I. pigment yellow 180 in Example 1, to provide a yellow toner.

Example 12

[0141] A yellow toner was obtained in the same manner as Example 1, except that melt-kneading was carried out using a continuous open-roller type twin-screw kneader "Kneadex," manufactured by NIPPON COKE & ENGINEERING CO., LTD. in place of same direction revolution twin-screw extruder. The continuous open-roller type twin-screw kneader had outer diameter of roller: 0.14 m and effective length of roller: 0.8 m, and an operational condition of a rotational speed of a high-rotation roller (front roller) of 75 r/min (a peripheral speed of 33 m/min), a rotational speed of a low-rotation roller (back roller) of 50 r/min (a peripheral speed of 22 m/min), and a gap between the rollers of 0.1 mm. The temperatures of the heating medium and the cooling medium inside the rollers are as follows. The temperature of the high-rotation roller was set at the raw material supplying side to 140°C, and at the kneaded product discharging side to 110°C, and a temperature at the low-rotation roller was set at the raw material supplying side to 65°C, and at the kneaded product discharging side to 30°C. In addition, the feeding rate of the raw material mixture was 10 kg/h, and the average residence time was about 5 minutes.

Example 13 [Emulsion Aggregation Method]

< Preparation of Water-Based Dispersion of Resin Particles for Core >

[0142] A 5-L container equipped with a stirrer, a reflux condenser, a dropping funnel, a thermometer and a nitrogen inlet tube was supplied with 600 g of methyl ethyl ketone, and 129 g of Resin AH1 and 21 g of Resin C1 were added thereto at 60°C, and the mixture was dissolved. To the resulting solution, 5% by mass of aqueous sodium hydroxide solution was added such that the solution had a degree of neutralization of 60% by mol to an acid value of a resin, and the solution was stirred for 30 minutes, to provide a mixture. Subsequently, 675 g of deionized water was added to the mixture over 77 minutes. Next, methyl ethyl ketone was distilled off at a temperature of 50°C or less under a reduced pressure while stirring the mixture at 250 r/min, and thereafter, the solid content concentration of the water-based dispersion was measured, the solid content concentration of the water-based dispersion was adjusted to 20% by mass with deionized water, to provide a resin dispersion for a core. Volume-median particle size D_{50} of resin particles in the dispersion was 200 nm, and CV value was 24%.

< Preparation of Water-Based Dispersion of Resin Particles for Shell >

[0143] A 5-L container equipped with a stirrer, a reflux condenser, a dropping funnel, a thermometer and a nitrogen inlet tube was supplied with 600 g of methyl ethyl ketone, and 150 g of Resin AL1 was added thereto at 60°C, and the mixture was dissolved. To the resulting solution, 5% by mass of aqueous sodium hydroxide solution was added such that the solution had a degree of neutralization of 60% by mol to an acid value of a resin, and the solution was stirred for 30 minutes, to provide a mixture. Subsequently, 675 g of deionized water was added to the mixture over 77 minutes. Next, methyl ethyl ketone and a part of water were distilled off at a temperature of 50°C or less under a reduced pressure while stirring the mixture at 250 r/min, and thereafter, the solid content concentration of the water-based dispersion was measured, the solid content concentration of the water-based dispersion was adjusted to 20% by mass with deionized water, to provide a resin dispersion for a shell. Volume-median particle size D_{50} of resin particles in the dispersion was 130 nm, and CV value was 22%.

< Preparation of Colorant Dispersion >

[0144] In a 1-L beaker, 116.2 g of a colorant "Toner Yellow HG," manufactured by Clariant, C.I. pigment yellow 180, 154.9 g of anionic surfactant "NEOPELEX (registered trademark) G-15," manufactured by Kao Corporation, 15% by mass of aqueous solution of sodium dodecylbenzenesulfonate and 260 g of deionized water were mixed, and the mixture was dispersed for 3 hours under room temperature with a homogenizer, and thereafter deionized water was added thereto such that the mixture had a solid content concentration of 24% by mass, thereby providing a colorant dispersion. Volume-median particle size D_{50} of colorant particles in the dispersion was 140 nm, and CV value was 28%.

< Preparation of Releasing Agent Dispersion >

[0145] Fifty grams of Fischer-Tropsch wax, manufactured by NIPPON SEIRO CO., LTD., trade name: FNP0090,

melting point: 90°C, 5 g of cationic surfactant, manufactured by Kao Corporation, trade name: SANISOL B50 and 200 g of deionized water were heated to 95°C, and the wax was dispersed using a homogenizer, and thereafter, the dispersed wax was subjected to a dispersion treatment with a pressurized discharging-type homogenizer, to provide a releasing agent dispersion having a solid content concentration of 20% by mass. Volume-median particle size D_{50} of releasing agent particles in the dispersion was 550 nm, and CV value was 26%.

< Preparation of Toner Particles >

[0146] In a 3-L four-necked flask equipped with a reflux condenser, a stirrer and a thermocouple, 500 g of the above resin dispersion for a core, 36 g of the above colorant dispersion, 33 g of the above releasing agent dispersion and 3.3 g of 15% by mass of aqueous solution of sodium dodecylbenzenesulfonate, "NEOPELEX G-15," manufactured by Kao Corporation, anionic surfactant, were mixed at 25°C. Next, a solution of which a pH was adjusted to 8.2 by adding 4.8% by mass of aqueous potassium hydroxide solution to an aqueous solution in which 40 g of ammonium sulfate was dissolved in 570 g of deionized water was added dropwise to the resulting mixture over 10 minutes at a temperature of 25°C, while stirring. Thereafter, the mixture was heated to 62°C over 2 hours, and the mixture was maintained at 62°C until the volume-median particle size D_{50} of the aggregated particles reached 7.1 μm , to provide a dispersion of aggregated particles (I).

[0147] To the resulting dispersion of aggregated particles (I), 215 g of the above resin dispersion for a shell was added dropwise at a rate of 0.6 mL/min (0.6 g/min), while keeping temperature of the dispersion at 62°C, to provide a dispersion of aggregated particles (II). Volume-median particle size D_{50} of the aggregated particles (II) was 7.0 μm .

[0148] To the resulting dispersion of aggregated particles (II), an aqueous solution in which 20 g of sodium polyoxyethylene laurylether sulfate, "EMAL E-27C," manufactured by Kao Corporation, anionic surfactant, effective concentration: 27% by mass, 280 g of deionized water and 40 g of aqueous sulfuric acid solution having a concentration of 0.1 mol/L were mixed was added. Thereafter, the mixture was heated to 80°C over 1 hour, and maintained at 80°C for 30 minutes, and then 10 g of aqueous sulfuric acid solution having a concentration of 0.1 mol/L was added thereto, and the mixture was further maintained at 80°C for 15 minutes. Next, 15 g of aqueous sulfuric acid solution having a concentration of 0.1 mol/L was added thereto again, and the mixture was maintained at 80°C until the circularity reached 0.970, thereby providing a dispersion of coalesced particles (core-shell particles) in which aggregated particles were coalesced.

[0149] The resulting dispersion of core-shell particles was cooled to 30°C, the dispersion was subjected to a suction filtration to separate a solid content, and thereafter, the solid content was washed with deionized water at 25°C, and the washed content was subjected to a suction filtration at 25°C for 2 hours. Thereafter, the filtrate was subjected to vacuum drying at 33°C for 24 hours using a vacuum drying oven "DRV622DA," manufactured by ADVANTEC, to provide toner particles. The resulting toner particles had a volume-mean particle size D_{50} of 7.0 μm , and circularity of 0.970. Here, the composition ratio (mass ratio) in a resin binder in the resulting toner particles is Resin AH1/Resin AL1/Resin C1 = 60/30/10.

[0150] One hundred parts by mass of the resulting toner particles, 1.0 parts by mass of hydrophobic silica "R972," manufactured by NIPPON AEROSIL CO., LTD., hydrophobically treating agent: DMDS, average particle size: 16 nm, and 1.0 parts by mass of a hydrophobic silica "RY-50," manufactured by NIPPON AEROSIL CO., LTD., hydrophobically treating agent: silicone oil, average particle size: 40 nm as external additives, were mixed for 3 minutes with a Henschel mixer at a rotational speed of 3000 r/min (peripheral speed of 32 m/sec), to provide yellow toners.

Test Example [Smearing Property of Printout]

[0151] A copying machine, tradename "AR-505," manufactured by Sharp Corporation was loaded with a toner, and a solid image before passing through a fusing machine was taken out, to provide a printout in an unfused state (printed area: 2 cm $\times$ 12 cm, attached amount: 0.5 mg/cm²). Further, an unfused image was printed on the same paper two times to make the attached amount of 1.5 mg/cm². The unfused image thus obtained was subjected to a fusing at 150°C, at a rate of 300 mm/s, to provide a printout.

[0152] A stainless weight having a size of a length of 3 cm, a width of 3 cm, and a height of 6.5 cm, and a weight of 500 g was loaded on the resulting printout, and the weight was moved back-and-forth on the printed image at a speed of 0.5 m/s. One back-and-forth movement was defined as one time, and 50 times was made upper limit. The number of times of black band-like toner smudges appear on the non-printed portion was visually confirmed, to evaluate a smearing property. The results are shown in Table 8. It is shown that the more the number, the more excellent the smearing property is. In the table, ">50" indicates that the toner smudges could not be confirmed even after 50 times.

[Table 8]

Table 8

	Resin binder										Colorant	Production method	Smearing property of printout (times)
	Amorphous polyester resin						Crystalline polyester resin [C]	AH/AL/C (mass ratio)					
	AH	PET content _H	AL	PET content _L	PET content _A	Ester group concentration A							
Ex. 1	Resin AH1	22	Resin AL1	22	22	4.7	Resin C1	60/30/10	PY180	8.2	Melt-kneading (twin screw)	>50	
Ex. 2	Resin AH2	22	Resin AL2	22	22	4.7	Resin C1	60/30/10	PY180	8.2	Melt-kneading (twin screw)	>50	
Ex. 3	Resin AH3	11	Resin AL3	11	11	4.3	Resin C1	60/30/10	PY180	8.2	Melt-kneading (twin screw)	48	
Ex. 4	Resin AH4	5	Resin AL4	5	5	4.0	Resin C1	60/30/10	PY180	8.2	Melt-kneading (twin screw)	45	
Ex. 5	Resin AH5	39	Resin AL5	39	39	5.5	Resin C1	60/30/10	PY180	8.2	Melt-kneading (twin screw)	47	
Ex. 6	Resin AH9	60	Resin AL9	65	62	9.4	Resin C1	60/30/10	PY180	8.2	Melt-kneading (twin screw)	44	
Ex. 7	Resin AH1	22	Resin AL1	22	22	4.7	Resin C1	60/30/10	PY185	11.9	Melt-kneading (twin screw)	>50	
Ex. 8	Resin AH6	22	Resin AL6	22	22	4.8	Resin C1	60/30/10	PY180	8.2	Melt-kneading (twin screw)	48	
Ex. 9	Resin AH7	22	Resin AL7	22	22	5.1	Resin C1	60/30/10	PY180	8.2	Melt-kneading (twin screw)	45	
Ex. 10	Resin AH8	18	Resin AL8	22	19	4.9	Resin C1	60/30/10	PY180	8.2	Melt-kneading (twin screw)	46	
Ex. 11	Resin AH10	22	Resin AL10	22	22	4.7	Resin C1	60/30/10	PY180	8.2	Melt-kneading (twin screw)	45	
Ex. 12	Resin AH1	22	Resin AL1	22	22	4.7	Resin C1	60/30/10	PY180	8.2	Melt-kneading (open-rolled)	47	

[0153]

(continued)

	Resin binder										Production method	Smearing property of printout (times)
	Amorphous polyester resin						Crystalline polyester resin [C]	AH/AL/C (mass ratio)	Colorant			
	AH	PET content H	AL	PET content L	PET content A	Ester group concentration A			Kinds	NH group amount		
Ex. 13	Resin AH1	22	Resin AL1	22	22	4.7	Resin C1	60/30/10	PY180	8.2	Emulsion ag-gregation	46
Ex. 14	Resin AH1	22	Resin AL1	22	22	4.7	-	60/40/0	PY180	8.2	Melt-kneading (twin screw)	>50
Ex. 15	Resin AH13	22	Resin AL13	22	22	4.5	Resin C1	60/30/10	PY180	8.2	Melt-kneading (twin screw)	>50
Ex. 16	Resin AH14	22	Resin AL14	22	22	4.8	Resin C1	60/30/10	PY180	8.2	Melt-kneading (twin screw)	>50
Ex. 17	Resin AH15	22	Resin AL15	22	22	4.8	Resin C1	60/30/10	PY180	8.2	Melt-kneading (twin screw)	>50
Ex. 18	Resin AH16	22	Resin AL16	22	22	4.5	Resin C1	60/30/10	PY180	8.2	Melt-kneading (twin screw)	>50
Comp. Ex. 1	Resin AH1	22	Resin AL1	22	22	4.7	Resin C1	60/30/10	PY155	2.8	Melt-kneading (twin screw)	34
Comp. Ex. 2	Resin AH11	0	Resin AL11	0	0	4.7	Resin C1	60/30/10	PY180	8.2	Melt-kneading (twin screw)	38
Comp. Ex. 3	Resin AH12	0	Resin AL12	0	0	3.8	Resin C1	60/30/10	PY180	8.2	Melt-kneading (twin screw)	25
Comp. Ex. 4	Resin AH1	22	Resin AL1	22	22	4.7	Resin C1	60/30/10	PY74	2.6	Melt-kneading (twin screw)	33
Note 1) PET content A is a weighted average of PET content H (mol%) and PET content L (mol%).												
Note 2) Ester group concentration A is a weighted average of ester group concentrations of Resin AH and Resin AL.												
Note 3) PY155: C.I. Pigment Yellow 155, PY74: C.I. Pigment Yellow 74												

[0154] It is found from the above results that toners of Examples 1 to 18 have excellent smearing property as compared to toners of Comparative Examples 1 and 4 containing an organic yellow pigment in which an NH group amount is small, and toners of Comparative Examples 2 and 3 without using a PET. Particularly, it is found from Comparative Example 2 that the use of an ethylene glycol and a terephthalic acid which are a monomeric component of a PET is not effective, and the use of a PET is important.

[0155] The toner for electrostatic image development of the present invention is suitably used in the development and the like of latent images formed in electrophotography, electrostatic recording method, electrostatic printing method and the like.

Claims

1. A toner for electrostatic image development comprising a resin binder and a colorant, wherein the resin binder comprises an amorphous polyester resin A which is a polycondensate of a polyethylene terephthalate, an alcohol component and a carboxylic acid component, and the colorant comprises an organic yellow pigment having an NH group amount of 4.0 mmol/g or more and 15.0 mmol/g or less, when a value of a total number of -NH-group and -NH₂ group present in a molecule divided by a molecular weight is defined as the NH group amount.
2. The toner for electrostatic image development according to claim 1, wherein the content of the polyethylene terephthalate is 5% by mol or more and 75% by mol or less in a total amount of the alcohol component, the carboxylic acid component and the polyethylene terephthalate, when a unit of terephthalic acid-ethylene glycol is defined as 1 mole.
3. The toner for electrostatic image development according to claim 1, wherein the content of the polyethylene terephthalate is 10% by mol or more and 50% by mol or less in a total amount of the alcohol component, the carboxylic acid component and the polyethylene terephthalate, when a unit of terephthalic acid-ethylene glycol is defined as 1 mole.
4. The toner for electrostatic image development according to any one of claims 1 to 3, wherein the polyethylene terephthalate has an IV value of 0.40 or more and 0.85 or less.
5. The toner for electrostatic image development according to any one of claims 1 to 4, wherein the organic yellow pigment is at least one selected from the group consisting of a benzimidazolone pigment, an isoindoline pigment and a condensed disazo pigment.
6. The toner for electrostatic image development according to any one of claims 1 to 4, wherein the organic yellow pigment is at least one selected from C.I. pigment yellow 180 and C.I. pigment yellow 185.
7. The toner for electrostatic image development according to any one of claims 1 to 6, wherein the amorphous polyester resin A has an ester group concentration of 3.5 mmol/g or more and 12.0 mmol/g or less.
8. The toner for electrostatic image development according to any one of claims 1 to 7, wherein the content of the organic yellow pigment is 1 part by mass or more and 20 parts by mass or less, based on 100 parts by mass of the amorphous polyester resin A.
9. The toner for electrostatic image development according to any one of claims 1 to 8, wherein the resin binder further comprises a crystalline polyester resin C.
10. The toner for electrostatic image development according to any one of claims 1 to 9, wherein the amorphous polyester resin A comprises resins having different softening points of which a difference of the softening points is 10°C or more.
11. A method of producing a toner for electrostatic image development as defined in any one of claims 1 to 10, comprising melt-kneading at least a resin binder and a colorant, and pulverizing the resulting kneaded product.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2024/041854

A. CLASSIFICATION OF SUBJECT MATTER

G03G 9/09(2006.01)i; **G03G 9/087**(2006.01)i
 FI: G03G9/09; G03G9/087 331

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
 G03G9/09; G03G9/087

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Published examined utility model applications of Japan 1922-1996
 Published unexamined utility model applications of Japan 1971-2025
 Registered utility model specifications of Japan 1996-2025
 Published registered utility model applications of Japan 1994-2025

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 2023-133117 A (RICOH COMPANY, LTD.) 22 September 2023 (2023-09-22) claims, paragraphs [0269]-[0303]	1-3, 5-9
Y		4
A		10-11
Y	JP 2017-090889 A (KAO CORPORATION) 25 May 2017 (2017-05-25) claims, paragraph [0107]	4
A		1-3, 5-11
Y	JP 2019-095515 A (KAO CORPORATION) 20 June 2019 (2019-06-20) claims, paragraph [0036]	4
A		1-3, 5-11
A	JP 2023-168265 A (RICOH COMPANY, LTD.) 24 November 2023 (2023-11-24) entire text, all drawings	1-11

☒ Further documents are listed in the continuation of Box C.☒ See patent family annex.

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“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

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C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2004/049075 A1 (MITSUI CHEMICALS, INC.) 10 June 2004 (2004-06-10) entire text, all drawings	1-11

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/JP2024/041854

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Patent document cited in search report			Publication date (day/month/year)	Patent family member(s)			Publication date (day/month/year)
JP	2023-133117	A	22 September 2023	US	2023/0288829	A1	
				claims, paragraphs [0339]-[0423]			
JP	2017-090889	A	25 May 2017	US	2018/0299799	A1	
				claims, paragraph [0108]			
				EP	3373071	A1	
JP	2019-095515	A	20 June 2019	(Family: none)			
JP	2023-168265	A	24 November 2023	US	2023/0367236	A1	
				EP	4276540	A1	
WO	2004/049075	A1	10 June 2004	US	2006/0078816	A1	
				EP	1569042	A1	

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- JP 2020154154 A [0004]
- JP 11133668 A [0040]
- JP HEI10239903 A [0040]
- JP 8020636 A [0040]