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# (54) Title: POLYESTER RESIN AND TONER INCLUDING THE SAME

**(57) Abstract:** An environmentally favorable polyester resin for toner, which has superior fixing property, storage stability, and image density in an electrophotographic image forming process is disclosed. The polyester resin is produced by carrying out esterification reaction and polycondensation reaction of reactant comprising branched aliphatic epoxy compound, aromatic dibasic acid, and aliphatic diol. The branched aliphatic epoxy compound has 1 to 5 of epoxy group(s), and is formed by the glycidylation of polyhydric alcohol. The amount of the branched aliphatic epoxy compound is 2 to 15 mol %, the amount of the aliphatic diol is 55 to 98 mol % with respect to the total alcohol components, and the amount of the aromatic dibasic acid is 60 to 100 mol % with respect to the total acid components.

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# Description

# POLYESTER RESIN AND TONER INCLUDING THE SAME

## Technical Field

[1] This invention relates to a polyester resin and toner including the same, and more particularly, to an environmentally favorable polyester resin for toner, which has superior fixing property, storage stability, and image density in an electrophotographic image forming process, and toner including the same.

## Background Art

[2] In general, an electrophotographic image forming process or an electrostatic printing process includes the steps of (a) forming an electrostatically charged image (hereinafter latent image ), which corresponds to a recording image, on a surface of an electrostatic recording medium, (b) developing the latent image with charged toner, (c) transferring the toner image to a recording material such as a paper or a recording film, and finally (d) fixing the transferred image on the recording material. The image forming process has advantages in that the copied or the printed material can be obtained with a high speed, the image formed on the electrostatic recording medium is stable, and an image-forming device is easy to manipulate. Therefore, the im age-forming process is widely used in the field of copiers and printers. In more detail, the image-forming process includes (1) a charging process for electrically charging a drum (for example, organic photoconductor drum: OPC) coated with a photoconductive or a photosensitive material, (2) an exposing process for forming an electrostatic latent image on the drum with the light reflected from an original image being copied, (3) a developing process for electrostatically adhering charged toner onto the latent image, (4) a transferring process for adhering a charged paper to the drum, and transferring the toner image on the drum to the adhered paper, (5) a fixing process for fixing the transferred toner image on the paper with a thermo-pressing roller, and (6) a cleaning process for removing the residual toner and the residual charge on the drum.

[3]

[4] The toner useful in the developing process may include a binder resin, a coloring agent, a charge control agent, and other additives. If a magnetic drum is used, the toner may include a magnetic material for developing the magnetic latent image formed on the drum. The toner is produced by melting, kneading and dispersing these components, and the toner of a particle shape is produced by pulverizing and classifying the kneaded components. The physical properties of the toner mainly depend on the binder resin, which is a main component of the toner. Accordingly, the desirable binder resin should have superior properties in dispersibility of the coloring

agent, fixing property, offset resisting property, and storage stability, and should be colorless to produce clear and vivid color images. In addition, the binder resin should provide superior image density on the copied material, and should be environmentally favorable.

[5]

[6] As the binder resin, a polyester resin is widely used due to its superior fixing property, transparency, and so on, in place of conventional resins such as polystyrene resin, styrene acrylic resin, epoxy resin, polyamide resin, and so on. For producing the polyester resin for toner, bisphenol A or its derivatives is generally used. However, bisphenol A is not an environmentally favorable material. Therefore, without using bisphenol A or its derivatives, it is required to develop a polyester resin for toner which has good characteristics in offset resisting property, fixing property at low temperature, sharp melting property, blocking resistance, charging property, pulverizing property, transparency, and long term endurance of a developed image. Recently, it is also required to produce the toner with a low cost.

[7]

[8] As a catalyst for producing the polyester resin, germanium catalyst, antimony catalyst, tin catalyst, etc., have been conventionally used. However, the conventional catalysts have a low activity and should be used in large amount, and are not favorable in an environmental aspect. In addition, the conventional catalyst have their characteristic colors in the produced polyester (for example, antimony catalyst produces gray color in the produced polyester), which deteriorates the transparency of the produced polyester resin. Therefore, it is tried to partially or fully replace the conventional catalysts with titanium catalyst such as tetraethyl titanate, acetyltripropyl titanate, tetrapropyl titanate, tetrabutyl titanate, polybutyl titanate, ethylacetoacetic ester titanate, isostearyl titanate, titanium dioxide, $TiO_2/SiO_2$ coprecipitates or $TiO_2/ZrO_2$ coprecipitates to improve the catalyst activity and the transparency of the polyester resin. The titanium catalyst is used in a small amount, and the catalyst activity is relatively superior compared with the antimony catalyst.

[9]

[10] The binder polyester resin for toner without bisphenol A or its derivatives is disclosed in Korean Patent Publication Nos. 10-2005-0051543 and 10-2005-0006232. In the Patent Publications, cross-linkage or gelation (non-dissolving property of the resin with respect to tetrahydrofuran (THF)) by using polyvalent acid and alcohol is carried out to improve the offset resisting property of the produced toner. However, the cross-linked or gelated polyester resin has a high softening temperature, which results in the deteriorated fixing property at low temperature and low fixing speed. For example, when a copying is carried out at a printing speed of 50 sheets/minute, the

toner s fixing property is deteriorated, and it is impossible to obtain a copied material having desirable toner fixing strength.

## Disclosure of Invention

## Technical Problem

[11] Therefore, it is an object of the present invention to provide a toner having superior offset resisting property and superior fixing property at low temperature, and a polyester resin for producing the toner.

[12] It is other object of the present invention to provide a toner which is environmentally favorable because of not using bisphenol A, its derivatives or heavy metal catalyst such as tin or antimony, and a polyester resin for producing the toner

## Technical Solution

[13] To accomplish these and other objects, the present invention provides a polyester resin for toner comprising branched aliphatic epoxy compound, aromatic dibasic acid, and aliphatic diol as polymerization components. The polyester resin is produced by carrying out esterification reaction and polycondensation reaction of the polymerization components. The branched aliphatic epoxy compound is a glycidylated compound of polyhydric alcohol, which is selected from the group consisting of erythritol, mannitol, sorbitol, 1,2,3,6-hexanetetrol, 1,4-sorbitane, pentaerythritol, dipentaerythritol, tripentaerythritol, sucrose, 1,2,4-butanetriol, 1,2,5-pentatriol, glycerol, 2-methylpropanetriol, 2-methyl-1,2,4-butanetriol, trimethylolethane, trimethylolpropane and mixture thereof, and the branched aliphatic epoxy compound has 1 to 5 of epoxy group(s). The amount of the branched aliphatic epoxy compound is 2 to15 mol%, and the amount of the aliphatic diol is 55 to 98mol% with respect to the total alcohol components, and the amount of the aromatic dibasic acid is 60 to 100mol% with respect to the total acid components. The reactant, if necessary, further includes a compound selected from the group consisting of titanium catalyst, aliphatic dibasic acid, polyvalent acid, monobasic acid, polyhydric alcohol, and monohydric alcohol.

## Mode for the Invention

[14] A more complete appreciation of the invention, and many of the attendant advantages thereof, will be better appreciated by reference to the following detailed description.

[15]

[16] The reactant for preparation of a polyester resin for toner according to the present invention includes branched aliphatic epoxy compound. The branched aliphatic epoxy compound has a structure of (poly)glycidyl ether of branched aliphatic polyhydric alcohol. Namely, the epoxy compound is glycidylated compound of polyhydric

alcohol. The branched aliphatic epoxy compound has 1 to 5 of epoxy group(s), and is formed by the glycidylation of polyhydric alcohol, for example, erythritol, mannitol, sorbitol, 1,2,3,6-hexanetetrol, 1,4-sorbitane, pentaerythritol, dipentaerythritol, tripentaerythritol, sucrose, 1,2,4-butanetriol, 1,2,5-pentatriol, glycerol, 2-methylpropanetriol, 2-methyl-1,2,4-butanetriol, trimethylolethane, trimethylolpropane, and so on. The amount of the branched aliphatic epoxy compound is 2 to15 mol%, preferably 5 to10 mol% with respect to the total alcohol components. In this specification, the total alcohol components includes monohydric alcohol, diol component, trihydric or higher alcohol and the branched aliphatic epoxy compound. If the amount of the branched aliphatic epoxy compound is more than 15 mol%, it is difficult to obtain a desirable resin, and is difficult to control the gelation of the polyester resin during the preparation of the resin. If the amount of the branched aliphatic epoxy compound is less than 2 mol%, the amount of gel in the polyester resin is not sufficient.

[17]

[18] In the present invention, the branched aliphatic epoxy compound is used instead of a conventional aromatic diol which is environmentally unfavorable. The conventional aromatic diol includes bisphenol A and its derivatives. Examples of bisphenol A derivative include polyoxyethylene-(2.0)-2,2-bis(4-hydroxyphenyl)propane, polyoxypropylene-(2.0)-2,2-bis(4-hydroxyphenyl)propane, polyoxypropylene-(2.2)-polyoxyethylene-(2.0)-2,2-bis(4-hydroxyphenyl)propane, polyoxyethylene-(2.3)-2,2-bis(4-hydroxyphenyl)propane, polyoxypropylene-(6)-2,2-bis(4-hydroxyphenyl)propane, polyoxypropylene-(2.3)-2,2-bis(4-hydroxyphenyl) propane, polyoxypropylene-(2.4)-2,2-bis(4-hydroxyphenyl)propane, polyoxypropylene-(3.3)-2,2-bis(4-hydroxyphenyl)propane, polyoxyethylene-(3.0)-2,2-bis(4-hydroxyphenyl)propane, polyoxyethylene-(6)-2,2-bis(4-hydroxyphenyl) propane, and so on.

[19]

[20] The reactant for preparation of the polyester resin for toner according to the present invention includes aromatic dibasic acid and/or alkyl ester thereof (hereinafter, collectively aromatic dibasic acid ) which is conventionally used in the preparation of a polyester resin. The representative examples of the aromatic dibasic acid include terephthalic acid and isophthalic acid. Examples of the alkyl ester of the aromatic dibasic acid include dimethyl terephthalate, dimethyl isophthalate, diethyl terephthalate, diethyl isophthalate, dibutyl terephthalate, dibutyl isophthalate, and so on. The aromatic dibasic acid and alkyl ester thereof can be used independently or in combination. The aromatic dibasic acid has a benzene ring of a high hydrophobic property, and thereby can improve the moisture-proof property of a toner and increase

the glass transition temperature (hereinafter, Tg ) of the produced resin, which results in the improved storage stability of the toner. The amount of the aromatic dibasic acid is 60 to 100mol% with respect to the total acid components, and more preferably 80 to 100mol%. The terephthalic acid increases toughness and Tg of the produced resin, and the isophthalic acid increases reactivity. Therefore, the ratio of terephthalic acid and isophthalic acid can be varied according to the desired property of the produced polyester resin.

[21]

[22] The reactant for preparation of the polyester resin for a toner according to the present invention includes aliphatic diol. Examples of the useful aliphatic diol include ethylene glycol, diethylene glycol, neopentyl glycol, propylene glycol, butane diol, and so on. Among the aliphatic diols, it is desirable to use propylene glycol when considering the reactivity control during the polycondensation reaction. The aliphatic diol except propylene glycol increases the polycondensation reaction rate, and thereby it is difficult to control the polycondensation reaction rate, which may result in the excess and abrupt increase of the molecular weight of a polyester resin or the gelation. Therefore, propylene glycol having secondary alcohol can be preferably used independently or in combination with other aliphatic diol. The preferable amount of the aliphatic diol is 55 to 98mol%, and more preferably 75 to 95mol% with respect to the total alcohol components. More preferably, the amount of propylene glycol is more than 55mol%, and the amount of other aliphatic diol is less than 43mol% with respect to the total alcohol components.

[23]

[24] The reactant for preparation of the polyester resin according to the present invention, if necessary, includes aliphatic dibasic acid, alkyl ester thereof, and/or acid anhydride thereof. Non-limiting examples of the compounds include aliphatic dibasic acid such as sebacic acid, isodecyl succinic acid, maleic acid, fumaric acid, adipic acid, azelaic acid, and so on, their monomethyl, monoethyl, dimethyl, diethylester and their acid anhydrides. The aliphatic dicarboxylic acid influences considerably on the fixing property and the storage stability of the toner. Therefore, the aliphatic dibasic acid should be properly used according to the demanded property of the resin, and the preferable amount of the aliphatic dibasic acid is equal or less than 10 mol%.

[25]

[26] The reactant for preparation of the polyester resin according to the present invention, if necessary, includes trivalent or higher acid. Non-limiting examples of the trivalent or higher acid include trimellitic acid, pyromellitic acid, 1,2,4-cyclohexanetricarboxylic acid, 2,5,7-naphthalenetricarboxylic acid, 1,2,4-naphthalenetricarboxylic acid, 1,2,5-hexanetricarboxylic acid,

1,2,7,8-octanetetracarboxylic acid, and their alkyl ester and acid anhydrides. The trivalent or higher acid can be used independently or in combination. The trivalent or higher acid increases the Tg of a produced resin, makes the resin to have a cohesive property, and improves the offset resisting property of a toner. The amount of trivalent or higher acid is preferably equal or less than 10 mol%, and more preferably less than 5 mol% with respect to the total acid components. If the amount of trivalent or higher acid is more than 10 mol%, it is difficult to obtain the desirable resin because it is difficult to control the gelation of the polyester resin during the preparation of the polyester resin.

[27]

[28] The reactant for preparation of the polyester resin according to the present invention may further include aliphatic or aromatic monobasic acid for controlling the polycondensation reaction rate. Non-limiting examples of the monobasic acid include aliphatic basic acid such as octanoic acid, decanoic acid, dodecanoic acid, myristic acid, palmitic acid, stearic acid, and so on, which may be branched, and may have unsaturated groups. Other examples of the monobasic acid include aromatic basic acid such as benzoic acid, naphthalenecarboxylic acid, and so on. The amount of the monobasic acid is equal or less than 20 mol%, and preferably equal or less than 10 mol% with respect to the total acid components. If the amount of the monobasic acid is more than 20mol%, the Tg of the resin decreases, which influences badly on the storage stability of a toner, and the desirable molecular weight of the polyester resin cannot be obtained.

[29]

[30] The reactant for preparation of the polyester resin according to the present invention, if necessary, includes trihydric or higher alcohol. Non-limiting examples of the trihydric or higher alcohol include sorbitol, 1,2,3,6-hexanetetrol, 1,4-sorbitane, pentaerythritol, dipentaerythritol, tripentaerythritol, sucrose, 1,2,4-butanetriol, 1,2,5-pentanetriol, glycerol, 2-methylpropanetriol, 2-methyl-1,2,4-butanetriol, trimethylolethane, trimethylolpropane, and 1,3,5-trihydroxymethylbenzene, and so on. The trihydric or higher alcohol can be used independently or in combination. The trihydric or higher alcohol increases the Tg of a produced resin, makes resin to have a cohesive property, and improves the storage stability of a toner. The amount of the trihydric or higher alcohol is less than equal or 10mol%, and preferably less than 5 mol% with respect to the total alcohol components. If the trihydric or higher alcohol is more than 10mol%, it is difficult to obtain a desirable resin because it is difficult to control the gelation of the polyester resin during the preparation of the polyester resin. In case of using the trihydric or higher alcohol in combination, the preferable total amount thereof is less than 10mol%.

[31]

[32] The reactant for preparation of the polyester resin according to the present invention may further include aliphatic monohydric alcohol for controlling the molecular weight of a produced resin. Non-limiting examples of the monohydric alcohol include aliphatic monohydric alcohol such as octanol, decanol, dodecanol, myristic alcohol, stearyl alcohol, and so on, which may be branched, and may have unsaturated groups. The amount of the monohydric alcohol is equal or less than 20 mol%, and more preferably equal or less than 10 mol% with respect to the total alcohol components. If the amount of the monohydric alcohol is more than 20mol%, the Tg of a resin decreases, which influences badly on the storage stability of a toner, and the desirable molecular weight of a polyester resin cannot be obtained.

[33]

[34] In the reactant for preparation of the polyester resin according to the present invention, the molar ratio of the total alcohol components (G) to the total acid components (A) is preferably 1.2 to 1.6. If the ratio (G/A) is less than 1.2, non-reacted acid component exists in the condensation reaction, and thereby the transparency of the produced resin can be deteriorated. If the ratio (G/A) is more than 1.6, the condensation reaction rate is so slow that the productivity of resin can be reduced.

[35]

[36] The polyester resin according to the present invention can be prepared by conventional two steps of an esterification reaction or ester exchange reaction and a polycondensation reaction. To prepare a polyester resin according to the present invention, the acid components and the alcohol components are charged into a reactor and heated to carry out the esterification or ester exchange reaction. Then, if necessary, conventional titanium catalyst for the esterification or ester exchange reaction, such as tetraethyl titanate, acetyltripropyl titanate, tetrapropyl titanate, tetrabutyl titanate, polybutyl titanate, ethylacetoacetic ester titanate, isostearyl titanate, titanium dioxide, $TiO_2/SiO_2$ coprecipitates or $TiO_2/ZrO_2$ coprecipitates and so on can be used. However, heavy metal catalysts such as antimony catalyst and tin catalyst(environmentally unfavorable materials) are not preferable. The esterification reaction is, for example, carried out under nitrogen flow at the reaction temperature of 230 to 260°C, while removing the water or alcohol produced from the reaction in conventional way. After completion of the reaction, the polycondensation reaction is carried out. The polycondensation reaction can also be carried out under the conventional conditions, for example, at the temperature of 240 to 260°C, and preferably at the temperature of less than 250°C. The polycondensation reaction can includes the steps of (a) reacting the reactant under high-vacuum and high speed stirring, as the first step, (b) then changing the high-vacuum to an atmospheric pressure by injecting nitrogen gas into the reactor

and reacting the reactant under the high speed stirring, and (c) reacting the reactant under an atmospheric pressure and low speed stirring. During the polycondensation reaction, the byproduct such as glycol can be removed by distillation. In the first step of the polycondensation reaction, the high vacuum means a pressure of equal to or less than 100mmHg, and preferably equal to or less than 30mmHg. By maintaining the high vacuum, the byproduct having low boiling point can be removed from the reaction products.

[37]

[38] The amount of a gelated portion(a non-dissolving portion of the resin with respect to tetrahydrofuran (THF)) in the polyester resin of the present invention is 5 to 30 weight%, and preferably 10 to 20 weight%. If the amount of the gelated portion is less than 5 weight%, the offset-resisting property of the toner is not sufficient. If the amount of the gelated portion is more than 30 weight%, the viscosity of the resin increase, and thereby industrially stable mass-production is impossible. The softening temperature of the polyester resin is preferably 140 to 180℃, and more preferably 150 to 170℃. If the softening temperature is less than 140℃, Tg can be lowered, and the storage stability can be deteriorated, and thereby the toner particles can be aggregated during a storage. If the softening temperature is more than 180℃, the fixing property at low-temperature can be deteriorated, and the offset may cause. The Tg of the polyester resin is preferably 50 to 75℃. If the Tg is less than 50℃, the storage stability of the toner can be deteriorated, and if the Tg is more than 75℃, the fixing property at low-temperature of the toner can be deteriorated, especially when the large size polyester particles are used as the binder, and the desirable image can not be obtained. The acid value of the polyester resin according to the present invention is preferably 1 to 25 KOHmg/g, and more preferably 5 to 20 KOHmg/g. If the acid value is less than 1 KOHmg/g, developing of a latent image with the toner and transferring of the developed toner image are not satisfactorily performed, and the image can be deteriorated. If the acid value is more than 25 KOHmg/g, the storage stability of the polyester resin can be deteriorated.

[39]

[40] The polyester resin according to the present invention is used as the main co mponent of a binder resin for the preparation of toner, and if necessary, other resin such as styrene resin or styrene-acryl resin can be used in combination with the polyester resin. The amount of the binder resin in toner is preferably 30 to 95 weight%, and more preferably 35 to 90 weight%. If the amount of the binder resin is less than 30 weight%, the offset resisting property of the toner can be deteriorated, and if the amount of the binder resin is more than 95 weight%, the charging stability of toner can be deteriorated.

[41]

[42] The polyester resin according to the present invention can be used with a coloring agent for toner. Examples of the coloring agent include carbon black, nigrosine dyes, lamp black, sudan black SM, naval yellow, mineral fast yellow, litol red, permanent orange 4R, and so on. Also, the polyester resin according to the present invention can be used with various additives, which are conventional in a production of toner, such as wax, charge control agent, offset preventing agent, magnetic material such as magnetic powder, and so on. Examples of the charge control agent include nigrosine, azine-based dye containing alkyl group, basic dye, monoazo dye and their metal complex, salicylic acid and its metal complex, alkyl salicylic acid and its metal complex, naphthoic acid and its metal complex, etc. Examples of the offset preventing agent include polyethylene, polypropylene, ethylene-polypropylene copolymer, etc., and examples of the magnetic powder include ferrite, magnetite, etc. The toner, which includes the polyester resin according to the present invention as the binder resin, can be prepared in conventional methods. For example, the toner can be prepared by kneading polyester resin as a binder resin, coloring agent, and additives with a uniaxial or biaxial extruder or mixer at the temperature of 15 to 30℃ higher than the softening temperature of the binder, and pulverizing the kneaded product to particles. The average size of the prepared toner particles is preferably 5 to 10□, and more preferably 7 to 9□. It is more preferable that the amount of the minute particles having the particle size of less than 5□ is less than 3 weight% with respect to the total toner.

[43]

[44] The following Examples and Comparative examples are provided to illustrate the present invention in more detail, but the present invention is not limited by the following examples. The test methods used in Examples are as follows:

[45]

[46] Amount of Gel portion (weight%)

[47] The gel amount is the amount of resin which is not dissolved with tetrahydrofuran (THF). This test is carried out in order to evaluate the cross-linking density of a resin. 0.1 g of resin was put into 100 ml of THF, and dissolved while stirring for 2 hours. After 22 hours, the solution was filtered with 200 mesh stainless filter. The amount of the remaining (not-dissolved) resin was measured, and is calculated in percentage with respect to the amount of the original resin.

[48]

[49] (2) Glass Transition Temperature (Tg, ℃)

[50] The glass transition temperature was measured with a differential scanning calorimeter (manufactured by TA Instruments) while increasing a sample temperature by 10℃/minute after melting and quenching the sample. The Tg was determined from

the mid value of tangent lines of the base lines of an endothermic curve.

[51]

[52] (3) Softening Temperature (℃)

[53] The softening temperature was determined with a flow tester(CFT-500D, manufactured by Shimadzu Laboratories), and is a temperature at the moment that the half of 1.5g sample flows out from a 1.0Φ×10 mm(height) nozzle under the conditions of 10 kgf of load, and temperature increase rate of 6℃/minute.

[54]

[55] (4) Acid Value (KOHmg/g): Resin was dissolved with dichloromethane, cooled, and titrated with 0.1N KOH-methanol solution.

[56]

[57] (5) Gelation of polymerization product

[58] In the polycondensation reaction, the case that the product cannot be obtained from the reactor because of the increase of viscosity was defined as gelation (gel amount: more than 30 weight%), and the case that the polymerization time is more than 300 minutes due to the slow reaction rate, and the case that non-reacted acid component is found were defined as non-reaction , and other normal reaction was defined as normal .

[59]

[60] (6) Pulverizing property

[61] During the preparation of a toner, the flake which was melt extruded was pulverized with Hosokawa Zet mill pulverizer, and the pulverized flake was classified with a wind-force classifier (100AFG, 50ATP, 50ZPS). The amount of a toner produced in one hour was evaluated as follow.

[62] ◎ : more than 0.4 kg/hr

[63] ○ : 0.2 to 0.4 kg/hr

[64] X : 0 to 0.2 kg/hr

[65]

[66] (7) Storage Stability: 100g of toner was put into a glass bottle and the bottle was sealed. After 48 hours at 50℃, the cohesion of the toner was observed by naked eyes. The cohesion degrees were evaluated as follow.

[67] ◎ : No cohesion and good storage stability

[68] ○ : Minute cohesion but good storage stability

[69] X : Serious cohesion and bad storage stability

[70]

[71] (8) Toner Image Density Evaluation: An image was printed on an OHP film or a paper with a black-and-white printer, which had a heat roller coated with Teflon and a temperature controller, and had a printing speed of 35 pages/minute. The image density of the printed image was measured with a Macbeth reflective densitometer RD918, and

then evaluated as follows.

[72] ◎ : The image density is equal to or more than 1.4.

[73] ○ : The image density is equal to or more than 1.2.

[74] X : The image density is less than 1.2.

[75]

[76] (9) Minimum Fixing Temperature and Offset Temperature: After coating a white paper with the produced toner, the paper was passed through a heat roller coated with silicon oil with a speed of 200mm/second. The lowest temperature at which more than 90% of toner was fixed was defined as the minimum fixing temperature. The highest temperature at which more than 90% of toner was fixed was defined as the offset temperature. The minimum fixing temperature and the offset temperature were measured within the range of 50 to 230°C of the heat roller. The temperature range between the minimum fixing temperature and the offset temperature was defined as the fixing temperature range.

[77]

[78] The abbreviations used in Examples and Comparative examples are as follows.

[79] TPA: terephthalic acid

[80] IPA: isophthalic acid

[81] AA: adipic acid

[82] SA: sebacic acid

[83] AzA: azelaic acid

[84] TMA: trimellitic acid

[85] PMDA: pyromellitic acid anhydride

[86] BzA: benzoic acid

[87] TMP: trimethylolpropane

[88] PG: propylene glycol

[89] NPG: neopentyl glycol

[90] EG: ethylene glycol

[91] DEG: diethylene glycol

[92] ODOL: octadecanol (=stearyl alcohol)

[93] GTE: glycerol triglycidyl ether (branched aliphatic epoxy compound)

[94] GDE: glycerol diglycidyl ether (branched aliphatic epoxy compound)

[95] G/A: molar ratio of the total alcohol components (including epoxy compound ) to the total acid components

[96]

[97] [Examples 1 to 11, Comparative examples 1 to 13]

[98] <u>Preparation of polyester resin</u>

[99] The reactant, of which the kind and amount are shown in Tables 1, 2 and 3, was

introduced into 2L reactor equipped with a stirring apparatus and a flow-out condenser. While slowly increasing the temperature to 250℃ and flowing out water (byproduct) from the reactor, the esterification reaction was carried out under nitrogen flow. After completion of generation and flow-out of water, the reactant was transferred to a polycondensation reactor equipped with a stirring apparatus, a cooling condenser, and a vacuum system, and 200ppm of catalyst with respect to the total acid components was added. While increasing the temperature to 250℃ and decreasing the pressure to 50mmHg for 30 minutes, excess diol was flowed out. Next, the pressure was slowly reduced to 0.1 mmHg. Under high vacuum, the reaction was carried out until a predetermined stirring torque occurred to obtain a polyester resin. The gel amount, softening temperature, Tg, and acid value of the prepared polyester resin were measured and represented in Tables 1, 2 and 3.

[100]

[101] Preparation of toner

[102] 50 weight part of the obtained polyester resin, 45 weight part of magnetite as a magnetic material, 2 weight part of azo-dye metal complex as an charge control agent, 3 weight part of polypropylene wax were mixed with a mixer, melted and kneaded in an extruder, pulverized with a zet mill pulverizer, classified with a wind-force classifier, and then were coated with 1 weight part of silica and 0.2 weight part of titanium dioxide to obtain toner particle having the volume average particle size of 8 to 9 □. The pulverizing property, minimum fixing temperature, offset temperature, storage stability and toner image density of the produced toner were measured and represented in Tables 1, 2 and 3.

[103] Table 1

| | Example | | | | | | Comparative example | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 1 | 2 | 3 | 4 | 5 |
| TPA (mole part) | 25 | 47.5 | 50 | 60 | 50 | 50 | 50 | 50 | 40 | 50 | 45 |
| IPA (mole part) | 60 | 47.5 | 50 | 25 | 50 | 37 | 50 | 50 | 40 | 45 | 45 |
| AA (mole part) | 0 | 0 | 0 | 5 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| AzA (mole part) | 5 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 5 | 0 |
| SA (mole part) | 0 | 0 | 0 | 0 | 0 | 3 | 0 | 0 | 0 | 0 | 0 |
| TMA (mole part) | 10 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 20 | 0 | 10 |
| PMDA (mole part) | 0 | 5 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| BzA (mole part) | 0 | 0 | 0 | 10 | 0 | 10 | 0 | 0 | 0 | 0 | 0 |
| PG (mole part) | 75 | 90 | 90 | 90 | 80 | 75 | 79 | 80 | 100 | 50 | 60 |
| EG (mole part) | 0 | 0 | 0 | 0 | 0 | 0 | 20 | 0 | 0 | 0 | 30 |
| NPG (mole part) | 15 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 30 | 0 |
| DEG (mole part) | 0 | 5 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| TMP (mole part) | 8 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 20 | 10 |
| ODOL(mole part) | 0 | 0 | 5 | 0 | 10 | 10 | 0 | 0 | 0 | 0 | 0 |
| GTE (mole part) | 2 | 0 | 5 | 10 | 0 | 0 | 1 | 20 | 0 | 0 | 0 |
| GDE (mole part) | 0 | 5 | 0 | 0 | 10 | 15 | 0 | 0 | 0 | 0 | 0 |
| G/A | 1.3 | 1.3 | 1.3 | 1.3 | 1.3 | 1.3 | 1.3 | 1.3 | 1.3 | 1.3 | 1.3 |
| Polymerization time (minute) | 120 | 110 | 140 | 105 | 120 | 60 | 180 | 20 | 85 | 120 | 60 |
| Polymerization product | normal | normal | normal | normal | normal | normal | normal | gelation | normal | gelation | gelation |
| Gel amount (weight%) | 14 | 15 | 8 | 10 | 13 | 30 | 0 | 54 | 30 | 39 | 35 |
| Softening temperature(℃) | 164 | 165 | 153 | 158 | 168 | 178 | 160 | 185 | 185 | 209 | 198 |
| Tg(℃) | 63 | 62 | 62 | 62 | 60 | 65 | 65 | 50 | 71 | 69 | 68 |
| Acid value (KOHmg/g) | 10 | 4 | 2 | 3 | 8 | 5 | 3 | - | 13 | - | - |
| pulverizing property | ◎ | ◎ | ◎ | ◎ | ◎ | ◎ | ◎ | - | ○ | - | - |
| Storage stability | ◎ | ◎ | ◎ | ◎ | ◎ | ◎ | ◎ | - | ◎ | - | - |
| Toner image density | ◎ | ◎ | ○ | ○ | ◎ | ◎ | X | - | ◎ | - | - |
| Minimum fixing temperature (℃) | 130 | 130 | 120 | 120 | 130 | 150 | 130 | - | 160 | - | - |
| Offset temperature (℃) | 190 | 200 | 180 | 180 | 200 | 210 | 170 | - | 210 | - | - |
| Fixing range(℃) | 60 | 70 | 60 | 60 | 70 | 60 | 40 | - | 50 | - | - |

[104] As shown in Table 1, the polyester resin produced according to Examples, in which the amount of the branched aliphatic epoxy compound is 2 to15 mol% with respect to the total alcohol components, had 5 to 30 weight% of gel amount, while the softening temperature was 140 to 180℃. As the softening temperature was lower and the gel amount(cross-linking density) was higher, the chain length of polymer(Namely, Mn: number average molecular weight) was reduced. Due to the low molecular weight of the resin, the resin can be melted at low temperature, and due to the gel portion of the resin, the resin can have an elastic property at high temperature. Accordingly, the toner of Examples had good pulverizing property, low temperature fixing property, high temperature fixing property, storage stability and image quality. On the contrary, when the amount of the branched aliphatic epoxy compound was less than 2 mol% with

respect to the total alcohol components (Comparative example 1), the gel amount was reduced to less than 5 weight%, and the high temperature fixing property of the toner was deteriorated. Therefore, the melted toner was adhered to a thermo-pressing roller in a fixing machine, which resulted in the unclear image. When the amount of the branched aliphatic epoxy compound was more than 15 mol% with respect to the total alcohol components (Comparative example 2), the gel amount of polycondensation reaction product was more than 30 weight%, and the pulverizing property and melting property of the resin were deteriorated. Therefore, industrially stable mass-production of a toner was impossible. In case of inducing the gelation with polyvalent acid and/or polyhydric alcohol during the preparation of polyester resin, without using the branched aliphatic epoxy compound (Comparative example 3, 4, and 5), the molecular weight increased during gelation, and the softening temperature also increased. Therefore, the low temperature fixing property of the toner was deteriorated. In addition, the melting property of the resin was also deteriorated, and it was difficult to control the polycondensation conditions. Particularly, it was difficult to obtain the resin from the reactor due to the gelation of the reactant during the polycondensation reaction, acid value measurement was impossible because the polyester resin was not dissolved with dichloromethane due to the gelation, and the toner production was impossible due to the high softening temperature of the polyester resin.

[105] Table 2

| | Example | | | Comparative example | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | 7 | 8 | 9 | 6 | 7 | 8 | 9 | 10 | 11 |
| TPA (mole part) | 50 | 60 | 70 | 50 | 45 | 45 | 70 | 50 | 50 |
| IPA (mole part) | 50 | 35 | 25 | 45 | 40 | 45 | 25 | 20 | 50 |
| AA (mole part) | 0 | 5 | 0 | 0 | 0 | 0 | 10 | 0 | 0 |
| AzA (mole part) | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| SA (mole part) | 0 | 0 | 5 | 0 | 0 | 0 | 5 | 0 | 0 |
| TMA (mole part) | 0 | 0 | 0 | 0 | 15 | 0 | 0 | 0 | 0 |
| PMDA (mole part) | 0 | 0 | 0 | 5 | 0 | 0 | 0 | 0 | 0 |
| BzA (mole part) | 0 | 0 | 0 | 0 | 0 | 10 | 0 | 30 | 0 |
| PG (mole part) | 95 | 70 | 50 | 25 | 85 | 60 | 75 | 85 | 65 |
| EG (mole part) | 0 | 20 | 45 | 70 | 0 | 20 | 0 | 0 | 0 |
| NPG (mole part) | 0 | 0 | 0 | 0 | 0 | 0 | 20 | 0 | 0 |
| DEG (mole part) | 0 | 5 | 0 | 0 | 0 | 0 | 0 | 10 | 0 |
| TMP (mole part) | 0 | 0 | 0 | 0 | 0 | 15 | 0 | 0 | 0 |
| ODOL(mole part) | 0 | 0 | 0 | 0 | 10 | 0 | 0 | 0 | 30 |
| GTE (mole part) | 5 | 0 | 5 | - | - | - | - | - | - |
| GDE (mole part) | 0 | 5 | 0 | - | - | - | - | - | - |
| G/A | 1.3 | 1.3 | 1.3 | 1.3 | 1.3 | 1.3 | 1.3 | 1.3 | 1.3 |
| Polymerization time (minute) | 165 | 70 | 60 | 30 | 25 | 70 | 65 | 140 | 200 |
| Polymerization product | normal | normal | normal | gelation | gelation | normal | normal | normal | normal |
| Gel (weight%) | 20 | 28 | 25 | 41 | 35 | 40 | 20 | 0 | 0 |
| Softening temperature(℃) | 172 | 175 | 179 | 220 | 192 | 205 | 175 | 120 | 115 |
| Tg(℃) | 64 | 61 | 58 | 69 | 65 | 68 | 30 | 45 | 25 |
| Acid value (KOHmg/g) | 4 | 4 | 4 | - | - | 2 | 4 | 18 | 20 |
| pulverizing property | ◎ | ○ | ○ | – | - | ○ | X | X | X |
| Storage stability | ◎ | ◎ | ○ | - | - | ◎ | - | - | - |
| Toner image density | ◎ | ◎ | ◎ | - | - | ◎ | - | - | - |
| Minimum fixing temperature (℃) | 140 | 150 | 160 | - | - | 190 | - | - | - |
| Offset temperature (℃) | 210 | 210 | 220 | - | - | 230 | - | - | - |
| Fixing area(℃) | 70 | 60 | 60 | - | - | 40 | - | - | - |

[106] As shown in Table 2, the polyester resin and toner produced according to Example 7, 8 and 9 had good physical properties. However, when the amount of propylene glycol was less than 55 mol% with respect to the total alcohol components and the amount of other aliphatic diol(ethylene glycol) having high reaction rate was relatively high(Comparative example 6), or when the amount of polyvalent acid was more than 10 mol% with respect to the total acid components(Comparative example 7), or when the amount of polyhydric alcohol was more than 10 mol% with respect to the total alcohol components(Comparative example 8), the reaction rate increased, and thereby it was difficult to obtain the resin from the reactor due to the gelation of the reactant during the polycondensation reaction, acid value measurement was impossible because the polyester resin was not dissolved with dichloromethane, and the toner production

was impossible due to the high softening temperature of the polyester resin.

[107]

[108] When the amount of aliphatic dibasic acid is more than 10 mol% with respect to the total acid components(Comparative example 9), the Tg was very low, and the pulverization of resin was impossible, and thereby the toner production was impossible. When the amount of monobasic acid is more than 20 mol% with respect to the total acid components(Comparative example 10) and when the amount of monohydric alcohol is more than 20 mol% with respect to the total alcohol components (Comparative example 11), polymer chain growing was limited due to the monohydric alcohol and monobasic acid component during the polycondensation reaction, and it was impossible to obtain a resin having the desirable softening temperature, and the Tg was too low to produce toner.

[109] Table 3

| | Example 10 | Example 11 | Comparative example 12 | Comparative example 13 |
|---|---|---|---|---|
| TPA (mole part) | 50 | 50 | 50 | 50 |
| IPA (mole part) | 50 | 50 | 50 | 50 |
| AA (mole part) | 0 | 0 | 0 | 0 |
| AzA (mole part) | 0 | 0 | 0 | 0 |
| SA (mole part) | 0 | 0 | 0 | 0 |
| TMA (mole part) | 0 | 0 | 0 | 0 |
| PMDA (mole part) | 0 | 0 | 0 | 0 |
| BzA (mole part) | 0 | 0 | 0 | 0 |
| PG (mole part) | 95 | 95 | 95 | 95 |
| EG (mole part) | 0 | 0 | 0 | 0 |
| NPG (mole part) | 0 | 0 | 0 | 0 |
| DEG (mole part) | 0 | 0 | 0 | 0 |
| TMP (mole part) | 0 | 0 | 0 | 0 |
| ODOL(mole part) | 0 | 0 | 0 | 0 |
| GTE (mole part) | 5 | 5 | - | - |
| GDE (mole part) | 0 | 0 | - | - |
| G/A | 1.2 | 1.6 | 1.1 | 2.0 |
| Polymerization time (minute) | 120 | 150 | 150 | 350 |
| Polymerization product | normal | normal | Non-reaction | Non-reaction |
| Gel (weight%) | 5 | 7 | - | 28 |
| Softening temperature(℃) | 169 | 164 | - | 192 |
| Tg(℃) | 62 | 62 | - | 68 |
| Acid value (KOHmg/g) | 15 | 1 | - | 4 |
| pulverizing property | ◎ | ◎ | - | ○ |
| Storage stability | ◎ | ◎ | - | ◎ |
| Toner image density | ○ | ○ | - | ◎ |
| Minimum fixing temperature (℃) | 130 | 130 | - | 170 |
| Offset temperature (℃) | 190 | 190 | - | 220 |
| Fixing area(℃) | 60 | 60 | - | 50 |

[110] As shown in Table 3, the polyester resin and toner produced according to Examples

10 and 11 had good characteristics in pulverizing property, fixing property and image density, and so on. However, when the molar ratio of the total alcohol components to the total acid components (G/A) is less than 1.2(Comparative example 12), non-reacted acid component was found during the condensation reaction, and thereby the transparency of resin was deteriorated. If the ratio(G/A) was more than 1.6(Comparative example 13), the condensation reaction rate was so slow that the productivity of resin was reduced.

[111]

[112] As described above, the toner including the polyester resin according to the present invention has superior offset-resisting property and low temperature fixing property. Also, in the present invention, it is possible to produce relatively inexpensive and environmentally favorable binder resin and toner because bisphenol A, its derivatives, or heavy metal compound such as tin or antimony is not used.

# Claims

[1] A polyester resin for toner comprising branched aliphatic epoxy compound, aromatic dibasic acid, and aliphatic diol as polymerization components.

[2] The polyester resin for toner according to claim 1, wherein the branched aliphatic epoxy compound is prepared by the glycidylation of polyhydric alcohol, which is selected from the group consisting of erythritol, mannitol, sorbitol, 1,2,3,6-hexanetetrol, 1,4-sorbitane, pentaerythritol, dipentaerythritol, tripentaerythritol, sucrose, 1,2,4-butanetriol, 1,2,5-pentatriol, glycerol, 2-methylpropanetriol, 2-methyl-1,2,4-butanetriol, trimethylolethane, trimethylolpropane and mixture thereof.

[3] The polyester resin for toner according to claim 1, wherein the amount of the branched aliphatic epoxy compound is 2 to15 mol%, the amount of the aliphatic diol is 55 to 98mol% with respect to the total alcohol components, and the amount of the aromatic dibasic acid is 60 to 100mol% with respect to the total acid components.

[4] The polyester resin for toner according to claim 1, wherein the polymerization components further includes a compound selected from the group consisting of aliphatic dibasic acid, trivalent or higher acid, monobasic acid, trihydric or higher alcohol and monohydric alcohol, and the amount of the aliphatic dibasic acid is equal or less than 10mol%, the amount of the trivalent or higher acid is equal or less than 10mol%, the amount of the monobasic acid is equal or less than 20mol% with respect to the total acid components, and the amount of the trihydric or higher alcohol is equal or less than 10mol%, the amount of the monohydric alcohol is equal or less than 20mol% with respect to the total alcohol components.

[5] The polyester resin for toner according to claim 1, wherein the molar ratio of total alcohol components to total acid components in the polymerization components is 1.2 to 1.6.

[6] The polyester resin for toner according to claim 1, wherein the polyester resin is produced by carrying out esterification reaction and polycondensation reaction of the polymerization components, and the esterification reaction is carried out in the presence of a titanium catalyst.

[7] The polyester resin for toner according to claim 1, wherein the gel amount of the polyester resin is 5 to 30wt% with respect to the total polyester resin, the softening temperature of the polyester resin is 140 to 180°C, the acid value of the polyester resin is 1 to 250 KOHmg/g, and the glass transition temperature of the polyester resin is 50 to 75°C.

[8] A toner including the polyester resin of claim 1 as a binder resin.

## INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR2006/002810

### A. CLASSIFICATION OF SUBJECT MATTER

*G03G 9/087(2006.01)i, G03G 9/13(2006.01)i*

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)
IPC8; G03G, C08F, C08G, B41M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean Patents and applications for invention since 1975
Korean Utility models and applications for Utility models since 1975
Japanese Utility models and application for Utility models since 1975

Electronic data base consulted during the intertnational search (name of data base and, where practicable, search terms used)
eKIPASS, Delphion, PAJ

### C. DOCUMENTS CONSIDERED TO BE RELEVANT

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

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|---|---|
| Date of the actual completion of the international search<br>18 OCTOBER 2006 (18.10.2006) | Date of mailing of the international search report<br>**18 OCTOBER 2006 (18.10.2006)** |
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