Title: RECYCLED METHOD FOR A WASTED POLYESTER AND RECLAIMED MATERIALS THEREOF

Abstract: The present invention relates to a method for recycling waste polyester resins and the reclaimed materials therefrom. The method for recycling waste polyester resins according to the present invention comprises phase 1 for producing a depolymerization composition of waste polyester resin after crushing it; phase 2 for producing a polyester polymer having an acid value range of 10 to 150 mg KOH/g by polycondensing the depolymerization composition using polyhydric alcohols; phase 3(a) for producing either a solid polyester resin or a liquid polyester resin if the polyester polymer from phase 2 has an acid value of more than 20 mg KOH/g; and phase 3(b) for producing a solid polyester resin in its entirety if the polyester polymer from phase 2 has an acid value of more than 20 mg KOH/g. The reclaimed polyester resin according to the present invention has the excellent compatibility, dispersibility, and adhesive property for various media, and can be easily neutralized and dissolved in water. Accordingly, the polyester resin can be used as a useful material for industrial products.
Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— with international search report

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RECYCLED METHOD FOR A WASTED POLYESTER AND
RECLAIMED MATERIALS THEREOF

Technical Field

(1) The present invention relates to a method for recycling waste polyester resins and the reclaimed materials therefrom, and more particularly, to a recycling method for making liquid or solid polyester resin compositions with excellent compatibility, solubility and dispersibility by depolymerizing and polycondensing crushed waste polyester resins and the reclaimed materials therefrom.

Background Art

(2) Polyester resins such as polyethylene terephthalate (hereinafter referred to as “PET”) have good heat resistance, processability and transparency, and non-toxicity compared with other materials, and, therefore are widely used for daily products and industrial supplies. Accordingly, a demand for polyester resins and production of that is increasing continuously and the polyester resin wastes also increase. As a result, environmental problems are looming large, concerning the treatment of these wastes. These polyester resin wastes are specified as recyclable in Korean Wastes Control Act but only a little amount of them is recycled, because the technological level of recycling method is merely to remelt physically the waste polyester resins, and make products and the quality of the reclaimed products is not satisfactory. Thus, treatment of the waste polyester resins becomes a serious problem, and methods for solving this problem are required desperately.
Disclosure of Invention

(3) Accordingly, the present invention is directed to a method for recycling waste polyester resins and reclaimed materials therefrom that substantially obviates one or more problems due to limitations and disadvantages of the related art.

(4) An object of the present invention is to provide a recycling method for making liquid or solid polyester resins with excellent compatibility, solubility and dispersibility by means of depolymerization and polycondensation of waste polyester resins.

(5) To achieve the object and in accordance with the purpose of the invention, as embodied and broadly described herein, there is provided a method for recycling waste polyester resins by depolymerizing and polycondensing waste polyester resins. The method for recycling waste polyester resins comprises:

phase 1 for producing a depolymerization composition of a waste polyester resin;

phase 2 for producing a polyester polymer having an acid value range of 10 to 150 mg KOH/g by adding polyhydric alcohols to the depolymerization composition and polycondensing them;

phase 3(a) for producing either a solid or a liquid polyester resin if the polyester polymer from phase 2 have an acid value of more than 20 mg KOH/g; and

phase 3(b) for producing a solid polyester resin in its entirety if the polyester polymer from phase 2 have an acid value of less than 20 mg KOH/g.
**Brief Description of the Drawings**

(6) Further objects and advantages of the invention can be more fully understood from the following detailed description taken in conjunction with the accompanying drawings, in which:

Fig. 1 is a flow chart of a method for recycling waste polyester resins in accordance with the present invention;

Fig. 2 is a flow chart of a method for recycling waste polyester resins according to another embodiment of the present invention;

Fig. 3 is a flow chart of a method for recycling waste polyester resins according to another embodiment of the present invention.

**Best mode for Carrying Out the Invention**

(7) Reference will now be made in detail to the preferred embodiments of the present invention, examples of which are illustrated in the accompanying drawings.

Fig. 1 is a flow chart of a method for recycling waste polyester resins in accordance with the present invention. As shown in Fig. 1, the composition of a reclaimed polyester resin in accordance with the present invention is produced through the phases comprising:

- phase 1 for producing a depolymerization composition of a waste polyester resin after crushing it;
- phase 2 for producing a polyester polymer having an acid value range of 10 to 150 mg KOH/g by adding polyhydric alcohols to the depolymerization composition and polycondensing it;
- phase 3(a) for producing either a solid polyester resin or a liquid
polyester resin if the polyester polymer from phase 2 has an acid value of more than 20 mg KOH/g; and

phase 3(b) for producing a solid polyester resin in its entirety if the polyester polymer from phase 2 has an acid value of less than 20 mg KOH/g.

The phase 1 further comprises:

a stage of the first depolymerization of a waste polyester resin using a solid resin solvent; and

a stage of the second depolymerization and an addition reaction by adding polybasic acids to the first depolymerization composition.

(8) As the solid resin solvent to be used in the first depolymerization of phase 1, one or more solvent can be selected from the group of gum rosin, wood rosin, dehydrogenated rosin, hydrogenated rosin, maleic rosin, rosin ester, pinene resin, dipentene resin, C5 petroleum resins, C9 petroleum resins, dammar resin, copal resin, dicyclopentadien(hereinafter referred to as "DCPD") resin, hydrogenated DCPD resin, and styrene maleic resin. The weight ratio of waste polyester resins to the solid resin solvent is 1:9 ~ 9:1. In addition, as the polybasic acid to be used in the second depolymerization of phase 1, one or more acids can be selected from the group of phthalic anhydride, isophthalic acid, terephthalic acid, adipic acid, azelaic acid, sebacic acid, tetrahydro phthalic anhydride, maleic anhydride, fumaric acid, itaconic acid, trimellitic acid, trimellitic anhydride, pyromellitic anhydride, succinic acid, cyclohexane dicarboxylic acid, naphthalene dicarboxylic acid, and benzoic acid. The amount of polybasic acid to be used is 10~70 w%, based on the amount of the composition from the first depolymerization.
(9) In the phase 2, there is produced a polyester polymer having an acid value range of 10 to 150 mg KOH/g by adding polyhydric alcohols to the depolymerization composition from the phase 1 and polycondensing it. The polyhydric alcohol, which adjust an acid value, to be used in the phase 2 may be, for example, ethylene glycol, propylene glycol, 1,3-propanediol, 1,3-butanediol, 1,6-hexanediol, neopentyl glycol, diethylene glycol, dipropylene glycol, polyethylene glycol, alkylene oxide adduct of bisphenol A, trimethylol propane, glycerin, pentaerythritol, and a mixture thereof. The amount of the polyhydric alcohol to be used is 10~70 w%, based on the amount of the depolymerization composition from the phase 1. The polyester polymer obtained via the phase 1 and the phase 2 is a solid resin. The weight average molecular weight of the polyester polymer is 3,000~50,000 and the softening point is 70~150℃.

(10) In the phase 1 and phase 2, the reactions are carried out under 0.05~0.5 w% of depolymerization and polycondensation catalysts at 200~250℃.

(11) The phase 3 has a two-stage procedure, i.e., phase 3(a) for producing either a solid or a liquid polyester resin if the polyester polymer from the phase 2 has an acid value of more than 20 mg KOH/g, and phase 3(b) for producing a solid polyester resin in its entirety if the polyester polymer from the phase 2 has an acid value of less than 20 mg KOH/g. The liquid polyester resin is produced via first process adding basic compounds to the polyester polymer to neutralize them, and second process dissolving and diluting said neutralized polyester resin using water, water-friendly solvents or a mixture of both of them.

(12) Here, as the basic compound to be used in the 3(a) phase one or more compounds can be selected from the group of sodium hydroxide, potassium hydroxide, ammonium hydroxide, lithium hydroxide, and amines. The amount
of the basic compound to be used is 3~30w%, based on the total amount of the polyester polymer from the phase 2. In addition, as the water-friendly solvent, one or more solvents can be selected from the group of alcohols, ethers, acetone, diacetone alcohol, dimethyl formamide, tetrahydrofuran, ethylglycol, propylglycol, butylglycol, and n-methyl pyrroldione. The amount of the water, water-friendly solvents, or a mixture of both of them to be added is 1~10 times, in comparison with the total amount of the neutralized polyester resin.

(13) The resulted polyester resin is either a liquid or a solid state, and, when measured by means of a constant load capillary extrusion rheometer, the polyester resin has a pour beginning temperature (T_{pb}) of 80~105°C, a pour ending temperature (T_{pe}) of 120~160°C, and a glass transition temperature (T_{g}) of 40~80°C. Moreover, the polymer resin has excellent reactivity and dispersibility because it has two or three carboxyl groups at the end of a polymer chain. The present invention can produce said polyester resin through recycling waste polyester resins, and said raw materials may have various composition ratios.

(14) The present invention will be described in further detail with reference to the examples thereof, which examples however are merely intended to be illustrative and not to be construed as limiting the scope of the invention.

**Example 1**

The reclaimed polyester resin according to the present invention can be used as a toner binder for an electrophotograph and an electrostatic development. The toner of the present invention is made of a polyester resin, a colorant, charge
control agents and release agents by means of polymerization or crushing method. The colorant that can be selected is a black pigment such as carbon black and magnetite, a yellow pigment such as iron oxide yellow, hansa yellow and permanent yellow, a blue pigment such as phthalocyanine blue and violet, a red pigment such as iron oxide red, carmine, toluidine red and quinacridone red, and a green pigment such as phthalocyanine green and chrome green. The amount of the colorant to be added is 1~40w%. The charge control agents can be selected from the group of negrosin-based dyes and quaternary ammonium salts such as BONTRON N-07 and BONTRON N-21 (available from Orient Chemical(Korea), Ltd.) as a plus(+) charge control agent, and azo metal complex and salicylic acid metal complex such as BONTRON S-34 and BONTRON E-84 (available from Orient Chemical(Korea), Ltd.) as a minus(−) charge control agent. The amount of the charge control agent to be used is 0.5~5w%, based on the amount of the binder resin. The release agent can be selected from the group of polyethylene wax, polypropylene wax, higher fatty acid esters, high aliphatic alcohols, carnauba wax and montan wax. One or more release agents can be used. The amount of the release agent to be used is 0.5~10w%, based on the amount of the binder resin. To obtain an excellent image, these additives have to be well dispersed in the binder resin. The reclaimed polyester resin of the present invention is well dispersed and dissolved in water, water-friendly solvents or a mixture thereof, and, therefore, a toner can be produced from polymerization method by dispersing said additives in the liquid polyester resin according to the present invention. In addition, in case of using crushing method, said additives can be well dispersed in the solid polyester resin according to the present invention because the solid polyester resin has functional group to play a role of a
surfactant, and, therefore, it is possible to produce a toner with a good performance. When measured by means of a rheometer, the toner from Example 1 has a pour beginning temperature \(T_{b}\) of 80–95°C and a pour ending temperature of 120–135°C. Moreover, the toner forms rapidly a very clear image, and has desirable low temperature fixing and offset properties.

**Example 2**

(15) The reclaimed polyester resin according to the present invention can be used as a composition of powder coating, which uses epoxy resin as a hardener. The polyester resin composition of the present invention has excellent reactivity and dispersibility because it has two or three carboxyl groups at the end of a polymer chain, and, therefore, by adding a little amount of anti-blocking agent to the polyester resin it can maintain good storage stability. In addition, because the polyester is resin with a low softening temperature, the hardening reaction is carried out in about ten minutes at less than 180°C. As a result, it is possible to lower the hardening temperature and to obtain high quality film of paint that has high gloss and excellent heat resistance and chemical resistance.

**Example 3**

(16) The reclaimed polyester resin according to the present invention can be used as a composition for oil modified alkyd vanish coatings and printing inks. The solid polyester resin of the present invention reacts with fatty acid and drying oil, and the product therefrom can dissolve well in aliphatic hydrocarbon solvents or aromatic hydrocarbon solvents, thereby providing a stable film of paint having excellent gloss, water resistance and weatherability, and a high quality image. In
gravure inks, the polyester resin of the present invention can provide a good printing image with high speed drying and excellent adhesive property, abrasion resistance and ruggedness, because it dissolves well in mixture solvents of ketone solvents and aromatic hydrocarbon solvents.

**Example 4**

(17) The reclaimed polyester resin according to the present invention can be used as a composition of an adhesive. The polyester resin of the present invention, which is used as a basic adhesive resin in a hotmelt adhesive, has a low softening temperature, a low melt viscosity, and excellent adhesive property, water resistance, chemical resistance, and compatibility. The hotmelt adhesive made of the polyester resin of the present invention provides excellent initial adhesive property and strong adhesive force for paper, boards, leathers, fabrics, woods, plastics and metals such as aluminum. These adhesives can also be used as liquid adhesives through dissolving them in various solvents.

(18) The said Examples will be described in further detail by referring to preparation examples, which examples however are merely intended to be illustrative and not to be construed as limiting the scope of the invention.

<Preparation Example 1>

(19) Crushed waste PET chips (400g), gum rosin (200g) and monobutyl tartaric acid (0.3g) are placed in a reactor which is equipped with an agitator, a reflux condenser, a separator, a thermometer and a nitrogen injection port. The mixture is heated to 250°C and maintained over 2 hours at that temperature. The mixture is agitated when the waste PET chips begin to be melted. After the mixture changes into a transparent state, the reactor is cooled to 150°C, and then,
maleic anhydride (180g) is added to the reactor. When the temperature of the mixture reaches to the point that ring-opening reaction is finished, the mixture is again heated to 235°C and maintained over 3 hours at that temperature for a depolymerization reaction. The acid value of the depolymerization product is 115 mg KOH/g. Then, the reactor is charged with 200 grams of ethylene oxide adduct of bisphenol A. The reactor is heated to 250°C and maintained over 5 hours at that temperature, and a polycondensation accompanied with a dehydration reaction is carried out. When the acid value reaches to 55 mg KOH/g, the reactor is cooled and charged with 50 grams of sodium hydroxide and 1,500 grams of per distilled water. Then, the mixture is stirred over 30 minutes at 85°C. The resultant water-soluble polyester resin has an acid value of 39 mg KOH/g, a weight average molecular weight of 11,000, a softening point of 80°C and pH of 8.5.

(20) Said water-soluble polyester resin can be used as a polymerization toner binder as follows. There are prepared the water-soluble polyester resin (100 g), carbon black(3g), charge control agents(0.1g), and release agents(1g). These reactants are mixed and dispersed, thereby making suspended particles. The suspended particles are filtrated, washed by water, and dried to form a toner composition. Then, the dried toner composition (100g) is mixed with external additives (1g), to produce a toner. A toner cartridge filled with said toner can provide a very clear developed image. The toner produced from the reclaimed polyester resin according to the present invention has excellent physical properties and a fusing property.

<Preparation Example 2>

(21) Crushed waste PET chips (400g), hydrogenated rosin (200g), monobutyl tartaric acid (0.3g), trimellitic anhydride (150g) and neopentyl glycol
(200g) are placed in a reactor which is equipped with an agitator, a reflux condenser, a separator, a thermometer and a nitrogen injection port. The reaction method is the same with Preparation Example 1. The resultant water-soluble polyester resin has an acid value of 30 mg KOH/g, a weight average molecular weight of 12,000, a softening point of 95°C and pH of 8.7.

(22) Said water-soluble polyester resin can be used as a polymerization toner binder as follows. There are prepared the water-soluble polyester resin (100 g), carbon black (3g), charge control agents (0.1g), and release agents (1g). These reactants are mixed and dispersed, thereby making suspended particles. The suspended particles are filtrated, washed by water, and dried to form a toner composition. Then, the dried toner composition (100g) is mixed with external additives (1g) to produce a toner. A toner cartridge filled with said toner can provide a very clear developed image. The toner produced from the reclaimed polyester resin according to the present invention has excellent physical properties and a fusing property.

<Preparation Example 3>

(23) Crushed waste PET chips (400g), rosin ester (200g), monobutyl tartaric acid (0.3g), fumaric acid (150g), neopentyl glycol (100g) and diethylene glycol (100g) are placed in a reactor which is equipped with an agitator, a reflux condenser, a separator, a thermometer and a nitrogen injection port. The reaction method is the same with Preparation Example 1, except that potassium hydroxide (55g) is used as a neutralizer instead of sodium hydroxide. The resultant water-soluble polyester resin has an acid value of 28 mg KOH/g, a weight average molecular weight of 12,000, a softening point of 105°C, and pH of 8.1.

<Preparation Example 4>
(24) Crushed waste PET chips (400g), C5 petroleum resins (200g),
monobutyl tartaric acid (0.3g), trimellitic anhydride (150g), ethylene glycol
(100g) and trimethylol- propane (80g) are placed in a reactor which is equipped
with an agitator, a reflux condenser, a separator, a thermometer and a nitrogen
injection port. The reaction method is the same with Preparation Example 1,
except that ammonium hydroxide (50g) is used as a neutralizer instead of sodium
hydroxide, and butyl glycol (200g) as a water-friendly solvent instead of per
distilled water. The resultant water-soluble polyester resin has an acid value of 30
mg KOH/g, a weight average molecular weight of 13,000, a softening point of
108 °C, and pH of 7.9.

<Preparation Example 5>

(25) Crushed waste PET chips (400g), C9 petroleum resins (200g),
monobutyl tartaric acid (0.3g), adipic acid (50g), maleic anhydride (100g),
propylene glycol (100g) and neopentyl glycol (100g) are placed in a reactor
which is equipped with an agitator, a reflux condenser, a separator, a thermometer
and a nitrogen injection port. The reaction method is the same with Preparation
Example 1, except that sodium hydroxide (30g) and trimethylamine (35g) are
used as a neutralizer instead of sodium hydroxide. The resultant water-soluble
polyester resin has an acid value of 31 mg KOH/g, a weight average molecular
weight of 13,000, and pH of 7.7.

<Preparation Example 6>

(26) Crushed waste PET chips (350g), maleic gum rosin (250g),
monobutyl tartaric acid (0.3g), trimellitic anhydride (100g), neopentyl glycol
(50g), and ethylene oxide adduct of bisphenol A (150g) are placed in a reactor
which is equipped with an agitator, a reflux condenser, a separator, a thermometer
and a nitrogen injection port. The reaction method is the same with Preparation Example 1. The resultant water-soluble polyester resin has an acid value of 45 mg KOH/g, a weight average molecular weight of 11,500, a softening point of 81°C, and pH of 8.7.

<Preparation Example 7>

(27) Crushed waste PET chips (350g), DCPD resin (250g), monobutyl tartaric acid (0.3g), maleic anhydride (150g), neopentyl glycol (100g) and polyethylene glycol (100g) are placed in a reactor which is equipped with an agitator, a reflux condenser, a separator, a thermometer and a nitrogen injection port. The reaction method is the same with Preparation Example 1, except that ammonium hydroxide (30g) and trimethylamine (50g) is used as a neutralizer instead of sodium hydroxide. The resultant water-soluble polyester resin has an acid value of 30 mg KOH/g, a weight average molecular weight of 12,000, a softening point of 95°C, and pH of 8.1.

<Preparation Example 8>

(28) Crushed waste PET chips (400g), DCPD resin (200g), monobutyl tartaric acid (0.3g), isophthalic acid (100g), adipic acid (50g), neopentyl glycol (70g) and ethylene oxide adduct of bisphenol A (120g) are placed in a reactor which is equipped with an agitator, a reflux condenser, a separator, a thermometer and a nitrogen injection port. The reaction method is the same with Preparation Example 1, except that neutralizing and solublizing processes are skipped. The resultant solid polyester resin has an acid value of 10 mg KOH/g, a weight average molecular weight of 20,000, and a softening point of 93°C.

<Preparation Example 9>

(29) Crushed waste PET chips (500g), gum rosin (200g), monobutyl
tartaric acid (0.3g), maleic anhydride (100g) and pentaerythritol (200g) are placed in a reactor which is equipped with an agitator, a reflux condenser, a separator, a thermometer and a nitrogen injection port. The reaction method is the same with Preparation Example 1, except that neutralizing and solublizing processes are skipped. The resultant solid polyester resin has an acid value of 11 mg KOH/g, a weight average molecular weight of 30,000, and a softening point of 145°C.

(30) Figs. 2~4 are flow charts of methods for recycling waste polyester resins according to other embodiments of the present invention. The following Examples are being provided to further illustrate various species of the present invention.

(31) **Example 5**

As shown in Fig. 2, a composition of reclaimed polyester resin in accordance with another embodiment of the present invention is produced through the phases comprising:

- phase 1 for producing a depolymerization composition of waste polyester resin by depolymerizing a waste polyester resin, eliminating excess polyhydric alcohols by means of decompression and stabilizing the composition by means of depolymerization stabilizer solid resins;

- phase 2 for producing a polyester polymer with 2~3 carboxyl groups at the end of a polymer chain by adding polybasic acids to said depolymerization composition to carry out an addition reaction and polycondensating the depolymerization composition using polyhydric alcohols, the polyester polymer having an acid value range of 10 to 150 mg KOH/g; and
phase 3 for producing a water-dispersible polyester resin by neutralizing said polyester polymers by means of basic compounds and dispersing the neutralized polyester resin in water, water-friendly solvents, or a mixture of both of them.

(32) As the depolymerization stabilizer solid resin to be used in the phase 1, one or more materials can be selected from the group of rosin, rosin derivatives, hydrogenated rosin, rosin ester, dehydrogenated rosin, maleic rosin, dammar resin, copal resin, petroleum resins, and derivatives of petroleum resins. The amount of the depolymerization stabilizer solid resin to be used is 10〜100w%, based on the total amount of the depolymerization composition. The polyhydric alcohol and polybasic acid to be used in the phase 2 and the basic compound to be used in the phase 3 are the same with the materials used at the making method of the present invention. The water-friendly solvent to be used in the phase 3 can be selected from the group of alcohols, acetone, diacetone alcohol, dimethyl formamide, dimethyl acetamide, ethyl cellsolve, butyl cellsolve, tetrahydrofuran, and N-methyl-2-pyrrolidone. The amount of the water-friendly solvent to be used is 10〜100w%, based on the total amount of the polyester polymer from the phase 2.

(33) The resultant polyester resin is either a liquid or a solid state, and has a pour beginning temperature \( T_{fb} \) of 80〜105°C, a pour ending temperature \( T_{end} \) of 120〜160°C, and a glass transition temperature \( T_g \) of 40〜80°C.

(34) Example 6

As shown in Fig. 3, a composition of reclaimed polyester resin in accordance with another embodiment of the present invention is produced through the phases comprising:
phase 1 for producing a depolymerization composition of waste polyester resin by depolymerizing a waste polyester resin, eliminating excess polyhydric alcohols by means of decompression and stabilizing the composition by means of depolymerization stabilizer solid resins;

phase 2 for producing a polyester polymer by adding polybasic acids, dimethyl-5-sodio sulpho iso phthalate (hereinafter referred to as "DMSSIP"), which is a monomer to provide a water-friendly functional group, or a mixture of both of them to said depolymerization composition to carry out a polycondensation reaction, and then, adding polyhydric alcohols to adjust an acid value; and

phase 3 for producing an aqueous solution from dissolving the polyester polymer in water, a liquid solution from dissolving the polyester polymer in water-friendly solvents, or a bulk resin without any treatment.

The depolymerization stabilizer solid resin in the phase 1, the polyhydric alcohol and the polybasic acid in the phase 2, and the basic compound and the water-friendly solvent in the phase 3 are the same with the materials used at the making method of the present invention. In addition, when the DMSSIP is mixed with the polybasic acid, the amount of DMSSIP to be used is 1~30w%, based on the total amount of the polybasic acid.

(35) The resultant polyester resin is either a liquid or a solid state, and has a pour beginning temperature \((T_{fb})\) of \(80\sim105\,^\circ C\), a pour ending temperature \((T_{end})\) of \(120\sim160\,^\circ C\), and a glass transition temperature \((T_g)\) of \(40\sim80\,^\circ C\).

(36) Example 7
As shown in Fig. 4, a composition of reclaimed polyester resin in accordance with another embodiment of the present invention is produced through the phases comprising:

- phase 1 for producing a polyester resin having sulfonic acid alkali metal salt of aromatic dicarboxylic acid including DMSSIP;

- phase 2 for producing a polyester polymer by adding said polyester resin from the phase 1 to a waste polyester resin to depolymerize them, and carrying out a polycondensation reaction accompanied with ester interchange; and

- phase 3 for producing an aqueous solution from dissolving the polyester polymer in water, a liquid solution from dissolving the polyester polymer in water-friendly solvents, or a bulk resin without any treatment.

The DMSSIP in the phase 1 is one of sulfonic acid alkali metal salts of aromatic dicarboxylic acids and functions as a compound causing depolymerization. The mixture of the DMSSIP and a polybasic acid can be used instead of DMSSIP. Here, the amount of the mixture to be used is the same with Example 6.

(37) The resultant polyester resin is either a liquid or a solid state, and has a pour beginning temperature \( (T_{\text{b}}) \) of \( 80 \sim 105^\circ\text{C} \), a pour ending temperature \( (T_{\text{end}}) \) of \( 120 \sim 160^\circ\text{C} \), and a glass transition temperature \( (T_g) \) of \( 40 \sim 80^\circ\text{C} \).

**Industrial applicability**

(38) The reclaimed polyester resin according to the present invention has the excellent compatibility, dispersibility, and adhesive property for various media,
and can be easily neutralized and dissolved in water. Accordingly, the polyester resin can be used as a useful material for industrial products such as a developer for electrophotograph, ink-jet inks, a textile finishing agent, an adhesive, a binder of film coatings, a toner, a hotmelt adhesive, and a binder of powder coating.
What Is Claimed Is:

1. A method for recycling waste polyester resins, the method comprising:
   phase 1 for producing a depolymerization composition of a waste polyester resin;
   phase 2 for producing a polyester polymer having an acid value range of 10 to 150 mg KOH/g by adding polyhydric alcohols to the depolymerization composition to polycondense the depolymerization composition;
   phase 3(a) for producing either a solid or a liquid polyester resin if the polyester polymer from the phase 2 has an acid value of more than 20 mg KOH/g; and
   phase 3(b) for producing a solid polyester resin in its entirety if the polyester polymer from the phase 2 has an acid value of less than 20 mg KOH/g.

2. The method for recycling waste polyester resins of claim 1, wherein the phase 1 producing a depolymerization composition of a waste polyester resin further comprises:
   a stage of the first depolymerization of a waste polyester resin using a solid resin solvent; and
   a stage of the second depolymerization and an addition reaction by adding polybasic acids to the first depolymerization composition.

3. The method for recycling waste polyester resins of claim 2, wherein the solid resin dissolvent is selected from the group of gum rosin, wood rosin, dehydrogenated rosin, hydrogenated rosin, maleic rosin, rosin ester, pinene resin,
dipentene resin, C5 petroleum resins, C9 petroleum resins, dammar resin, copal resin, dicyclopentadien resin, hydrogenated dicyclopentadien resin, styrene maleic resin, and a mixture thereof.

4. The method for recycling waste polyester resins of claim 2, wherein the weight ratio of the waste polyester resin to the solid resin solvent is 1:9~9:1.

5. The method for recycling waste polyester resins of claim 2, wherein the polybasic acid to be used in the second depolymerization accompanied with the addition reaction is selected from the group of phthalic anhydride, isophthalic acid, terephthalic acid, adipic acid, azelaic acid, sebamic acid, tetrahydro phthalic anhydride, maleic anhydride, fumaric acid, itaconic acid, trimellitic acid, trimellitic anhydride, pyromellitic anhydride, succinic acid, cyclohexane dicarboxylic acid, naphthalene dicarboxylic acid, benzoic acid, and a mixture thereof.

6. The method for recycling waste polyester resins of claim 2, wherein the amount of the polybasic acid to be added is 10~70w%, based on the amount of the composition from the first depolymerization.

7. The method for recycling waste polyester resins of claim 1, wherein the reactions in the phase 1 and the phase 2 are carried out under 0.05~0.5 w% of depolymerization and polycondensation catalysts.

8. The method for recycling waste polyester resins of claim 1, wherein the
reactions in the phase 1 and the phase 2 are carried out at 200~250°C.

9. The method for recycling waste polyester resins of claim 1, wherein the polyhydric alcohol to be used in the phase 2 is selected from the group of ethylene glycol, propylene glycol, 1,3-propanediol, 1,3-butanediol, 1,6-hexanediol, neopentyl glycol, diethylene glycol, dipropylene glycol, polyethylene glycol, alkylene oxide adduct of bisphenol A, trimethylol propane, glycerin, pentaerythritol, and a mixture thereof.

10. The method for recycling waste polyester resins of claim 1 or claim 9, wherein the amount of the polyhydric alcohol to be used in the phase 2 is 10~70w%, based on the amount of the depolymerization composition from the phase 1.

11. The method for recycling waste polyester resins of claim 1, wherein the polyester polymer from the phase 2 is a solid resin having a weight average molecular weight of 3,000~50,000.

12. The method for recycling waste polyester resins of claim 1, wherein the polyester polymer from the phase 2 has a softening point at 70~150°C.

13. The method for recycling waste polyester resins of claim 1, wherein the liquid polyester resin from the phase 3(a) is produced by a procedure comprising:

   a stage for adding basic compounds to the polyester polymer from the phase 2 to neutralize the polyester polymer; and
a stage for dissolving and diluting the neutralized polyester polymer using water, water-friendly solvent or the mixture of both of them.

14. The method for recycling waste polyester resins of claim 13, wherein the basic compound for use in neutralization is selected from the group of sodium hydroxide, potassium hydroxide, ammonium hydroxide, lithium hydroxide, amines and a mixture thereof.

15. The method for recycling waste polyester resins of claim 13, wherein the amount of the basic compound to be used is 3~30w%, based on the amount of the polyester polymer from the phase 2.

16. The method for recycling waste polyester resins of claim 13, wherein the water-friendly solvent is selected from the group of alcohols, ethers, acetone, diacetone alcohol, dimethyl formamide, tetrahydrofuran, ethyl glycol, propyl glycol, butyl glycol, n-methyl pyrrolidone, and a mixture thereof.

17. The method for recycling waste polyester resins of claim 13, wherein the amount of the water, water-friendly solvent or the mixture of both of them to be added is 1~10 times, in comparison with the total amount of the neutralized polyester resin.

18. A method for recycling waste polyester resins, the method comprising:

   phase 1 for producing a depolymerization composition of a waste polyester resin by depolymerizing waste polyester resin, eliminating excess polyhydric
alcohol by means of decompression, and stabilizing the composition using depolymerization stabilizer solid resin;

phase 2 for producing a polyester polymer with 2~3 carboxyl groups at the end of a polymer chain by adding polybasic acids to the depolymerization composition to carry out an addition reaction, and, then, carrying out polycondensation using polyhydric alcohol, the polyester polymer having an acid value range of 10~150 mg KOH/g; and

phase 3 for producing water-dispersible polyester resin by neutralizing the polyester polymer using basic compound and dispersing the neutralized polyester resin in water, water-friendly solvent or the mixture of both of them.

19. The method for recycling waste polyester resins of claim 18, wherein the basic compound for use in neutralization in the phase 3 is selected from the group of sodium hydroxide, potassium hydroxide, ammonium hydroxide, lithium hydroxide, amines, and a mixture thereof.

20. The method for recycling waste polyester resins of claim 18, wherein the amount of the basic compound to be used is 3~30w%, based on the total amount of the polyester polymer from the phase 2.

21. A method for recycling waste polyester resins, the method comprising:

phase 1 for producing a depolymerization composition of a waste polyester resin by depolymerizing the waste polyester resin, eliminating excess polyhydric alcohol by means of decompression, and stabilizing the composition using depolymerization stabilizer solid resin;
phase 2 for producing a polyester polymer by adding polybasic acids, 
DMSSIP or the mixture of both of them to the depolymerization composition to 
carry out a polycondensation reaction, and then, adding polyhydric alcohols to 
adjust an acid value; and 

phase 3 for producing an aqueous solution from dissolving the polyester 
polymer in water, a liquid solution from dissolving the polyester polymer in 
water-friendly solvent, or a bulk resin without any treatment.

22. The method for recycling waste polyester resins of claim 18 or claim 21, 
wherein the depolymerization stabilizer solid resin in the phase 1 is selected from 
the group of rosin and derivatives thereof, hydrogenated rosin, rosin ester, 
dehydrogenated rosin, maleic rosin, dammar resin, copal resin, petroleum resin 
and derivatives thereof, and a mixture thereof.

23. The method for recycling waste polyester resins of claim 18 or claim 21, 
wherein the amount of the depolymerization stabilizer solid resin to be used is 
10~100w%, based on the total amount of the depolymerization composition.

24. The method for recycling waste polyester resins of claim 18 or claim 21, 
wherein the polyhydric alcohol to adjust an acid value in the phase 2 is selected 
from the group of ethylene glycol, propylene glycol, 1,3-propanediol, 1,3-
butanediol, 1,6-hexanediol, neopentyl glycol, diethylene glycol, dipropylene 
glycol, polyethylene glycol, alkylene oxide adduct of bisphenol A, trimethylol 
propane, glycerin, pentaerythritol, and a mixture thereof.
25. The method for recycling waste polyester resins of claim 18 or claim 21, wherein the polybasic acid in the phase 2 is selected from the group of phthalic anhydride, isophthalic anhydride, terephthalic acid, adipic acid, azelaic acid, sebacic acid, tetrahydro phthalic anhydride, maleric anhydride, fumaric acid, itaconic acid, trimellitic acid, trimellitic anhydride, pyromellitic anhydride, succinic acid, cyclohexane dicarboxylic acid, naphthalene dicarboxylic acid, benzoic acid, and a mixture thereof.

26. The method for recycling waste polyester resins of claim 18 or claim 21, wherein the amount of the polybasic acid to be used in the phase 2 is 10~50w%, based on the amount of the depolymerization composition from the phase 1.

27. A method for recycling waste polyester resins, the method comprising:

phase 1 for producing a polyester resin having sulfonic acid alkali metal salt of aromatic dicarboxylic acid including DMSSIP;

phase 2 for producing a polyester polymer by adding the polyester resin from phase 1 to a waste polyester resin to depolymerize the waste polyester resin, and carrying out polycondensation reaction accompanied with ester interchange reaction; and

phase 3 for producing an aqueous solution from dissolving the polyester polymer in water, a liquid solution from dissolving the polyester polymer in water-friendly solvent, or a bulk resin without any treatment.

28. The method for recycling waste polyester resins of claim 21 or 27, wherein the amount of the DMSSIP to be mixed with the polybasic acid is 1~30w%,
based on the total amount of the polybasic acid.

29. The method for recycling waste polyester resins of claim 18, claim 21 or claim 27, wherein the water-friendly solvent in the phase 3 is selected from the group of alcohols, acetone, diacetone alcohol, dimethyl formamide, dimethyl acetamide, ethyl cellsolve, butyl cellsolve, tetrahydrofuran, and N-methyl-2-pyrrolidone.

30. The method for recycling waste polyester resins of claim 18, claim 21 or claim 27, wherein the amount of the water-friendly solvent to be used in the phase 3 is 10~100w%, based on the total amount of the polyester polymer from the phase 2.

31. A reclaimed polyester resin composition produced according to the claim 1, claim 18, claim 21 or claim 27, the state of the reclaimed polyester resin composition being either solid or liquid.

32. The reclaimed polyester resin composition of claim 31, wherein the polyester resin has a pour beginning temperature \( (T_{fb}) \) of 80~105°C.

33. The reclaimed polyester resin composition of claim 31, wherein the polyester resin has a pour ending temperature \( (T_{end}) \) of 120~160°C.

34. The reclaimed polyester resin composition of claim 31, wherein the polyester resin has a glass transition temperature \( (T_g) \) of 40~80°C.
35. The reclaimed polyester resin composition of claim 31, wherein the reclaimed polyester resin is used as a developer for use in electrophotograph, ink-jet inks, a textile finishing agent, an adhesive, a binder of film coatings, a toner, a hotmelt adhesive, and a binder of powder coatings.
Fig. 1

Waste polyester resin

First depolymerization of waste polyester resin

Addition of solid resin dissolvent

Second depolymerization and addition reaction of waste polyester resin

Addition of polybasic acid

Polycondensation using polyhydric alcohol

Phase 1

Phase 2: preparation of polyester polymer

Acid value: more than 20 mg KOH/g

Acid value: less than 20 mg KOH/g

Phase 3(a): preparation of solid or liquid resin

Phase 3(b): preparation of solid resin in its entirety

Polyester resin
Fig. 2

Waste polyester resin
Depolymerization using polyhydric alcohol
Addition of depolymerization stabilizer solid resin

Phase 1: preparation of depolymerization composition of waste polyester resin
Addition reaction by adding polybasic acid
Polycondensation using polyhydric alcohol

Phase 2: preparation of polyester polymer
Neutralization by adding basic compound
Dispersing in water/water-friendly solvent

Phase 3: preparation of water-dispersible polyester resin

Polyester resin
Fig. 3

Waste polyester resin

- Depolymerization using polyhydric alcohol
- Addition of depolymerization stabilizer solid resin

Phase 1: preparation of depolymerization composition of waste polyester resin

- Addition reaction by adding polybasic acid/DMSSIP
- Polycondensation using polyhydric alcohol

Phase 2: preparation of polyester polymer

Phase 3: preparation of liquid or solid polyester resin

Polyester resin
Fig. 4

Phase 1: preparation of polyester resin having sulfonic acid alkali metal salt

Waste polyester resin

Depolymerization and polycondensation

Phase 2: preparation of polyester polymer

Phase 3: preparation of liquid or solid polyester resin

Polyester resin
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

IPC7 C08G 63/00

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)

IPC7 C08G 63/00, C08G 63/183, C08J 11/04, C08J 11/24

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

Korean Patents and applications for inventions since 1975

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

KIPASS, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>P,Y</td>
<td>KR 02-18220A(PARK WOO HEUN) 08 March 2002 see the whole documents</td>
<td>1,5,9</td>
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<tr>
<td>Y</td>
<td>JP 08-253596A(KAO CORP.) 01 October 1996 see the whole documents</td>
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<td>A</td>
<td>US 5,635,584(EASTMAN CHMICAL CO.) 03 June 1997 see the whole documents</td>
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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
26 MARCH 2003 (26.03.2003)

Date of mailing of the international search report
27 MARCH 2003 (27.03.2003)

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Form PCT/ISA/210 (second sheet) (July 1998)