POLYESTER MELT-PHASE COMPOSITIONS HAVING IMPROVED THERMO-OXIDATIVE STABILITY, AND METHODS OF MAKING AND USING THEM

CROSS-REFERENCE TO RELATED APPLICATIONS

[001] This application claims priority to U.S. Provisional Application Serial No. 61/098,043, filed September 18, 2008 the disclosure of which is incorporated herein by reference in its entirety.

FIELD OF THE INVENTION

[002] The invention relates to polyester compositions, and more specifically, to polyester compositions that include a melt-phase polyethylene terephthalate polyester having incorporated therein residues of a monomer having two or more fused aromatic rings.

BACKGROUND OF THE INVENTION

[003] Certain polyester compositions, suitable for molding, are useful in packaging, such as in the manufacture of beverage containers. For example, some poly(ethylene terephthalate) polymers ("PET") are useful for that purpose, and PET has become popular because of its lightness, transparency and chemical inertness.

[004] PET is normally produced in a two-stage process, beginning with a melt-phase stage followed by a solid stating stage. The melt-phase stage is typically a three-phase process. First, in the esterification stage, ethylene glycol is reacted with terephthalic acid in a slurry under positive pressure and a temperature of 250-280°C yielding oligomeric PET. Next, the oligomer is heated to a slightly higher temperature, usually 260-290°C, and the positive pressure is changed to a mild vacuum, usually 20-100 mm, to yield the prepolymer. Finally, the prepolymer is converted to the final polymer by continuing to reduce the pressure to 0.5-3.0 mm and sometimes raising the temperature. After the three-phase melt process is complete, typically pellets at the end of the polymer stage are increased in molecular weight by

a solid state process. Typically, both the melt-phase and solid state process stages are conducted in the presence of an antimony catalyst.

[005] Antimony can be problematic, however. When it is used as a polycondensation catalyst for polyester and the polyester is molded into a bottle, for example, the bottle is generally hazy and often has a dark appearance from the antimony catalyst that is reduced to antimony metal.

[006] Disadvantages with the use of antimony, as well as other factors, have led to the development of an antimony-free melt-phase only process. However, the oxidative stability of PET prepared by such a method may be reduced and may result in a breakdown in molecular weight when the PET is exposed to air at temperatures around or exceeding 165°C. This is a problem because PET must be dried before it is processed, and the drying of PET is generally carried out above 165°C.

[007] Thus, there remains a need in the art for PET that can be produced by a melt-phase only process and that possesses higher oxidative stability. Increased stability may allow drying at higher temperatures. Additionally, it may eliminate the need to produce higher molecular weight PET to compensate for subsequent molecular weight breakdown.

SUMMARY OF THE INVENTION

[008] In one aspect, the invention relates to polyester compositions that include a melt-phase polyethylene terephthalate polyester having incorporated therein residues of a monomer having two or more fused aromatic rings, in an amount from about 0.1mole% to about 10 mole%, based on a total amount of dicarboxylic acid residues in the melt-phase polyethylene terephthalate polyester comprising 100 mole%; and that also include titanium.

[009] In another aspect, the invention relates to polyester compositions that include a melt-phase polyethylene terephthalate polyester having incorporated therein residues of 2,6-naphthalenedicarboxylic acid, in an amount from about 0.1 mole% to about 3 mole%, based on a total amount of dicarboxylic acid residues in the melt-phase polyethylene terephthalate polyester comprising 100 mole%; and titanium,

present in an amount from about 3 ppm to about 100 ppm titanium atoms, based on the total weight of the polyester composition.

[010] In yet another aspect, the invention relates to articles that include a melt-phase polyethylene terephthalate polyester having incorporated therein residues of 2,6-naphthalenedicarboxylic acid, in an amount from about 0.1 mole% to about 3 mole%, based on a total amount of dicarboxylic acid residues in the melt-phase polyethylene terephthalate polyester comprising 100 mole%; and titanium present in an amount from about 3 ppm to about 100 ppm titanium atoms, based on the total weight of the article.

[011] In a further aspect, the invention relates to processes for making melt-phase polyethylene terephthalate polyesters, that include the steps of forming a mixture comprising ethylene glycol, at least one acid chosen from terephthalic acid and derivatives of terephthalic acid, and a monomer having two or more fused aromatic rings, wherein the monomer having two or more fused aromatic rings is present in an amount from about 0.1 mole% to about 3 mole%, based on a total amount of dicarboxylic acid residues in the mixture comprising 100 mole%; and reacting the mixture in the presence of titanium to obtain the melt-phase polyethylene terephthalate polyester.

[012] Further aspects of the invention are as disclosed and claimed herein.

DETAILED DESCRIPTION OF THE INVENTION

[013] The present invention may be understood more readily by reference to the following detailed description of the invention, including the appended figures, and to the examples provided. It is to be understood that this invention is not limited to the specific processes and conditions described in the examples, because specific processes and process conditions for processing plastic articles may vary. It is also to be understood that the terminology used is for the purpose of describing particular embodiments only and is not intended to be limiting.

[014] As used in the specification and the claims, the singular forms "a," "an," and "the" include plural referents unless the context clearly dictates otherwise.

For example, reference to a "preform," "container" or "bottle" or an "article" is intended to include a plurality of preforms, containers, bottles, or articles.

[015] By "comprising" or "containing" we mean that at least the named compound, element, particle, etc. must be present in the composition or article, but does not exclude the presence of other compounds, materials, particles, etc., even if the other such compounds, material, particles, etc. have the same function as what is named.

[016] It is also to be understood that the mention of one or more process steps does not preclude the presence of additional process steps before, after, or intervening between those steps expressly identified, unless such a process step is expressly excluded by the claim.

[017] Expressing a range includes all integers and fractions thereof within the range. Expressing a temperature or a temperature range in a process, or of a reaction mixture, or of a melt or applied to a melt, or of a polymer or applied polymer means in all cases that the reaction conditions are set to the specified temperature or any temperature, continuous or intermittently, within the range; and that the reaction mixture, melt, or polymer are subjected to the specific temperature.

[018] By "atoms" as used in conjunction with a metal we mean the metal atom occupying any oxidation state, any morphological state, any structural state, and any chemical state, whether as added to or as present in the polymer or composition of matter.

[019] The terms "melt phase," "melt-phase product," and "melt-phase polyethylene terephthalate polyester," etc. are intended to refer to melt-phase reactions and to the products of such reactions. Melt-phase products may be isolated in the form of pellets or chips, or may be fed as a melt directly from the melt-phase finishers into extruders and directed into molds for making shaped articles such as bottle preforms (e.g. "melt to mold" or "melt to preform"). Unless otherwise specified, the melt-phase product may take any shape or form, including amorphous pellets, crystallized pellets, solid stated pellets, preforms, sheets, bottles, tray, jar, and so forth. In one aspect, the melt-phase polyethylene terephthalate polyesters useful

according to the invention may be limited to those not having undergone an increase in molecular weight in the solid state, that is, those having substantially all of their increase in molecular weight occurring while in the melt phase. Inherent viscosity is used by those skilled in the art to estimate molecular weight build, so that those polyesters made entirely in the melt phase and without subsequent solid-stating will have an inherent viscosity at the time of use that is not substantially greater than the inherent viscosity achieved during the melt phase polymerization. These polyesters may be described as or considered to be "melt-phase only" polyesters

[020] The term "melt" in the context of a melt-phase product is a broad umbrella term referring to a stream undergoing reaction at any point in the melt phase for making a polyester polymer, and includes the stream in esterification phase even though the viscosity of this stream is typically not meaningful, and also includes the stream in the polycondensation phase including the prepolymer and finishing phases, between each phase, and up to the point where the melt is solidified. The term "melt" in intended to refer to a polyester product not having undergone an increase in molecular weight in the solid state, although a melt-phase product may, of course, optionally undergo an increase in molecular weight in the solid state, as evidenced, for example, by an increase in inherent viscosity, after which it would no longer be considered a "melt".

[021] The intrinsic viscosity is the limiting value at infinite dilution of the specific viscosity of a polymer. It is defined by the following equation:

$$\eta_{int} = \lim_{c \to 0} (\eta_{sp}/C) = \lim_{c \to 0} \ln (\eta_r/C)$$

Where η_{int} = Intrinsic viscosity

η_r = Relative viscosity = t_s/t_o

η_{sp} = Specific viscosity = $\eta_r - 1$

[022] Instrument calibration involves replicate testing of a standard reference material and then applying appropriate mathematical equations to produce the "accepted" I.V. values.

$$\text{Calibration Factor} = \frac{\text{Accepted Ih.V. of Reference Material}}{\text{Average of Triplicate Determinations}}$$

Corrected Ih.V. = Calculated Ih.V. x Calibration Factor

The intrinsic viscosity (It.V. or η_{int}) may be estimated using the Billmeyer equation as follows:

$$\eta_{int} = 0.5\,[e^{0.5 \times \text{Corrected Ih.V.}} - 1] + (0.75 \times \text{Corrected Ih.V.})$$

[023] Inherent viscosity (I.V.) is calculated from the measured solution viscosity. The following equations describe these solution viscosity measurements:

$$IV = \eta_{inh} = [\ln (t_s/t_o)]/C$$

where η_{inh} = Inherent viscosity at 25°C at a polymer concentration of 0.50 g/ 100 mL of 60% phenol and 40% 1,1,2,2-tetrachloroethane

ln = Natural logarithm

t_s = Sample flow time through a capillary tube

t_o = Solvent-blank flow time through a capillary tube

C = Concentration of polymer in grams per 100 mL of solvent (0.50%)

Herein, inherent viscosity (IV) measurements were made under the conditions described above (at 25°C at a polymer concentration of 0.50 g/ 100 mL of 60% phenol and 40% 1,1,2,2-tetrachloroethane).

[024] L*, a*, and b* color coordinates are measured on transparent injection-molded disks, according to the following method. A Mini-Jector model 55-1 is used to mold a circular disk which has a diameter of 40 mm and a thickness of 2.5 mm. Before molding, the pellets are dried for at least 120 minutes and no more than 150 minutes in a forced air mechanical convection oven set at 170 °C. The Mini-Jector settings are the following: rear heater zone = 275 °C; front two heater zones = 285 °C;

cycle time = 32 seconds; and inject timer 30 seconds. The color of the transparent injection-molded disk is measured using a HunterLab UltraScan XE® spectrophotometer. The HunterLab UltraScan XE® spectrophotometer is operated using a D65 illuminant light source with a 10° observation angle and integrating sphere geometry. The HunterLab UltraScan XE® spectrophotometer is zeroed, standardized, UV calibrated, and verified in control. The color measurement is made in the total transition (TTRAN) mode. The L* value indicates the transmission/opacity of the sample. The "a*" value indicates the redness (+)/greenness (-) of the sample. The "b* value indicates the yellowness (+)/blueness (-) of the sample.

[025] Alternatively, color values are measured on crystallized polyester pellets or crystallized polymer ground to a powder passing a 3 mm screen. The polyester pellets or polymer specimens which are ground to a powder have a minimum degree of crystallinity of 15%. The HunterLab UltraScan XE® spectrophotometer is operated using a D65 illuminant light source with a 10° observation angle and integrating sphere geometry. The HunterLab UltraScan XE® spectrophotometer is zeroed, standardized, UV calibrated, and verified in control. The color measurement is made in the reflectance (RSIN) mode. The results are expressed in the CIE 1976 L*, a*, b* (CIELAB) color scale. The "L*" value indicates the lightness/darkness of the sample. The "a*" indicates the redness (+)/greenness (-) of the sample. The "b*" indicates the yellowness (+)/blueness (-) of the sample.

[026] In one aspect, the invention relates to polyester compositions that include a melt-phase polyethylene terephthalate polyester having incorporated therein residues of a monomer having two or more fused aromatic rings, in an amount from about 0.1mole% to about 10 mole%, based on a total amount of dicarboxylic acid residues in the melt-phase polyethylene terephthalate polyester comprising 100 mole%. Alternatively, the amount of residues of the monomer having two or more fused aromatic rings may be from about 0.1 mole% to about 3 mole%, or from about 0.5 mole% to about 2.5 mole%, in each case based on the total amount of dicarboxylic

acid residues in the melt-phase polyethylene terephthalate polyester comprising 100 mole%.

[027] In other aspects, the amount of residues of the monomer having two or more fused aromatic rings may be at least 0.05 mole%, or at least 0.1 mole%, or at least 0.25 mole%. Further, the amount of residues of the monomer having two or more fused aromatic rings may be up to about 3 mole%, or up to 5 mole%, or up to 10 mole%, in each case based on the total amount of dicarboxylic acid residues in the melt-phase polyethylene terephthalate polyester comprising 100 mole%.

[028] According to the invention, the melt-phase polyethylene terephthalate polyester may comprise, for example, residues of terephthalic acid, present in an amount of at least 90 mole%, based on the total amount of dicarboxylic acid residues in the melt-phase polyethylene terephthalate polyester comprising 100 mole%, and residues of ethylene glycol, present in an amount of at least 90 mole%, based on a total amount of diol residues in the melt-phase polyethylene terephthalate polyester comprising 100 mole%. In alternative embodiments, the residues of terephthalic acid may be present in an amount of at least 92 mole%, or at least 95 mole%, in each case based on the total amount of dicarboxylic acid residues in the melt-phase polyethylene terephthalate polyester comprising 100 mole%, and the residues of ethylene glycol may be present in an amount of at least 92 mole%, or at least 95 mole%, in each case based on a total amount of diol residues in the melt-phase polyethylene terephthalate polyester comprising 100 mole%.

[029] The melt-phase polyethylene terephthalate polyesters useful according to the invention include one or more monomers having two or more fused aromatic rings, for example 2,6-naphthalenedicarboxylic acid; dimethyl 2,6-naphthalenedicarboxylate; 9-anthracenecarboxylic acid; 2,6-anthracenedicarboxylic acid; dimethyl-2,6-anthracenedicarboxylate; 1,5-anthracenedicarboxylic acid; dimethyl-1,5-anthracenedicarboxylate; 1,8-anthracenedicarboxylic acid; or dimethyl-1,8-anthracenedicarboxylate. Thus, in one aspect the invention relates to polyester compositions in which the monomer having two or more fused aromatic rings comprises 2,6-naphthalenedicarboxylic acid present in an amount, for example, from about 0.1 mole% to about 3 mole%. Alternatively, the 2,6-naphthalenedicarboxylic

acid may be present, for example, in an amount from about 0.5 mole% to about 2.5 mole%, or as disclosed elsewhere herein with respect to the one or more monomers having two or more fused aromatic rings.

[030] The polyester compositions of the invention further comprise titanium.

[031] The polyester compositions of the invention may further comprise residues of phosphoric acid.

[032] In some aspects of the invention, the polyester compositions may not comprise metals other than titanium having catalytic effect, and may, for example, not comprise antimony, or germanium. Such compositions and the polyesters in them may therefore be prepared in the absence of antimony, or germanium, or both.

[033] The titanium of the polyester compositions may be provided in a variety of forms, as described elsewhere herein, and may be provided in various amounts, for example in an amount from about 1 ppm to about 150 ppm titanium atoms, or from 3 ppm to 100 ppm titanium atoms, or from 5 ppm to 60 ppm titanium atoms, in each case based on the total weight of the polyester composition.

[034] In another aspect, the titanium may be present in an amount from about 5 ppm to about 40 ppm titanium atoms, based on the total weight of the polyester composition.

[035] In yet another aspect, the polyester compositions of the invention may further comprise phosphorus, present in an amount from about 10 ppm to about 300 ppm phosphorus atoms, or from 12 ppm to 250 ppm, or from 15 ppm to 200 ppm, in each case based on the total weight of the polyester composition. Alternatively, the amount of phosphorus present may be defined as a molar ratio of phosphorus to titanium, and thus may range, for example, from about 0.25 moles of phosphorus per mole of titanium to about 3 moles of phosphorus per mole of titanium.

[036] The phosphorus may be provided as a phosphorus compound containing one or more phosphorus atoms, and especially phosphate triesters, acidic phosphorus compounds or their ester derivatives, and amine salts of acidic phosphorus-containing compounds.

[037] Specific examples of phosphorus compounds include phosphoric acid, pyrophosphoric acid, phosphorous acid, polyphosphoric acid, carboxyphosphonic acids, alkylphosphonic acids, phosphonic acid derivatives, and each of their acidic salts and acidic esters and derivatives, including acidic phosphate esters such as phosphate mono- and di- esters and non-acidic phosphate esters (e.g. phosphate tri-esters) such as trimethyl phosphate, triethyl phosphate, tributyl phosphate, tributoxyethyl phosphate, tris(2- ethylhexyl) phosphate, oligomeric phosphate tri-esters, trioctyl phosphate, triphenyl phosphate, tritolyl phosphate, (tris)ethylene glycol phosphate, triethyl phosphonoacetate, dimethyl methyl phosphonate, tetraisopropyl methylenediphosphonate, mono-, di-, and tri-esters of phosphoric acid with ethylene glycol, diethylene glycol, or 2-ethylhexanol, or mixtures of each.

[038] In a further aspect, the melt-phase polyethylene terephthalate polyesters of the invention may have an I.V., obtained from a melt-phase polymerization reaction, of at least 0.72 dL/g, or at least 0.75 dL/g, or at least 0.78 dL/g, or at least 0.80 dL/g, or as described elsewhere herein. These polyesters may thereafter undergo a further increase in molecular weight in the solid state, as evidenced by an increase in inherent viscosity, or alternatively, may have substantially all of their increase in molecular weight occur while in the melt phase. Thus, the melt-phase polyethylene terephthalate polyesters of the invention may have an I.V. achieved during melt-phase polymerization of at least 0.72 dL/g, or at least 0.75 dL/g, or at least 0.78 dL/g, or at least 0.80 dL/g, or as described elsewhere herein. The inherent viscosity may thereafter decrease due to subsequent processing, especially if at elevated temperatures, such that a higher inherent viscosity may be desired in order to account for this subsequent loss in molecular weight.

[039] In a further aspect, polyester compositions are provided that include a melt-phase polyethylene terephthalate polyester having incorporated therein residues of 2,6-naphthalenedicarboxylic acid, in an amount from about 0.1 mole% to about 3 mole%, based on a total amount of dicarboxylic acid residues in the melt-phase polyethylene terephthalate polyester comprising 100 mole%; and titanium, present in an amount from about 5 ppm to about 60 ppm titanium atoms, based on the total weight of the polyester composition.

[040] In yet another aspect, articles are provided that include a melt-phase polyethylene terephthalate polyester having incorporated therein residues of 2,6-naphthalenedicarboxylic acid, in an amount from about 0.1 mole% to about 3 mole%, based on a total amount of dicarboxylic acid residues in the melt-phase polyethylene terephthalate polyester comprising 100 mole%; and titanium, present in an amount from about 5 ppm to about 60 ppm titanium atoms, based on the total weight of the article. These articles may be, for example, in the form of a bottle, a preform, a jar, or a tray.

[041] In yet another aspect, the invention relates to processes for making a melt-phase polyethylene terephthalate polyester, that include the steps of forming a mixture comprising ethylene glycol, at least one acid chosen from terephthalic acid and derivatives of terephthalic acid, and a monomer having two or more fused aromatic rings, wherein the monomer having two or more fused aromatic rings is present in an amount from about 0.1 mole% to about 3 mole%, based on a total amount of dicarboxylic acid residues in the mixture comprising 100 mole%; and reacting the mixture in the presence of titanium to obtain the melt-phase polyethylene terephthalate polyester. Alternatively, the monomer having two or more fused aromatic rings may be present in an amount from about 0.5 mole% to about 2.5 mole%.

[042] In a further aspect, the mixture may comprise terephthalic acid, present in an amount of at least 90 mole%, based on the total amount of dicarboxylic acid residues in the mixture comprising 100 mole%, and the ethylene glycol may be present in the mixture in an amount of at least 90 mole%, based on a total amount of diols in the mixture comprising 100 mole%.

[043] In yet another aspect the monomer having two or more fused aromatic rings provided to the mixture may include one or more of: 2,6-naphthalenedicarboxylic acid; dimethyl 2,6-naphthalenedicarboxylate; 9-anthracenecarboxylic acid; 2,6-anthracenedicarboxylic acid; dimethyl-2,6-anthracenedicarboxylate; 1,5-anthracenedicarboxylic acid; dimethyl-1,5-anthracenedicarboxylate; 1,8-anthracenedicarboxylic acid; or dimethyl-1,8-anthracenedicarboxylate, and may be especially, for example, 2,6-

naphthalenedicarboxylic acid, present in the mixture in an amount, for example, from about 0.5 mole% to about 2.5 mole%.

[044] In yet another aspect, the titanium may be present in the reaction mixture in an amount from about 1 ppm to about 200 ppm titanium atoms, or from 1 ppm to 150 ppm titanium atoms, or from 5 ppm to 60 ppm titanium atoms, in each case based on the total weight of the melt-phase polyethylene terephthalate polyester obtained.

[045] In yet another aspect, the titanium may be provided to the mixture in an amount from about 5 ppm to about 60 ppm titanium atoms, based on the total weight of the melt-phase polyethylene terephthalate polyester obtained.

[046] In yet another aspect, the processes of the invention include a further step of adding phosphorus to the melt-phase polyethylene terephthalate polyester obtained, in an amount from about 10 ppm to about 300 ppm phosphorus, based on the total weight of the melt-phase polyethylene terephthalate polyester obtained, or as described elsewhere herein.

[047] In a further aspect, the melt-phase polyethylene terephthalate polyester obtained may have an I.V. of at least 0.72 dL/g, or at least 0.78 dL/g, or as further described herein. In yet another aspect, the processes of the invention may exclude a solid state polymerization step, and thus may optionally exclude compositions having had a significant increase in molecular weight in the solid state. In this aspect, the I.V. may be achieved entirely in the melt phase.

[048] We have unexpectedly discovered that in melt-phase processes for making polyethylene terephthalate polyesters, whether homopolymers or copolymers, and especially those carried out in the absence of antimony, for example including titanium as a catalyst, or aluminum and an alkali metal or an alkaline earth metal as described and claimed in an application copending herewith, the inclusion of a comonomer containing two or more fused aromatic rings, such as 2,6-naphthalenedicarboxylic acid, significantly improves the thermo-oxidative stability of these PET resins. Specifically, less molecular weight loss during simulated drying in air is observed.

[049] We have found that compositions made using an antimony-free catalyst system is thermo-oxidatively unstable in customer dryers at temperatures routinely employed. This instability causes the polymer to lose molecular weight and develop color when dried at temperatures necessary to ensure reliable processing and defect-free preform manufacture. As shown in the examples, the inclusion of comonomers with two or more fused aromatic rings significantly decreases the amount of molecular weight lost during simulated drying.

[050] We have found that the use of at least one source of titanium and a comonomer with two or more fused aromatic rings in the comonomer backbone, in a melt-phase process for producing polyethylene terephthalate polyesters, results in a polyester product having improved thermo-oxidative stability. Examples of acceptable comonomers include 2,6-naphthalenedicarboxylic acid, dimethyl 2,6-naphthalenedicarboxylate, 9-anthracenecarboxylic acid, 2,6-anthracenedicarboxylic acid, dimethyl-2,6-anthracenedicarboxylate, 1,5-anthracenedicarboxylic acid, dimethyl-1,5-anthracenedicarboxylate, 1,8-anthracenedicarboxylic acid, dimethyl-1,8-anthracenedicarboxylate, and similar derivatives of anthracene, naphthalene, phenanthrene, and pyrene.

[051] The polyester compositions according to the invention allow drying at standard drying temperatures, while maintaining satisfactory molecular weight.

[052] The melt-phase polyethylene terephthalate polyesters of the invention include at least one melt-phase polyethylene terephthalate polyester. In an embodiment, the melt-phase polyethylene terephthalate polyester is virgin (e.g., non-recycled) polyethylene terephthalate polyester. In an embodiment, the melt-phase polyethylene terephthalate polyester does not comprise any post-consumer recycled polyethylene terephthalate. In an embodiment, the at least one polyethylene terephthalate polyester does not comprise any pre-consumer recycled polyethylene terephthalate.

[053] In one aspect, the melt-phase polyethylene terephthalate polyester comprises:

(a) residues of at least one carboxylic acid component wherein at least 90 mole% of the residues are residues of terephthalic acid based on 100 mole% of the residues of at least one carboxylic acid component, and

(b) residues of at least one hydroxyl component wherein at least 90 mole% of the residues are residues of ethylene glycol, based on 100 mole% of the residues of at least one hydroxyl component. In an embodiment, the melt-phase polyethylene terephthalate polyester further comprises up to 10 mole% of residues chosen from residues of isophthalic acid, residues of diethylene glycol, residues of 1,4-cyclohexanediol (CHDM), and residues of derivatives thereof. Non-limiting exemplary ranges for residues of isophthalic acid are 0.5-5.0 mole% relative to the total diacid components, for residues of diethylene glycol are 0.5-4.0 wt% based on the weight of the polymer, and for residues CHDM are 0.5-4.0 mole % relative to glycol components. In an embodiment, the polyester compositions further comprise residues of phosphoric acid.

[054] In one aspect, the polyester compositions comprise titanium. In another aspect, the amount of titanium may be from 3 ppm to 60 ppm, based on the total weight of the polyester composition.

[055] The titanium useful in the compositions and processes of the invention may be provided in a variety of forms and amounts. For example, the titanium will typically be present as a titanium residue, that is, a moiety remaining in a polymer melt upon addition of titainum atoms to the melt-phase process for making the polyester polymer, and the oxidation state, morphological state, structural state, or chemical state of the titanium compound as added or of the residue present in the compositions is not limited. The titanium residue may be in the same form as the titanium compound added to the melt-phase reaction, but typically will be altered since the titanium participates in accelerating the rate of polycondensation.

[056] By the term "titanium atoms" or "titanium" is meant the presence of titanium in the polyester polymer detected through any suitable analytical technique regardless of the oxidation state of the tiatinum. Suitable detection methods for the presence of titanium include inductively coupled plasma optical emission spectroscopy (ICP-OES). The concentration of titanium is reported as the parts per

million of metal atoms based on the weight of the polymer compositions. The term "metal" does not imply a particular oxidation state.

[057] Titainum may be added to the processes of the invention as a compound or as a metal, so long as the titanium is ultimately active as a catalyst in the polycondensation phase. Titanium oxides are not included within the meaning of an titainum compound or metal because they are insoluble and have little, if any, catalytic activity in the polymer melt. It is desirable to select a titanium compound which can be dissolved in a diluent or a carrier that is volatile and/or reactive with the polyester forming ingredients. Titanium compounds can also be added as slurries or suspensions in a liquid that is volatile and/or reactive with the polyester forming ingredients. A mode of addition of titanium compounds is addition to a catalyst mix tank, which is part of the polyester melt-phase process equipment. The catalyst mix tank may also contain a suitable solvent, for example ethylene glycol.

[058] Examples of suitable titanium compounds include titanium tetraisopropoxide, titanium (IV) ethoxide, acetyl tri-isopropyltitanate, titanium (IV) 2-ethylhexanoate, titanium (IV) 2-ethylhexoxide, titanium (IV) n-propoxide, titanium (IV) n-butoxide, and titanium (IV) t-butoxide. A wide variety of titanium alkoxides are suitable for use according to the invention, including those corresponding to the general form $Ti(OR)_4$, and $Ti(OR)_x(OR')_y$, wherein R and R' are alkoxy species derived from alcohols such as ethyl, propyl, isopropyl, butyl, t-butyl, and the like, and in which x=1 to 4, y=0 to 2.

[059] The amount of titanium present according to the invention may be at least 1 ppm, or at least 3 ppm, or at least 5 ppm, or at least 8 ppm, or at least 10 ppm, or at least 20 ppm, or at least 30 ppm, and up to about 150 ppm, or up to about 100 ppm, or up to about 75 ppm, or up to about 60 ppm titanium atoms, based on the total weight of the polyester composition, or based on the total weight of the reaction mixture, as the case may be.

[060] This invention can be further illustrated by the following examples, although it will be understood that these examples are included merely for purposes of illustration and are not intended to limit the scope of the invention unless otherwise specifically indicated.

EXAMPLES

Examples 1-7

[061] Oligomer synthesis: Polyethylene terephthalate oligomers were prepared from terephthalic acid and virgin ethylene glycol, and in some cases with various amounts of 2,6-naphthalenedicarboxylic acid purchased from Aldrich Chemical Company (Part # 301353 , [1141-38-4]), or with isophthalic acid or cyclohexane dimethanol as described below. An aqueous mixture of tetramethylammonium hydroxide (TMAH) in water was charged to each batch to reduce the amount of diethylene glycol formed during the esterification reaction. The TMAH was purchased from Aldrich Chemical Company (part # 328251, [75-59-2]) and diluted 1 part in 10 parts distilled water prior to use. In every case, all the raw materials were mixed together in a 2 liter polyethylene beaker and then charged into a Parr high pressure reactor. A control oligomer containing two mole percent of isophthalate modification was also prepared from BP-Amoco's isophthalic acid starting material. Another control oligomer was prepared containing Eastman cyclohexane dimethanol starting material.

[062] A typical charge of reactants to the esterification reactor is shown in the table below. The "as charged mol ratio" was 1.6 moles of glycol to 1.0 moles of total acids and the expected yield of water was 144 grams. No catalyst was present during the esterification step.

Table 1

Reactant	**Example 1**	**Example 2**	**Example 3**	**Example 4**	**Example 6**	**Example 7**
Terephthalic Acid	664.64g [4.00 moles]	661.35g [3.98 moles]	651.40g [3.92 moles]	654.65g [4.00 moles]	651.38g [3.92 moles]	**611g 3.68 moles]**
Ethylene Glycol	397.28g [6.40 moles]	397.25g [6.40 moles]	397.28g [6.40 moles]	397.28g [6.40 moles]	397.32g 6.40 moles]	397.28g 6.40 moles]
2,6-Napthalene dicarboxylic acid	0	4.32g [0.02 moles]	8.71g [0.04 moles]	12.96g [0.06 moles]	17.20g [0.08 moles]	69.6g 0.32 moles]
TMAH – H_2O solution	0.5g	0.5g	0.4g	0.7g	0.7g	0.5g

[063] The reactor used to carry out the esterification had a 2 liter volume and was fitted with a heated, packed, column for reaction by-product separation and removal. The packed column was connected to a water cooled condenser which was, in turn, connected to a pressure regulator and house nitrogen source. The flow of nitrogen into the system was controlled by this regulator. The volume of nitrogen to be 'bled' into the system was determined based on the output from a pressure transducer located on the head of the reactor. The reaction vapor output, which was cooled in the condenser section, was collected and its mass was continuously measured to estimate the extent of reaction. The unit had a "propeller" style stirrer to provide agitation.

[064] The reaction conditions were controlled and monitored using a Camile® distributed data acquisition and control system. The target reaction parameters were as shown in Table 2 below.

Table 2

Stage	Duration (minutes)	Reactor Temperature (° C)	Reactor Pressure (psig)	Stir Rate (rpm shaft)	Column Temperature (° C)
1	5	25	40	180	25
2	60	245	40	180	25
3	5	245	40	180	150
4	200	245	40	180	150
5	25	245	0	0	25
6	1	25	0	0	0

[065] After completion of the reaction sequence, the product was removed from the Parr reactor via a ram-seal valve fitted to the reactor's bottom section. A small portion of the reaction mixture was collected in a three-inch diameter, one-half inch deep aluminum pan for color evaluation. The remaining oligomer was drained into a stainless steel pan and allowed to solidify before being immersed in liquid nitrogen. The cold oligomer was pulverized using a hammer to produce a coarse powder suitable for polymerization.

[066] The product oligomer was analyzed by proton NMR to determine composition, molar ratio of EG to total acids, degree of polymerization, and diethylene glycol content. Color was measured on the cooled disk of oligomer

collected in the aluminum pan as described above. The measurement was made using a Hunter Ultrascan XE instrument.

[067] Polymer synthesis (**Examples 1-7**): Samples of the granular oligomer from each Parr run were charged to a series of 500-ml heavy walled, round-bottom flasks for polymerization. Titanium was introduced into the oligomer as a solution of titanium isopropoxide in n-butanol (Aldrich 377996). The addition of this catalyst mix was done using a syringe.

[068] A stainless steel stirrer (2" diameter paddle) was next inserted into the flask and then each flask was fitted with a polymer adapter head. This head included a nipple for the attachment of a nitrogen purge line, a septum port for injection of additives, a smooth bore tubular section for the stirring shaft and two standard taper 24/40 male joints; one for insertion into the flask's female joint and the second, which is oriented at a 45° angle to the first, was connected to a section of glass tubing terminating at a vacuum condenser system. A Teflon tubular bushing was inserted into the smooth bore section of the adapter. The stainless steel stirring shaft was passed through the inner diameter of this bushing and a section of rubber hose was fitted around the stirring shaft and over the outside diameter of the glass tubing. This assembly provides a low friction, vacuum tight seal between the stirring shaft and the adapter head of the reaction flask. The assembled apparatus was clamped into a polymerization "rig", and the stirring shaft connected to a 1/8 horsepower stirring motor. The polymerization rig included a molten metal bath which could be raised to provide heat input to the flask. The stirring motor could also be raised or lowered to ensure that the stirrer's blade was fully immersed in the molten oligomer/polymer as the reaction was carried out.

[069] Typical melt-phase polymerization reaction conditions are as shown in Table 3. As with the esterification sequence reaction, parameters were monitored and controlled using a Camile® system.

Table 3

Stage Number	Duration (minutes)	Temperature (° C)	System pressure (mm Hg)	Stirring rate (rpm shaft)
1	0.1	275	760	0
2	10	275	760	150
3	2	275	140	300
4	1	275	141	300
5	10	275	51	300
6	5	275	51	300
7	2	275	140	300
8	2	275	140	300
9	2	275	4.5	300
10	20	275	4.5	300
11	10	275	0.5	30
12	180	275	0.5	30
13	0.1	275	0.5	30
14	1	275	600	30
15	1	275	600	30
16	1	275	600	30
17	1	275	600	0

[070] At the end of Stage 13shown in the table above a solution of phosphoric acid (Aldrich Chemical Co. part 452289, [7664-38-2]) in diethylene glycol diethyl ether (diglyme, Aldrich Chemical Co. part 281662, [111-96-6]) was injected into the polymer mass using a glass syringe fitted with a stainless steel needle. At the titanium loading of 7 parts per million the target loading of phosphorus was 9 parts per million and at the 20 ppm titanium loading the target level of phosphorus was 26 parts per million.

[071] At the end of the reaction sequence the metal bath was lowered and the polymer mass was allowed to cool. After ten to fifteen minutes the polymer had solidified and the heating bath was raised to re-melt the polymer and permit it to be pulled free of the flask walls. After cooling for an additional fifteen minutes the flask was broken and the solid polymer mass was immersed into liquid nitrogen. The cold polymer mass was removed from the stirring rod using a hydraulic ram fitted with a chisel attachment. The collected "lumps" of polymer were cooled again in liquid nitrogen and finally ground in a Wiley mill. The mill was fitted with a screen having 3-mm diameter holes. The resulting coarsely ground polymer was collected and submitted for various analytical tests.

[072] Themo-oxidative stability (TOS) testing: Examples 1-7 were evaluated for thermo-oxidative stability by passing dry, heated air through the PET particles at 12 scfh and 192°C. The laboratory apparatus consisted of a glass jacketed filter frit with the sample placed above the frit. Dry air was pushed into the sample from below after passing through a glass coil and being heated by indirect contact with refluxing 1-octanol. Sample temperature was measured by a thermo-couple placed directly into the sample. Samples were removed at t = 1, 2, 4, 6, 8, and 24 hours and analyzed for inherent viscosity as described above.

Table 4. TOS testing of samples 1-11

Ex. #	Compositional Description (as charged to the esterification reactor)	Titanium Level (ppm)	I.V. after heating in air stream for 0 hours	1 hour	2 hours	4 hours	6 hours	8 hours	24 hours	I.V. Change over 24 hours
1	98 mole % terephthalate, 2 mole % isophthalate, 100 mole % ethylene glycol	7	0.796	0.613	0.542	0.501	0.467	0.416	0.336	-0.460
2	99.5 mole % terephthalate, 0.5 mole % naphthalate, 100 mole % ethylene glycol	7	0.782	0.759	0.749	0.735	0.716	0.708	0.646	-0.136
3	99 mole % terephthalate, 1 mole % naphthalate, 100 % ethylene glycol	7	0.776	0.763	0.756	0.750	0.745	0.734	0.697	-0.079
4	98.5% terephthalate, 1.5 mole % naphthalate, 100 mole % ethylene glycol	7	0.725	0.721	0.726	0.734	0.747	0.765	0.778	+0.050
5	98 mole % terephthalate, 2 mole % naphthalate, 100 mole % ethylene glycol	7	0.788	0.783	0.779	0.787	0.785	0.798	0.810	+0.022

6	92 mole % terephthalate, 8 mole % naphthalate, 100 mole percent ethylene glycol	7	0 .656			0 .721	0 .766		0 .877	+0. 221
7	98 mole % terephthalate, 2 mole % isophthalate, 100 mole % ethylene glycol	20	0 .684	0 .548	0 .513	0 .483	0 .452	0 .419	0 .354	- 0.330
8	99.5 mole % terephthalate, 0.5 mole % naphthalate, 100 mole % ethylene glycol	20	0 .694	0 .667	0 .644	0 .623	0 .615	0 .607	0 .599	- 0.095
9	98.5% terephthalate, 1.5 mole % naphthalate, 100 mole % ethylene glycol	20	0 .781	0 .749	0 .739	0 .732	0 .734	0 .734	0 .729	- 0.052
10	98 mole % terephthalate, 2 mole % naphthalate, 100 mole % ethylene glycol	20	0 .693	0 .690	0 .689	0 .725	0 .733	0 .682	0 .691	- 0.002
11	92 mole % terephthalate, 8 mole % naphthalate, 100 mole percent ethylene glycol	20	0 .737	0 .739	0 .744	0 .748	0 .757	0 .760	0 .788	+0. 051

[073] The results in Table 4 show that the inclusion of 2,6-naphthalenedicarboxylic acid moiety in titanium catalyzed PET substantially increased the thermo-oxidative stability of the resin. Specifically, less molecular weight loss, and thus less IV break, is observed versus the controls without 2,6-naphthalenedicarboxylate modification.

Claims:

1. A process for making a melt-phase polyethylene terephthalate polyester, comprising:

forming a mixture comprising ethylene glycol, at least one acid chosen from terephthalic acid and derivatives of terephthalic acid, and a monomer having two or more fused aromatic rings, wherein the monomer having two or more fused aromatic rings is present in an amount from about 0.1 mole% to about 3 mole%, based on a total amount of dicarboxylic acid residues in the mixture comprising 100 mole%; and

reacting the mixture in the presence oftitanium to obtain the melt-phase polyethylene terephthalate polyester.

2. The process according to claim 1, wherein the monomer having two or more fused aromatic rings is present in an amount from about 0.5 mole% to about 2.5 mole%.

3. The process according to claim 2, wherein:

the mixture comprises terephthalic acid, present in an amount of at least 90 mole%, based on the total amount of dicarboxylic acid residues in the mixture comprising 100 mole%, and

the ethylene glycol is present in the mixture in an amount of at least 90 mole%, based on a total amount of diols in the mixture comprising 100 mole%.

4. The process according to claim 3, wherein the monomer having two or more fused aromatic rings comprises one or more of: 2,6-naphthalenedicarboxylic acid; dimethyl 2,6-naphthalenedicarboxylate; 9-anthracenecarboxylic acid; 2,6-anthracenedicarboxylic acid; dimethyl-2,6-anthracenedicarboxylate; 1,5-anthracenedicarboxylic acid;, dimethyl-l ,5-anthracenedicarboxylate; 1,8-anthracenedicarboxylic acid; or dimethyl-I ,8-anthracenedicarboxylate.

5. The process according to claim 2, wherein the monomer having two or more fused aromatic rings comprises 2,6-naphthalenedicarboxylic acid, present in an

amount from about 0.5 mole% to about 2.5 mole%.

6. The process according to claim 1, wherein the mixture does not comprise antimony.

7. The process according to claim 1, wherein the mixture does not comprise germanium.

8. The process according to claim 1, wherein the titanium is present in an amount from about 1 ppm to about 150 ppm titanium atoms, based on the total weight of the melt-phase polyethylene terephthalate polyester obtained.

9. The process according to claim 1, comprising a further step of:

adding phosphorus to the melt-phase polyethylene terephthalate polyester obtained, in an amount from about 5 ppm to about 300 ppm phosphorus, based on the total weight of the melt-phase polyethylene terephthalate polyester obtained.

10. The process according to claim 1, wherein the melt-phase polyethylene terephthalate polyester obtained has an I.V. of at least 0.72 dL/g achieved in the melt phase.

11. The process according to claim 1, wherein the process does not comprise solid state polymerization.