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(54) Title: TITANIUM NITRIDE PARTICLES, METHODS OF MAKING THEM, AND THEIR USE IN POLYESTER COMPO-
SITIONS

(57) Abstract: Polyester compositions are disclosed that include polyester polymers or copolymers having incorporated therein titanium nitride particles that improve the reheat properties of the compositions. Processes for making such compositions are also disclosed. The titanium nitride particles are made from titanium oxide particles by heating the titanium oxide particles in a nitrogen-containing gas to a temperature sufficient to convert at least a portion of the titanium oxide particles to titanium nitride particles. The particles are then mixed with a liquid carrier to obtain a slurry of titanium nitride particles, and the slurry is introduced to a polyester polymerization process to obtain a polyester composition having improved reheat.



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Titanium Nitride Particles, Methods of Making Them, and Their Use in Polyester Compositions

FIELD OF THE INVENTION

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This invention relates to titanium nitride particles, methods of making them, and their use in polyester compositions.

BACKGROUND OF THE INVENTION

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Many plastic packages, such as those made from poly(ethylene terephthalate) (PET) and used in beverage containers, are formed by reheat blow-molding, or other operations that require heat softening of the polymer.

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In reheat blow-molding, bottle preforms, which are test-tube shaped injection moldings, are heated above the glass transition temperature of the polymer, and then positioned in a bottle mold to receive pressurized air through their open end. This technology is well known, as shown, for example, in U.S. Pat. No. 3,733,309, incorporated herein by reference. In a typical blow-molding operation, radiation energy from quartz infrared heaters is generally used to reheat the preforms.

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In the preparation of packaging containers using operations that require heat softening of the polymer, the reheat time, or the time required for the preform to reach the proper temperature for stretch blow molding (also called the heat-up time), affects both the productivity and the energy required. As processing equipment has improved, it has become possible to produce more units per unit time. Thus it is desirable to provide polyester compositions which provide improved reheat properties, by reheating faster (increased reheat rate), or with less

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reheat energy (increased reheat efficiency), or both, compared to conventional polyester compositions.

5 A variety of black and gray body absorbing compounds have been used as reheat agents to improve the reheat characteristics of polyester preforms under reheat lamps. These conventional reheat additives include carbon black, graphite, antimony metal, black iron oxide, red iron oxide, inert iron compounds, spinel pigments, and infrared-absorbing dyes. The amount of absorbing compound that can be added to a
10 polymer is limited by its impact on the visual properties of the polymer, such as brightness, which may be expressed as an L^* value, and color, which is measured and expressed as an a^* value, a b^* value, and haze, as further described below.

15 To retain an acceptable level of brightness and color in the preform and resulting blown articles, the quantity of reheat additive may be decreased, which in turn decreases reheat rates. Thus, the type and amount of reheat additive added to a polyester resin may be adjusted to strike the desired balance between increasing the reheat rate and
20 retaining acceptable brightness and color levels.

U.S. Pat. Appln. Nos. 11/095,834 and 11/228,672, having common assignee herewith and incorporated herein by reference in their entirety, disclose and claim polyester compositions that comprise a polyester
25 polymer and titanium nitride particles, the particles serving, for example, to increase the reheat properties of the polyester compositions.

We have found titanium nitride to be effective in imparting desirable reheat characteristics in polyesters. This is especially the case with so-
30 called nanosize or ultrafine particles, which offer the advantage of improving the near infrared absorbing characteristics of polyester

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compositions without significantly affecting the color properties of the molded polyester articles.

- 5 JP Publ. No. 61-278558 discloses a polyester composition containing microparticulate titanium nitride, preferably in an amount between 0.05 and 10 % by weight, obtained by heating titanium metal or titanium oxide in nitrogen. The polyester composition is said to have excellent black spin-dyeing and light blocking properties.
- 10 U.S. Pat. No. 5,998,004 discloses a biaxially oriented polyester film, having excellent scratch resistance and chipping resistance by the inclusion of particles having an average primary particle diameter of 5-300 nm, an average degree of aggregation of 5-100 and a Mohs' hardness of 6-10 by the content of 0.01-5 wt. %. The scratch resistance and chipping resistance of the film can be further increased by the
- 15 inclusion of particles having an average particle diameter of 0.3-3 μ m, a Mohs' hardness less than that of the previously described particles, and/or non-incorporated particles.
- 20 There remains a need in the art for polyester compositions having improved reheat, that incorporate titanium nitride particles that provide the desired properties while being economical to produce.

SUMMARY OF THE INVENTION

- 25 In one aspect, the invention relates to processes for producing a suspension of titanium nitride particles in a carrier suitable for use in a polyester polymerization process that may be used to obtain a polyester composition having an amount of titanium nitride particles sufficient to
- 30 improve the reheat properties of the composition. The processes according to the invention for producing the titanium nitride particles use titanium oxide particles as a reactant.

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Thus, in various embodiments, titanium dioxide particles are heated in a gas containing a source of nitrogen, hereinafter a "nitrogen-containing gas," for example ammonia, to a temperature sufficient to effect either
5 partial or essentially complete nitridation of the titanium oxide particles, so as to obtain titanium nitride particles. The resulting titanium nitride particles may then be combined with a carrier to form a slurry, and the slurry introduced to a polyester polymerization process. In those
10 embodiments in which only partial nitridation is achieved, the resulting titanium nitride particles will also include unreacted or only partially reacted titanium oxide particles, such that when suspended, the residual titanium oxide particles may have a whitening effect on the resulting polymer compositions. In those cases where substantial or essentially
15 complete nitridation is achieved, the absence of unreacted particles may allow the use of fewer particles to achieve the intended reheat improvement. The titanium nitride particles produced according to the invention may also result in polyester compositions having reduced yellowness, and/or increased blueness, as well as an increased
20 resistance of the contents of a package made from the polyester composition to the effects of ultraviolet light.

Although the particles may be hereinafter referred to as titanium nitride particles for convenience, the term is intended to also encompass mixtures of titanium nitride particles and titanium oxide particles, unless
25 otherwise specified. Further, in those cases in which carbon is present in the titanium oxide particles used as a reactant, or in the nitrogen-containing gas, the titanium particles produced may comprise significant amounts of titanium carbide.

30 The polyester compositions according to the invention thus comprise polyester polymers or copolymers, and especially thermoplastic polyester polymers or copolymers, having incorporated therein titanium

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nitride particles that provide one or more of: improved reheat, reduced yellowness, and increased resistance of the contents to the effects of ultraviolet light. The titanium nitride particles are incorporated into the polyesters during polymerization as a suspension in one or more
5 carriers, and especially one or more liquid carriers. A range of particle sizes may be used, as well as a range of particle size distributions. The polyester compositions may comprise a single type of polyester polymer, or may be blends of polyesters having one or more other polymers blended therein, and especially one or more polyamides or other
10 polymers that provide advantages not possible with the use of a single polymer, such as improved oxygen-scavenging effect, or improved acetaldehyde scavenging effect, or the like.

15 DETAILED DESCRIPTION OF THE INVENTION

The present invention may be understood more readily by reference to the following detailed description of the invention, and to the examples provided. It is to be understood that this invention is not limited to the
20 specific processes and conditions described, 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. It is further understood that although the various
25 embodiments may achieve one or more advantages, the claimed invention is not restricted to those advantages, nor need all the advantages be obtained in every instance.

As used in the specification and the claims, the singular forms "a," "an,"
30 and "the" include plural referents unless the context clearly dictates otherwise. For example, reference to processing a thermoplastic

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"preform," "container" or "bottle" is intended to include the processing of a plurality of thermoplastic preforms, articles, containers, or bottles.

- By "comprising" or "containing" we mean that at least the named compound, element, particle, etc. is 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.
- As used herein, a "d₅₀ particle size" is the median diameter, where 50% of the volume is composed of particles larger than the stated d₅₀ value, and 50% of the volume is composed of particles smaller than the stated d₅₀ value. As used herein, the median particle size is the same as the d₅₀ particle size.
- Thus, in one aspect, the invention relates to processes for producing polyester compositions that include the steps of : heating titanium oxide particles in a nitrogen-containing gas at a temperature sufficient to obtain titanium nitride particles; suspending the titanium nitride particles in a carrier to obtain a suspension of titanium nitride particles; and introducing the suspension of titanium nitride particles to a polyester polymerization process to obtain a polyester composition having the titanium nitride particles dispersed therein.
- The nitrogen-containing gas may be, for example N₂, trimethylamine, triethylamine, or ammonia, or mixtures of any of these, and especially, ammonia.
- The reaction may be carried out, for example at a temperature from about 700°C to about 1,500°C.

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The titanium oxide particles comprise titanium dioxide particles, which may be in the form, for example, of one or more of the following crystalline forms: anatase, brookite, or rutile.

- 5 The titanium oxide particles used may have a median particle size, for example, from about 0.5 nm to about 1,000 nm, or from about 0.5 nm to about 500 nm, or from 1 nm to 100 nm, or from 1 nm to 50 nm.

- 10 The carrier used may comprise, for example, one or more of: ethylene glycol, a fatty acid ester, an ethoxylated fatty acid ester, a paraffin oil, a polyvalent alcohol, a polyvalent amine, a silicone oil, a hydrogenated castor oil, a hydrogenated ricinus oil, a stearic ester of pentaerythritol, soybean oil, or an ethoxylated alcohol.

- 15 The titanium nitride particles obtained may have a median particle size, for example, of from about 0.5 nm to about 1,000 nm, or from about 0.5 nm to about 500 nm, or from 1 nm to 100 nm, or from 1 nm to 50 nm.

- 20 In one aspect, the titanium nitride particles of the invention may be dispersed in the polyester composition in an amount, for example, from about 0.5 ppm to about 1,000 ppm, or from 5 ppm to 50 ppm, in each case with respect to the total weight of the polyester composition.

- 25 The polyester composition may comprise, for example polyethylene terephthalate, and may be in the form of a beverage bottle preform, or in the form of a beverage bottle, or in the form of a molded article.

- 30 The polyester compositions of the invention may comprise, for example, a polyester polymer as a continuous phase, with the titanium nitride particles dispersed within the continuous phase.

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The titanium nitride particles may have a median particle size, for example, from 1 nm to 1,000 nm, and may thus provide the beverage bottle preform with a reheat improvement temperature (RIT) of at least 5°C while maintaining a preform L* value of 70 or more, and a b* value
5 from about minus 0.8 to about plus 2.5.

The polyester composition of the invention may demonstrate, for example, a reduction in the percent of UV transmission of at least 10% at a wavelength of 370nm, as measured at a sample thickness of about
10 0.012 inches, when compared with a polyester composition lacking the titanium nitride particles.

The titanium nitride particles useful according to the invention may comprise, for example, particles coated with titanium nitride.
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The titanium nitride particles used may comprise a titanium nitride having an empirical formula from about $\text{TiN}_{0.42}$ to about $\text{TiN}_{1.16}$.

The titanium nitride particles used may comprise titanium nitride in an amount, for example of at least about 90 wt.%, with respect to the total weight of the titanium nitride particles. The titanium nitride particles of
20 the invention may further comprise titanium carbide.

When in the form of a beverage bottle preform, the compositions may, for example, exhibit a reheat improvement temperature greater than
25 5°C.

According to an aspect of the invention, the polyester polymerization process may comprise the following steps, with the
30 suspension of titanium nitride particles is introduced into the polyester polymerization process before, during, or after any of these steps: a) an esterification step comprising transesterifying a dicarboxylic acid diester

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with a diol, or directly esterifying a dicarboxylic acid with a diol, to obtain one or more of a polyester monomer or a polyester oligomer; b) a polycondensation step comprising reacting the one or more of a polyester monomer or a polyester oligomer in a polycondensation
5 reaction in the presence of a polycondensation catalyst to produce a molten polyester polymer having an It.V. from about 0.50 dL/g to about 1.1 dL/g; c) a particulation step in which the molten polyester polymer is solidified into particles; and d) an optional solid-stating step in which the solid polymer is polymerized to an It.V. from about 0.70 dL/g to about
10 1.2 dL/g.

According to an aspect of the invention, the polyester polymerization process may further comprise a forming step, following the solid-stating step, the forming step comprising melting and extruding the resulting
15 solid polymer to obtain a formed item having the titanium nitride particles dispersed therein.

According to an aspect of the invention, the suspension of titanium nitride particles may be dispersed in a thermoplastic polymer to form a
20 thermoplastic concentrate in which the titanium nitride particles are present in an amount from about 100 ppm to about 5,000 ppm, with respect to the weight of the thermoplastic concentrate, and the thermoplastic concentrate thereafter introduced into the polyester polymerization process prior to or during the forming step. In this
25 aspect, the titanium nitride particles may have a median particle size, for example, from about 1 nm to about 100 nm.

In the process of the invention, the suspension of titanium nitride particles may be added, for example, to the polyester polymerization
30 process prior to or during the polycondensation step, or prior to or during the esterification step.

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According to the processes of the invention, the dicarboxylic acid used may comprise, for example, terephthalic acid, or a dicarboxylic acid diester may be used that comprises dimethyl terephthalate. The diol used, may comprise, for example, ethylene glycol.

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In those cases in which a thermoplastic concentrate is used, it may be added to the molten polyester polymer; for example, when the molten polyester polymer has an It.V. which is within +/- 0.2 It.V. units of the It.V. of the thermoplastic concentrate.

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In another aspect, the invention relates to processes for producing polyester compositions that includes the steps of heating titanium oxide particles in a nitrogen-containing gas to a temperature sufficient to convert a portion of the titanium oxide particles to titanium nitride particles; suspending the titanium oxide particles and the titanium nitride particles in a carrier to obtain a suspension of titanium oxide particles and titanium nitride particles; and introducing the suspension of titanium oxide particles and titanium nitride particles to a polyester polymerization process to obtain a polyester composition having the titanium oxide particles and the titanium nitride particles dispersed therein.

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Other aspects of the invention are as further disclosed hereinafter.

Thus, according to the invention, titanium nitride particles may be used in polyester compositions to obtain one or more of the following advantages: to improve the reheat properties of the polyester compositions in which they are distributed; as a bluing agent to increase the blue tint of the polyester compositions in which they are distributed; or to improve the UV-blocking properties of the polyester compositions in which they are distributed. Of course, the polyester compositions of the invention may have additional advantages beyond those just given, and

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the invention is intended to encompass such additional advantages as well.

When we say that the polyester compositions of the invention may have improved reheat properties, we mean that the compositions may reheat faster (increased reheat rate), or with less reheat energy (increased reheat efficiency), or both, compared to conventional polyester compositions that do not include the titanium nitride particles of the invention, when exposed, for example, to similar infrared heating, or radiation. A convenient measure is the reheat improvement temperature (RIT) of the compositions, as further defined herein.

When we say that the polyester compositions of the invention may have reduced yellowness, or that the titanium nitride particles may act as a bluing agent, we mean that the resulting compositions may appear to be less yellow, or more blue, or both, or that the b^* value, as measured using the tristimulus CIE $L^*a^*b^*$ scale, as further described herein, is lower than it would be in the absence of the titanium nitride particles of the invention. For example, the b^* value may be lowered by at least 1 unit, or at least 2 units, or at least 3 units.

When we say that the polyester compositions of the invention may have UV-blocking effect, we mean that the compositions may provide increased resistance of the contents to the effects of ultraviolet light. This phenomenon can be determined by visual inspection of contents such as dyes that degrade over time in the presence of UV light. Alternatively, the UV-blocking effect of the polyester compositions of the invention can be measured by UV-VIS measurements, such as by using a HP8453 Ultraviolet-Visible Diode Array Spectrometer, performed from a wavelength ranging from 200nm to 460nm. An effective comparison measure using this equipment would be a reduction in the percent of UV transmission rate at 370nm, the polyester compositions of the invention

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typically obtaining a reduction of at least 5%, or at least 10%, or at least 20% when compared with polyester compositions without the titanium nitride particles of the invention. For example, if the unmodified polymer exhibits a transmission rate of about 80%, and the modified polymer
5 exhibits a transmission rate of about 60%, the reduction would be a reduction of 25%. Any other suitable measure of the ability of the polyester compositions to block a portion of the UV light incident upon the compositions may likewise be used. A suitable sample thickness, for purposes of approximating the thickness of a bottle side-wall, might be,
10 for example, about 0.012 inches thick, or from about 0.008 to about 0.020 inches thick.

While the polyester compositions of the invention in the broadest sense may provide any or all of the foregoing advantages within a wide range
15 of polymer types and amounts, and titanium nitride particle concentration, particle size, purity, and various other properties described herein, in some cases particular ranges of materials and types may be especially suited to particular uses, and these embodiments will be further described in the appropriate portions of the specification.

20 The term "titanium oxide" as used herein should be understood to include titanium metal having significant amounts of oxygen dissolved therein, for example, in amounts in which the ratio of oxygen to titanium is from about 0.4:1 to about 2:1. For example, any of the lower oxides of
25 titanium are included, including titanium monoxide, TiO ; titanium dioxide, TiO_2 ; titanium sesquioxide, Ti_2O_3 ; and trititanium pentoxide, Ti_3O_5 . Titanium monoxide and titanium dioxide are both well suited for use according to the invention, with titanium dioxide being particularly well-suited, based on cost and availability, the three common crystalline
30 forms available being anatase, brookite, and rutile. Titanium oxides useful according to the invention include those further described in Kirk-Othmer Encyclopedia of Chemical Technology, Vol 24, 4th ed., (1997)

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pp. 225 – 349, and especially pp. 233– 250, the relevant portions of which are incorporated herein by reference.

5 The titanium oxide particles useful in the processes according to the invention to produce titanium nitride particles may themselves be produced by a variety of methods, and may be in a variety of forms, either naturally derived or synthetic, for example as titanium dioxide solids or crystals in brookite, rutile, or anatase forms, or combinations thereof. Titanium dioxide particles may be used, and may be surface
10 treated in order to prevent sintering.

Titanium dioxide particles may be produced, for example, by making an aqueous solution of titanium, for example as an alkoxide or a chloride salt. TiO_2 may then be generated by heating the solution, causing
15 hydrolysis. The resulting TiO_2 precipitate may be further processed by drying and calcining, that is, heating to drive off volatiles, to form the titanium dioxide particles.

The titanium oxide particles useful according to the invention include a
20 wide range of particle sizes and particle size distributions. The size of the titanium oxide particles may thus vary within a broad range depending on the desired particle size for the titanium nitride particles to be produced, and will vary by the method of production, and the numerical values for the particle sizes may also vary somewhat
25 according to the shape of the particles and the method of measurement. Particle sizes useful according to the invention may vary within a large range, especially when the titanium nitride particles to be produced are provided for reheat improvement or UV-blocking effect, such as in a range from about 0.0005 μm to about 100 μm , or from 0.001 μm to 10
30 μm , or from 0.001 μm to 1 μm , or from 0.001 μm to 0.1 μm . When the polyester composition comprises PET, we expect that particle sizes from

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0.0005 μm to 1 μm , or from 0.001 μm to 0.1 μm , would be especially suitable.

5 In certain embodiments, such as those in which a bluing effect is desired, the titanium oxide used to produce the titanium nitride may range even smaller, such as from about 1 nm to about 1,000 nm, or from 1 nm to 500 nm, or from 1 nm to 300 nm, or from 1 nm to 200 nm, or from 1 nm to 100 nm. In these embodiments, the particles may thus be at least 1 nm in diameter, or at least 2 nm, or at least 5 nm, up to about 10 50 nm, or up to about 100 nm, or up to about 200 nm, or up to about 500 nm. The size may thus vary within a wide range, depending upon the intended effect, such that particles from about 1 nm to about 100 nm, or from 1 nm to 75 nm, or from 1 nm to 60 nm, would be especially suited to improve one or more of the reheat properties, the color properties, or 15 the UV-blocking properties, of the compositions.

In other embodiments, such as those in which UV-blocking effect is a significant or primary motivation for providing the titanium nitride particles, the size of the titanium oxide used to produce the titanium 20 nitride particles may vary, for example, from about 1 nm to about 100 nm, or from 1 nm to 50 nm, and will typically be present in a concentration from about 5 ppm to about 200 ppm, or from 5 ppm to 50 ppm.

25 In further embodiments, such as those in which a reheat additive effect is a significant or primary motivation for providing the titanium nitride particles, the size of the titanium oxide used to produce the titanium nitride particles may vary, for example, from about 1 nm to about 500 nm, or from 1 nm to 300 nm, and will typically be present in a 30 concentration from about 1 ppm to about 100 ppm, or from 5 ppm to 30 ppm.

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In yet other embodiments, such as those in which a bluing effect is a significant or primary motivation for providing the titanium nitride particles, the size of the titanium oxide used to produce the titanium nitride particles may vary, for example, from about 1 nm to about 100 nm, or from 5 nm to 60 nm, and will typically be present in a concentration from about 5 ppm to about 100 ppm, or from 5 ppm to 50 ppm.

The titanium oxide particles used to produce the titanium nitride particles, and having a mean particle size suitable for the invention, may have irregular shapes and form chain-like structures, although roughly spherical particles may be preferred. The particle size and particle size distribution may be measured by methods such as those described in the Size Measurement of Particles entry of Kirk-Othmer *Encyclopedia of Chemical Technology*, Vol. 22, 4th ed., (1997) pp. 256 – 278, incorporated herein by reference. For example, particle size and particle size distributions may be determined using a Fisher Subsieve Sizer or a Microtrac Particle-Size Analyzer manufactured by Leeds and Northrop Company, or by microscopic techniques, such as scanning electron microscopy or transmission electron microscopy.

A range of particle size distributions may be useful according to the invention. The particle size distribution, as used herein, may be expressed by "span (**S**)," where **S** is calculated by the following equation:

$$S = \frac{d_{90} - d_{10}}{d_{50}}$$

where d_{90} represents a particle size in which 90% of the volume is composed of particles having a diameter smaller than the stated d_{90} ; and d_{10} represents a particle size in which 10% of the volume is composed of

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particles having a diameter smaller than the stated d_{10} ; and d_{50} represents a particle size in which 50% of the volume is composed of particles having a diameter larger than the stated d_{50} value, and 50% of the volume is composed of particles having a diameter smaller than the stated d_{50} value.

Thus, particle size distributions of the titanium oxide particles, in which the span (S) is from 0 to 10, or from 0 to 5, or from 0.01 to 2, for example, may be used according to the invention. Alternatively, the particle size distribution (S) may range even broader, such as from 0 to 15, or from 0 to 25, or from 0 to 50.

Of course, since we expect there to be a correlation between the size of the titanium oxide particles used and the titanium nitride particles obtained, the particle size of the titanium oxide particles will be chosen so as to produce the desired titanium nitride particle size. In general, we expect that the size of the titanium nitride particles produced will typically be slightly larger than the size of the titanium oxide particles used to produce them.

According to the present invention, heating titanium oxide particles in the presence of a nitrogen-containing gas effects a chemical reaction, described herein as a nitridation, in which at least a portion of the titanium oxide particles are converted to titanium nitride particles.

A variety of nitrogen-containing gases may be used according to the invention, for example those that include one or more of: NO; N_2O ; NO_2 ; N_2 ; amines such as alkylamines, and especially trimethylamine and triethylamine; or NH_3 . Particularly effective are nitrogen-containing gases that include ammonia. Another example of a nitrogen-containing gas is a mixture of ammonia and hydrogen gases. Still another example

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of a nitrogen-containing gas is a mixture of trimethylamine and hydrogen gases.

Preferably, the gas is a mixture of ammonia and hydrogen gases,
5 although the presence of other gases is not excluded provided that these gases do not unduly affect the nitridation. For example, moisture and residual oxygen impurities may adversely affect titanium nitride powder quality by hindering conversion of the oxide to the nitride form. Generally, it may be helpful to keep oxygen impurity levels less than
10 about five (5) parts per million parts of gas, or even less than one (1) part per million parts of gas. If the moisture content is too high, it may be necessary or helpful to pass the nitrogen-containing gas through a drying bed or dessicant. The gas may also be purified by conventional means to reduce oxygen content. For example, a nitrogen-containing
15 gas comprising a mixture of ammonia, hydrogen, and nitrogen gases may be used. The gases may be introduced individually or in combination into the presence of the titanium oxide particles.

For example, titanium dioxide particles may be first exposed to hydrogen
20 gas, or a mixture of gases that includes hydrogen gas, to form a lower oxide or a mixture of lower oxides of titanium. The lower oxide or lower oxides of titanium may be characterized, for example, by the chemical formula Ti_nO_m wherein the ratio m/n is a value less than 2 (the ratio m/n of 2 being that of the dioxide). Some examples of lower oxides of
25 titanium include, but are not limited to, Ti_2O_3 and Ti_3O_5 . Subsequently, the lower oxides of titanium may be exposed to a gas comprising ammonia either with or without the presence of hydrogen gas wherein titanium oxide particles are converted to titanium nitride particles.

30 Heating of the titanium oxide particles may be accomplished with any means known in the art. An electrical resistance heated tube furnace is a well suited apparatus that may be used to heat the particles and the

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nitrogen-containing gas. Other apparatus suitable for effecting heating include, but are not limited to, kilns, direct fired heaters, furnaces, and ovens. Additionally, radio frequency or microwave radiation may be used to effect heating. The actual temperature of heating may be
5 determined by optical pyrometry or other suitable means.

Heating and maintaining titanium oxide particles at temperatures in the range, for example, from about 700°C to about 1,500°C, is generally effective to convert titanium oxide to titanium nitride in the presence of a
10 suitable nitrogen-containing gas. Alternatively, the heating temperature may be, for example, from 750°C to 1,000°C, or from 800°C to 1,000°C. It may be advantageous to heat at relatively low temperatures, thereby slowing the nitridation process, resulting in longer reaction times allowing a nearly complete conversion of titanium oxide particles to
15 titanium nitride particles. Conversely, at higher temperatures, the nitriding may proceed rapidly, but sintering may occur, leading to undesirable particle characteristics such as nonuniformity in particle size and a general increase in average particle size. When titanium oxide powder is exposed to the nitrogen-containing gas, the exposure time is
20 suitably within a range, for example, from about one (1) to about six (6) hours.

Normally, it is desirable to convert all or nearly all of the titanium oxide particles to titanium nitride particles. In this instance, the titanium oxide
25 particles should be exposed to at least the stoichiometric quantity of nitrogen-containing gas necessary to completely convert the titanium oxide particles to titanium nitride particles. For example, one technique that may be particularly effective is to expose the titanium oxide particles to a continuous stream of nitrogen-containing gas while maintaining the
30 particle temperature in the range from 700°C to 1,500°C.

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Alternatively, it may be desirable to instead produce a mixture of titanium oxide and titanium nitride particles. It may also be desirable to produce a mixture of ultrafine titanium oxide particles and ultrafine titanium nitride particles. In the instance where it is desirable to produce a mixture of
5 titanium oxide and titanium nitride particles, the titanium oxide particles may be exposed to quantities of nitrogen-containing gas inadequate (i.e. substoichiometric quantities of nitrogen) to produce complete conversion of the titanium oxide particles to titanium nitride particles. Another
10 example of producing a mixture of titanium oxide and titanium nitride particles may be to heat titanium oxide particles in the presence of stoichiometric or excess stoichiometric amounts of a nitrogen source at a temperature from about 700°C to 1,500°C, for a time from about one
(1) to about six (6) hours, controlling the desired degree of chemical conversion of oxide to nitride by selecting the appropriate time,
15 temperature, and amount of nitrogen in the nitrogen-containing gas.

According to the invention, the titanium nitride particles so produced, which may be a mixture of titanium nitride and titanium oxide particles, are used as an additive to enhance the reheat characteristics of
20 polyester compositions in which they are dispersed. For this purpose, the particles are suspended in a carrier to form a suspension, and the suspension thereafter effectively dispersed uniformly within a polyester polymer, for example during or after polyester polymerization, to produce the polyester composition.

25 Hence, after a portion or all of the titanium oxide particles are converted to titanium nitride particles, the resultant particles are suspended in a carrier, for example a liquid carrier, to produce a suspension of titanium nitride particles, or a suspension of titanium nitride and titanium oxide
30 particles, as the case may be.

- 20 -

As a carrier for the particles so produced, a variety of carriers, and especially liquid carriers, may be advantageously used, such as those that are compatible with polyester polymerization processes used to form the polyesters. Carriers which react to form a portion of the
5 polymer backbone through ester linkages, for example ethylene glycol, may be especially suited as carriers for use according to the invention. Suitable carriers thus include, for example, ethylene glycol, diethylene glycol, fatty acid esters, ethoxylated fatty acid esters, paraffin oils, polyvalent alcohols, polyvalent amines, silicone oil, hydrogenated castor
10 oil, hydrogenated ricinus oil, stearic esters of pentaerythritol, soybean oil, and ethoxylated alcohols such as polyethylene glycol, or combinations thereof.

When we describe the carriers useful according to the invention as
15 preferably being liquids, we mean that the carriers are in an amorphous (non-crystalline) form of matter intermediate between gases and solids that is negligibly sensitive to compression but that yields easily to pressure such that the liquid will conform itself to the shape of the containing vessel.

20

The heated titanium nitride particles or the mixture of titanium nitride and titanium oxide particles produced by the methods described above may be first cooled at a rapid rate sufficient to mitigate the tendency for solid particles to fuse together, thereby avoiding the formation of undesirable
25 agglomerates or large grains of powder product. The cooled particles may then be combined with a carrier, and especially a liquid carrier, to form a suspension of the particles in the carrier. Thus, for example, titanium particles at a temperature from about 700°C to about 1,500°C may be rapidly cooled in a pool of liquid carrier, for example ethylene
30 glycol at a temperature of 25°C, thereby forming a suspension of the titanium nitride particles.

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Thus, according to the invention, in various embodiments, there are also provided suspension compositions comprising titanium nitride particles in a liquid carrier in an amount of mass ratio of liquid carrier to titanium, for example, greater than 1 to 1.

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The suspension thereby obtained may be added to a bulk polyester or anywhere along the different stages for manufacturing a polyester, in a manner such that the suspension is compatible with the bulk polyester or its precursors. In general, it is desirable to provide a suspension
10 composition and a feed introduction system such that the titanium nitride particles or the mixture of titanium nitride and titanium oxide will be uniformly dispersed within the polymer. For example, the point of addition or the intrinsic viscosity (It.V.) (which is a measure of the polymer's molecular weight) of the suspension may be chosen such that
15 the It.V. of the polyethylene terephthalate and the It.V. of the concentrate are similar, e.g. +/- 0.2 dL/g It.V. measured at 25°C in a 60/40 wt/wt phenol/tetrachloroethane solution. In one aspect, the suspension of titanium nitride particles is first dispersed in a thermoplastic polymer to form a thermoplastic concentrate, for example having an It.V. ranging
20 from 0.3 dL/g to 1.1 dL/g, to match the typical It.V. of a polyester, for example a polyethylene terephthalate, under manufacture in the polycondensation stage. Alternatively, a concentrate can be made with an It.V. similar to that of solid-stated pellets used at the injection molding stage (e.g. It.V. from 0.6 dL/g to 1.1 dL/g):

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It should be understood that as used herein, the term polyester is intended to include polyester derivatives, including, but not limited to, polyether esters, polyester amides, and polyetherester amides.

Therefore, for simplicity, throughout the specification and claims, the
30 terms polyester, polyether ester, polyester amide, and polyetherester amide may be used interchangeably and are typically referred to as polyester, but it is understood that the particular polyester species is

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dependent on the starting materials, i.e., polyester precursor reactants and/or components.

5 The polyester compositions according to the invention are suitable for use in packaging, such as those in which a reheat step may be desirable, and are provided with titanium nitride particles in an amount sufficient to improve the reheat efficiency, or reduce the yellowness, or increase the resistance of the contents to the effects of ultraviolet light, or any combination of the foregoing benefits. These compositions may
10 be provided as a melt, in solid form, as preforms such as for blow molding, as sheets suitable for thermoforming, as concentrates, and as bottles, the compositions comprising a polyester polymer, with titanium nitride particles dispersed in the polyester. Suitable polyesters include polyalkylene terephthalates and polyalkylene naphthalates.

15 The invention relates also to processes for the manufacture of polyester compositions in which a suspension of titanium nitride particles may be added to any stage of a polyester polymerization process, such as during the melt phase for the manufacture of polyester polymers. The
20 suspension of titanium nitride particles may also be added, and especially in the form of a thermoplastic concentrate, to the polyester polymer which is in the form of solid-stated pellets, or to an injection molding machine for the manufacture of preforms from the polyester polymers.

25 The titanium nitride particles of the invention are the reaction product of titanium oxide particles with a nitrogen-containing gas. Titanium nitride is commonly considered to be a compound of titanium and nitrogen in which there is approximately a one-to-one correspondence between
30 titanium atoms and nitrogen atoms. However, it is known in the art of metallurgy that titanium nitride, having a cubic NaCl-type structure, is stable over a wide range of anion or cation deficiencies, for example in

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relative amounts from about $\text{TiN}_{0.42}$ to about $\text{TiN}_{1.0}$, or even, for example, to about $\text{TiN}_{1.16}$, (for example, if titanium nitride is prepared at low temperatures by reacting NH_3 with TiCl_4 , see pg. 87, Transition Metal Carbides and Nitrides, by Louis E. Toth, 1971, Academic Press.

5 (London), incorporated herein by reference) all of which compounds are intended to fall within the scope of the invention. Indeed, so long as the particles according to the invention comprise significant amounts of titanium nitride, for example in an amount sufficient to provide measurable reheat in the absence of any other material, the remainder
10 of the particles may well be elemental titanium, or titanium with small amounts of nitrogen dissolved, such that the average amount of nitrogen in the particles may be even lower than that stated in the formulas.

Titanium nitride particles useful according to the claimed invention may
15 comprise significant amounts of titanium carbide and/or titanium oxide, so long as the titanium nitride particles are the reaction product of titanium oxide particles with a nitrogen-containing gas, and are comprised of significant amounts of the titanium nitride, or so long as the total amount of titanium nitride and titanium carbide is at least 50 wt.%,
20 for example. Significant levels of titanium carbide may be obtained by including in the titanium oxide particles significant amounts of carbon. Thus, the titanium nitride may have relative amounts of titanium, carbon, and nitrogen within a wide range, such as a relative stoichiometry up to about $\text{TiC}_{0.5}\text{N}_{0.5}$, or to about $\text{TiC}_{0.8}\text{N}_{0.2}$, or to about $\text{TiC}_{0.7}\text{N}_{0.3}$ or even
25 greater, with the carbon replacing nitrogen, and with the relative amounts of titanium to nitrogen (or nitrogen and carbon) as already described. Of course, the amount of titanium carbide phase which is present in the particles is not at all critical, so long as the desired effect is achieved. We expect that titanium nitride having significant amounts
30 of titanium carbide present would be entirely suited for practice according to the invention, especially for use as a reheat additive, since we have found titanium nitride containing significant amounts of titanium

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carbide to be entirely suitable as a reheat additive. Significant amounts of titanium carbide may be introduced into the titanium nitride particles, for example, by providing either the titanium oxide, or the nitrogen-containing gas, or both, with significant amounts of carbon.

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Titanium nitride obtained according to the claimed invention may have properties such as the titanium nitride further described in Kirk-Othmer *Encyclopedia of Chemical Technology*, Vol 24, 4th ed., (1997) pp. 225 – 349, and especially pp. 231– 232, the relevant portions of which are
10 incorporated herein by reference.

Titanium nitride particles obtained according to the claimed invention may be distinguished from titanium compounds such as those used as condensation catalysts, for example titanium alkoxides or simple
15 chelates. That is, if titanium compounds are used as condensation catalysts to form the polymer in the compositions of the claimed invention, polyester polymers obtained according to the invention will additionally contain titanium nitride particles, as described herein. The titanium nitride particles obtained according to the invention may also be
20 distinguished from elemental titanium and titanium alloys, as further described in Kirk-Othmer *Encyclopedia of Chemical Technology*, Vol. 24, 4th ed., (1997) pp. 186 – 224, incorporated herein by reference, although the invention does not exclude the presence of elemental titanium or titanium alloys in the titanium nitride particles, so long as the
25 particles are obtained as the reaction product of titanium oxide particles with a nitrogen-containing gas, and are comprised of significant amounts of titanium nitride, as already described.

The titanium nitride particles obtained according to the invention are
30 useful for the improvement of one or more of reheat, color, or UV-blocking in polyester compositions and include those having a range of particle sizes and particle size distributions, although we have found

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certain particle sizes and relatively narrow particle size distributions to be especially suitable in certain applications. For example, in some embodiments, such as those in which the polyester comprises PET, titanium nitride particles having a median particle size of about 0.02 micrometers (μm), and a relatively narrow particle size distribution, are advantageous as both bluing agents and reheat additives.

The titanium nitride particles according to the claimed invention may include one or more other metals or impurities, so long as the particles are comprised of significant amounts of titanium nitride, for example in an amount of at least 50 wt.%. Metals or non-metals that may be present in minor amounts up to a total of 50 wt.% or more include aluminum, tin, zirconium, manganese, germanium, iron, chromium, tungsten, molybdenum, vanadium, palladium, ruthenium, niobium, tantalum, cobalt, nickel, copper, gold, silver, silicon, and hydrogen, as well as carbon and oxygen, as already described.

Not wishing to be bound by any theory, we believe that the effectiveness of titanium nitride particles as a reheat additive and a UV-blocking additive may be a function of the absorptive properties of the titanium nitride, so that titanium nitrides containing amounts of other materials are suitable for use according to the invention so long as the particles are comprised of significant amounts of titanium nitride. Thus, the titanium nitride particles may comprise at least 50 wt.% titanium nitride, or at least 75 wt.% titanium nitride, or at least 90 wt.% titanium nitride, or at least 95 wt.% titanium nitride.

Again, not wishing to be bound by any theory, we think it likely that the effect of the titanium nitride particles of the invention as a bluing agent is due to the ability of such particles, especially with sizes in the range from about 1 nm to about 60 nm, to efficiently remove the light with about 600nm wavelength (or yellow light) from the incident light. This removal

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of yellow light by the polyester compositions would cause the polyester article to appear to be blue. We note that larger, micron-scale particles provide much less of a bluing effect than do the submicron or nanometer-scale particles just described.

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The titanium nitride particles may thus include elemental titanium, or may include other materials, such as other metals, so long as such other materials do not substantially affect the ability of the titanium nitride particles to increase the reheat properties of the polymer compositions, for example, or to increase the bluing effect, or the UV-blocking effect, as the case may be.

The titanium nitride particles obtained according to the invention may include titanium oxide particles, or may be coated with a fine layer of titanium oxide, and are useful according to the invention so long as the oxide coating does not substantially affect the ability of the titanium nitride particles to effect one of the intended advantages already described, such as to increase the reheat efficiency of the polymer compositions.

20

In one aspect, the titanium nitride particles of the invention include composite TiO_2/TiN particles in which, because of mass transfer effects, the nitridation occurs preferentially on the outer surface of the titanium dioxide particles. In this aspect, since the reheat properties of reheat additives are believed to be primarily controlled by the effective surface area of infrared absorption, it may only be necessary to have the outer surface of nanosized particles covered with titanium nitride. Thus, in this aspect, the particles may have an inner core of titanium dioxide and an outer shell of titanium nitride. By controlling the degree of the reaction, a shell with a controlled thickness may be thereby obtained. We think it likely that these particles may be especially suited, compared with solid titanium nitride particles, for use according to the invention. These

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particles may be formed, for example, by exposing rutile TiO_2 powder to ammonia and hydrogen at a temperature of about $1,000^\circ\text{C}$, to thereby obtain particles in which titanium nitride is present in an amount, for example, of about 20 wt.%.

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Depending upon the form of the titanium oxide particles used as a reactant, the particles may thus contain or include titanium nitride hollow spheres or titanium nitride-coated spheres, in which the core may be comprised of titanium nitride, of mixtures of titanium nitride with other materials, or of other materials in the substantial absence of titanium nitride. Again, not wishing to be bound by any theory, we think it likely that the effectiveness of titanium nitride as a reheat additive is a function of the absorptive properties of the titanium nitride, so that titanium nitride-coated particles are suitable for use according to the invention, so long as the coating thickness of titanium nitride is sufficient to provide adequate reheat properties. Thus, in various embodiments, the thickness of a coating may be from about $0.005\ \mu\text{m}$ to about $10\ \mu\text{m}$, or from $0.01\ \mu\text{m}$ to $5\ \mu\text{m}$, or from $0.01\ \mu\text{m}$ to $0.5\ \mu\text{m}$. Alternatively, the coating thickness may range even smaller, such as from about $0.5\ \text{nm}$ to about $100\ \text{nm}$, or from $0.5\ \text{nm}$ to $50\ \text{nm}$, or from $0.5\ \text{nm}$ to about $10\ \text{nm}$. Such titanium nitride coatings may also comprise small amounts of other materials, as already described.

The amount of titanium nitride particles present in the polyester compositions obtained according to the invention may vary within a wide range, for example from about $0.5\ \text{ppm}$ to about $1,000\ \text{ppm}$, or from $1\ \text{ppm}$ to $500\ \text{ppm}$, or from $1\ \text{ppm}$ to $200\ \text{ppm}$, or from $1\ \text{ppm}$ to $100\ \text{ppm}$, or from $1\ \text{ppm}$ to $50\ \text{ppm}$. The amount used may, of course, depend upon the desired effect(s), and the amounts may therefore vary, as further described elsewhere herein, depending upon whether the particles are provided as a reheat additive, as a bluing agent, or as a UV-blocking agent, or for any combination of these benefits.

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For example, in some instances, loadings from about 1 ppm to about 10 ppm may be entirely adequate for improved reheat. Similarly, when a bluing effect is desired, amounts from about 5 ppm to about 50 ppm might be suitable. When significant UV-blocking protection is desired, such as in juice containers, the titanium nitride loading may be from about 1 ppm up to about 100 ppm, or even greater, when used as the primary or sole UV-blocking agent. Thermoplastic concentrates according to the invention may, of course, have amounts much greater than these, as further described elsewhere herein.

When used for UV-blocking effect, the titanium nitride particles of the invention may be used alone, or in combination with one or more known UV absorbers. When used in combination with known UV absorbers, the need for conventional UV absorbers might thereby be reduced. Also, because known UV absorbers tend to yellow the polymers in which they are used, the bluing effect of the titanium nitride particles would be an added benefit when used in combination with such UV absorbers, resulting in less need of additional bluing agents. And further, even in those cases in which the primary motivation is not to improve reheat, the resulting compositions might nonetheless exhibit improved reheat, making them suitable for uses that might otherwise require the presence of a separate reheat agent.

The shapes of the titanium nitride particles obtained follow from the shapes of the titanium oxide particles used as a reactant and include, but are not limited to, the following: acicular powder, angular powder, dendritic powder, equi-axed powder, flake powder, fragmented powder, granular powder, irregular powder, nodular powder, platelet powder, porous powder, rounded powder, and spherical powder. The particles may be of a filamentary structure, where the individual particles may be loose aggregates of smaller particles attached to form a bead or chain-

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like structure. The overall size of the particles will vary generally as function of the size of the titanium oxide particles used and may also vary in chain length and degree of branching, based on differences in reaction time and temperature, for example.

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The size of the titanium nitride particles are thus a function of the size of the titanium oxide particles used as a reactant, and may thus vary within a broad range depending on the method of production, and the numerical values for the particle sizes may vary according to the shape of the particles and the method of measurement. Particle sizes useful according to the invention may vary within a large range, especially when provided for reheat improvement or UV-blocking effect, such as from about 0.001 μm to about 100 μm , or from 0.01 μm to 45 μm , or from 0.01 μm to 10 μm , or from 0.01 μm to 5 μm . When the polyester composition comprises PET, we expect that particle sizes from 0.01 μm to 5 μm , or from 0.001 μm to 0.1 μm , would be especially suitable.

In certain embodiments, such as those in which a bluing effect is desired, the particles may range even smaller, such as from about 1 nm to about 1,000 nm, or from 1 nm to 500 nm, or from 1 nm to 300 nm, or from 1 nm to 200 nm, or from 1 nm to 50 nm. In these embodiments, the particles may thus be at least 1 nm in diameter, or at least 5 nm, up to about 200 nm, or up to about 300 nm, or up to about 500 nm. The size may thus vary within a wide range, such that particles, for example, from about 1 nm to about 100 nm, or from 1 nm to 75 nm, or from 5 nm to 60 nm, would be especially suited to improve one or more of the reheat properties, the color properties, or the UV-blocking properties, of the compositions.

30 In other embodiments, such as those in which UV-blocking effect is a significant or primary motivation for providing the titanium nitride particles, the size of the particles may vary, for example, from about 1

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nm to about 100 nm, or from 1 nm to 50 nm, and will typically be present, for example, in a concentration from about 5 ppm to about 200 ppm, or from 5 ppm to 50 ppm.

- 5 In further embodiments, such as those in which a reheat additive effect is a significant or primary motivation for providing the titanium nitride particles, the size of the particles may vary, for example, from about 1 nm to about 500 nm, or from 1 nm to 300 nm, and will typically be present, for example, in a concentration from about 1 ppm to about 100
10 ppm, or from 5 ppm to 30 ppm.

- In yet other embodiments, such as those in which a bluing effect is a significant or primary motivation for providing the titanium nitride particles, the size of the particles may vary, for example, from about 1
15 nm to about 100 nm, or from 5 nm to 50 nm, and will typically be present in a concentration, for example, from about 5 ppm to about 100 ppm, or from 5 ppm to 50 ppm.

- The titanium nitride particles, which have a mean particle size suitable
20 for the invention, may have irregular shapes and form chain-like structures, although roughly spherical particles may be preferred. The particle size and particle size distribution may be measured by methods such as those described in the Size Measurement of Particles entry of Kirk-Othmer *Encyclopedia of Chemical Technology*, Vol. 22, 4th ed.,
25 (1997) pp. 256 – 278, incorporated herein by reference. For example, particle size and particle size distributions may be determined using a Fisher Subsieve Sizer or a Microtrac Particle-Size Analyzer manufactured by Leeds and Northrop Company, or by microscopic techniques, such as scanning electron microscopy or transmission
30 electron microscopy.

A range of particle size distributions may be useful according to the

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invention. The particle size distribution, as used herein, may be expressed by "span (**S**)," where **S** is calculated by the following equation:

$$S = \frac{d_{90} - d_{10}}{d_{50}}$$

where d_{90} represents a particle size in which 90% of the volume is composed of particles having a diameter smaller than the stated d_{90} ; and d_{10} represents a particle size in which 10% of the volume is composed of particles having a diameter smaller than the stated d_{10} ; and d_{50} represents a particle size in which 50% of the volume is composed of particles having a diameter larger than the stated d_{50} value, and 50% of the volume is composed of particles having a diameter smaller than the stated d_{50} value.

Thus, particle size distributions in which the span (**S**) is from 0 to 10, or from 0 to 5, or from 0.01 to 2, for example, may be used according to the invention. Alternatively, the particle size distribution (**S**) may range even broader, such as from 0 to 15, or from 0 to 25, or from 0 to 50.

In order to obtain a good dispersion of titanium nitride particles in the polyester compositions, a concentrate, containing for example about 300 ppm to about 1000 ppm titanium nitride particles, or from 300 ppm to 1 wt%, or up to 10 wt%, or even higher, may be prepared from the suspension of particles using a polyester such as a commercial grade of PET. The concentrate may then be let down into a polyester at the desired concentration, ranging, for example, from 1 ppm to 500 ppm, or as already described.

Due to the properties of titanium nitride, the polyester compositions of this invention which contain titanium nitride particles as the reheat

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additive would not be expected to suffer from the problem of re-oxidation in the presence of an oxygen leak during solid-stating, as is the case with the antimony metal particles mentioned earlier. Thus, we expect that the reheat rate will tend to be less variable with titanium nitride
5 particles, and fewer adjustments will need to be made to the reheat lamp settings during the reheat blow molding process.

The amount of titanium nitride particles used in the polyester will depend upon the particular application, the desired reduction in reheat time, and
10 the toleration level in any reduction of a^* or b^* away from zero along with the movement of L^* brightness values away from 100. Thus, in various embodiments, the quantity of titanium nitride particles may be at least 0.5 ppm, or at least 1 ppm, or at least 5 ppm. In some applications, the quantity of titanium nitride particles may be at least 10 ppm, in some
15 cases at least 20 ppm, and even at least 25 ppm. The maximum amount of titanium nitride particles may be limited by one or more of the desired reheat rate, or maintenance in L^* , a^* , b^* and other appearance properties, which may vary among applications or customer requirements. In some embodiments, the amount may be up to 500
20 ppm or more, or up to about 300 ppm, or up to about 250 ppm. In those applications where color, haze, and brightness are not important features to the application, however, the amount of titanium nitride particles used may be up to 1,000 ppm, or up to 5,000 ppm, or even up to 10,000 ppm. The amount can even exceed 10,000 ppm, especially
25 when formulating a concentrate with titanium nitride particles, as discussed elsewhere herein.

The method by which the suspension of titanium nitride particles is incorporated into the polyester composition is illustrated by but not
30 limited to the following. The suspension of titanium nitride particles can be added to the polymer reactant system, during or after polymerization, to the polymer melt, or to the molding powder or pellets or molten

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polyester in the injection-molding machine from which the bottle preforms are made. In those cases in which the suspension is to be added to a polymer or prepolymer having a significant viscosity, the suspension may first be added to a thermoplastic polymer to obtain a thermoplastic concentrate, as described elsewhere herein, and the concentrate thereafter added to the polyester polymer or prepolymer. The suspension may be added at locations including, but not limited to, proximate the inlet to an esterification reactor, proximate the outlet of an esterification reactor, at a point between the inlet and the outlet of an esterification reactor, anywhere along a recirculation loop, proximate the inlet to a prepolymer reactor, proximate the outlet to a prepolymer reactor, at a point between the inlet and the outlet of a prepolymer reactor, proximate the inlet to a polycondensation reactor, or at a point between the inlet and the outlet of a polycondensation reactor, or at a point between the outlet of a polycondensation reactor and a die for forming pellets, sheets, fibers, bottle preforms, or the like.

The suspension of titanium nitride particles may be added to a polyester polymer such as PET, either as a neat suspension or as a thermoplastic concentrate, and fed to an injection molding machine by any method, including feeding the suspension to the molten polymer in the injection molding machine, or by combining the suspension with a feed of PET to the injection molding machine, either melt blending or dry blending pellets. The titanium nitride particles may be supplied as the suspension, or the suspension used to form a concentrate in a polymer such as PET or another thermoplastic polymer, as the dispersion in a liquid or solid carrier. Examples of suitable carriers include but are not limited to polyethylene glycol, mineral oil, hydrogenated castor oil, and glycerol monostearate, or as described elsewhere herein.

Alternatively, the suspension of titanium nitride particles may be added to an esterification reactor, such as with and through the ethylene glycol

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feed optionally combined with phosphoric acid, to a prepolymer reactor, to a polycondensation reactor, or to solid pellets in a reactor for solid stating, or at any point in-between any of these stages. In each of these cases, the suspension of titanium nitride particles may be combined with
5 PET or its precursors, as used to from a concentrate containing PET. As already described, the carrier may be reactive to PET or may be non-reactive.

The impact of a reheat additive on the color of the polymer can be
10 judged using a tristimulus color scale, such as the CIE $L^*a^*b^*$ scale. The L^* value ranges from 0 to 100 and measures dark to light. The a^* value measures red to green with positive values being red and negative values green. The b^* value measures yellow to blue with yellow having positive values and blue negative values.

15 Color measurement theory and practice are discussed in greater detail in *Principles of Color Technology*, pp.25-66 by Fred W. Billmeyer, Jr., John Wiley & Sons, New York (1981), incorporated herein by reference.

20 L^* values for the polyester compositions as measured on twenty-ounce bottle preforms discussed herein should generally be greater than 45, or at least 60, or at least 65, or at least 70. Specifying a particular L^* brightness does not imply that a preform having a particular sidewall cross-sectional thickness is actually used, but only that in the event the
25 L^* is measured, the polyester composition actually used is, for purposes of testing and evaluating the L^* of the composition, injection molded to make a preform having a thickness of 0.154 inches.

The color of a desirable polyester composition, as measured in twenty-
30 ounce bottle preforms having a nominal sidewall cross-sectional thickness of 0.154 inches, is generally indicated by an a^* coordinate value preferably ranging from about minus 4.4 to plus 1.6, or minus 2.0 to about plus 0.5 or from about minus 2.0 to about plus 0.1. With

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respect to a b^* coordinate value, it is generally desired to make a bottle preform having a b^* value coordinate ranging from minus 8.6 to plus 10.2, or from minus 3.0, or from minus 1.5, to a positive value of less than plus 5.0, or less than plus 4.0, or less than plus 3.8, or less than 2.6.

The measurements of L^* , a^* and b^* color values are conducted according to the following method. The instrument used for measuring b^* color should have the capabilities of a HunterLab UltraScan XE, model U3350, using the CIE Lab Scale (L^* , a^* , b^*), D65 (ASTM) illuminant, 10° observer and an integrating sphere geometry. Clear plaques, films, preforms, and bottles are tested in the transmission mode under ASTM D1746 "Standard Test Method for Transparency of Plastic Sheeting." The instrument for measuring color is set up under ASTM E1164 "Standard Practice for Obtaining Spectrophotometric Data for Object-Color Evaluation."

More particularly, the following test methods can be used, depending upon whether the sample is a preform or a bottle. Color measurements should be performed using a HunterLab UltraScan XE (Hunter Associates Laboratory, Inc., Reston VA), which employs diffuse/ 8° (illumination/view angle) sphere optical geometry, or equivalent equipment with these same basic capabilities. The color scale employed is the CIE $L^*a^*b^*$ scale with D65 illuminant and 10° observer specified.

Preforms having a mean outer diameter of 0.846 inches and a wall thickness of 0.154 inches are measured in regular transmission mode using ASTM D1746, "Standard Test Method for Transparency of Plastic Sheeting". Preforms are held in place in the instrument using a preform holder, available from HunterLab, and triplicate measurements are averaged, whereby the sample is rotated 90° about its center axis

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between each measurement.

The intrinsic viscosity (It.V.) values described throughout this description are set forth in dL/g unit as calculated from the inherent viscosity (Ih.V.) measured at 25°C in 60/40 wt/wt phenol/tetrachloroethane. The inherent viscosity is calculated from the measured solution viscosity. The following equations describe these solution viscosity measurements, and subsequent calculations to Ih.V. and from Ih.V. to It.V:

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

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%)

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

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

where η_{int} = Intrinsic viscosity
 η_r = Relative viscosity = t_s/t_o
 η_{sp} = Specific viscosity = $\eta_r - 1$

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

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Calibration Factor = Accepted IV of Reference Material /
Average of Replicate Determinations

Corrected IhV = Calculated IhV x Calibration Factor

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

10
$$\eta_{int} = 0.5 [e^{0.5 \times \text{Corrected IhV}} - 1] + (0.75 \times \text{Corrected IhV})$$

15 Thus, a beneficial feature provided by polyester compositions containing
titanium nitride particles is that the compositions and preforms made
from these compositions typically have an improved reheat rate,
expressed as a twenty-ounce bottle preform Reheat Improvement
Temperature (RIT), relative to a control sample with no reheat additive.

20 The following test for reheat improvement temperature (RIT) is used
herein, in order to describe the reheat improvement of the compositions
described herein. Twenty-ounce bottle preforms (with an outer diameter
of 0.846 inches and a sidewall cross-sectional thickness of 0.154 inches)
are run through the oven bank of a Sidel SBO2/3 blow molding unit. The
25 lamp settings for the Sidel blow molding unit are shown in Table 1. The
preform heating time in the heaters is 38 seconds, and the power output
to the quartz infrared heaters is set at 64%.

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TABLE 1. Sidel SBO2/3 lamp settings.

Heating zone	Lamps ON=1 OFF=0			
	Lamp power setting (%)	Heater 1	Heater 2	Heater 3
Zone 8	0	0	0	0
zone 7	0	0	0	0
Zone 6	0	0	0	0
Zone 5	90	1	0	1
Zone 4	90	1	0	1
Zone 3	90	1	0	1
Zone 2	90	1	0	1
Zone 1	90	1	1	1

- 5 In the test, a series of fifteen preforms is passed in front of the quartz infrared heaters and the average preform surface temperature of the middle five preforms is measured. All preforms are tested in a consistent manner. The preform reheat improvement temperature (RIT) is then calculated by comparing the difference in preform surface
- 10 temperature of the target samples containing a reheat additive with that of the same polymer having no reheat additive. The higher the RIT value, the higher the reheat rate of the composition.

Thus, in various embodiments, the twenty-ounce bottle preform reheat improvement temperature of the polyester compositions according to the

15 claimed invention containing titanium nitride particles, may be from about 0.1°C to about 11°C, from 1°C to 11°C, or from 1°C to values even higher than 11°C, such as 32°C, depending on the desired applications.

20

In some embodiments, the polyester compositions containing titanium nitride particles, and preforms made from these compositions, may have a b* color of less than 10.2, or less than 3.5, or less than 3, and in any case greater than minus 2, or greater than minus 9. Similarly,

25 preforms from the polyester compositions according to the invention may

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have an L^* brightness of at least 45, or at least 60, or at least 65, or at least 70.

Preforms containing titanium nitride according to the invention may show
5 a blue tinge (a lower b^* value than control samples).

The polyester compositions according to the invention may have improved solid-stating stability compared to polyester compositions containing conventional reheat additives. The solid-stating stability is
10 here defined as little or no change in the reheat rate after the polymer undergoes solid-state polymerization in the presence of an air leak during the process. Constant reheat rate is important for certain bottle making processes, such as blow-molding. If the reheat rate varies as a result of the oxidation of the reheat additive, as is the case with antimony
15 metal, then constant adjustments must be made to the oven power settings of the blow molding machine in order to maintain a consistent preform surface temperature from one preform to another.

According to the invention, in various embodiments, there are also
20 provided concentrate compositions comprising titanium nitride particles in an amount of at least 0.05 wt.%, or at least 2 wt.%, and up to about 20 wt.%, or up to 35 wt.%, and a thermoplastic polymer normally solid at 25°C and 1 atm such as a polyester, polyolefin, polyamide, or polycarbonate in an amount of at least 65 wt.%, or at least 80 wt.%, or
25 up to 99 wt.% or more, each based on the weight of the concentrate composition. The concentrate may be in liquid, molten state, or solid form. The converter of polymer to preforms has the flexibility of adding titanium nitride particles to bulk polyester at the injection molding stage continuously, or intermittently, in liquid molten form or as a solid blend,
30 and further adjusting the amount of titanium nitride particles contained in the preform by metering the amount of concentrate to fit the end use application and customer requirements.

- 40 -

The concentrate may be made by mixing the suspension of titanium nitride particles with a polymer such as a polycarbonate, a polyester, a polyolefin, or mixtures of these, in a single or twin-screw extruder, and optionally compounding with other reheat additives. A suitable polycarbonate is bisphenol A polycarbonate. Suitable polyolefins include, but are not limited to, polyethylene and polypropylene, and copolymers thereof. Melt temperatures should be at least as high as the melting point of the polymer. For a polyester, such as PET, the melt temperatures are typically in the range of 250°-310°C. Preferably, the melt compounding temperature is maintained as low as possible. The extrudate may be withdrawn in any form, such as a strand form, and recovered according to the usual way such as cutting.

The concentrate may be prepared in a similar polyester as used in the final article. However, in some cases it may be advantageous to use another polymer in the concentrate, such as a polyolefin. In the case where a polyolefin/ titanium nitride particles concentrate is blended with the polyester, the polyolefin can be incorporated as a nucleator additive for the bulk polyester.

The concentrate may be added to a bulk polyester or anywhere along the different stages for manufacturing PET, in a manner such that the concentrate is compatible with the bulk polyester or its precursors. For example, the point of addition or the lt.V. of the concentrate may be chosen such that the lt.V. of the polyethylene terephthalate and the lt.V. of the concentrate are similar, e.g. +/- 0.2 lt.V. measured at 25°C in a 60/40 wt/wt phenol/tetrachloroethane solution. A concentrate can be made with an lt.V. ranging from 0.3 dL/g to 1.1 dL/g to match the typical lt.V. of a polyethylene terephthalate under manufacture in the polycondensation stage. Alternatively, a concentrate can be made with

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an It.V. similar to that of solid-stated pellets used at the injection molding stage (e.g. It.V. from 0.6 dL/g to 1.1 dL/g).

Other components can be added to the polymer compositions of the present invention to enhance the performance properties of the polyester composition. For example, crystallization aids, impact modifiers, surface lubricants, denesting agents, stabilizers, antioxidants, ultraviolet light absorbing agents, catalyst deactivators, colorants, nucleating agents, acetaldehyde reducing compounds, other reheat enhancing aids, fillers, anti-abrasion additives, and the like can be included. The resin may also contain small amounts of branching agents such as trifunctional or tetrafunctional comonomers such as trimellitic anhydride, trimethylol propane, pyromellitic dianhydride, pentaerythritol, and other polyester forming polyacids or polyols generally known in the art. All of these additives and many others and their use are well known in the art. Any of these compounds can be used in the present composition.

The polyester compositions of the present invention may be used to form preforms used for preparing packaging containers. The preform is typically heated above the glass transition temperature of the polymer composition by passing the preform through a bank of quartz infrared heating lamps, positioning the preform in a bottle mold, and then blowing pressurized air through the open end of the mold.

A variety of other articles can be made from the polyester compositions of the invention, including those in which reheat is neither necessary nor desirable. Articles include sheet, film, bottles, trays, other packaging, rods, tubes, lids, fibers and injection molded articles. Any type of bottle can be made from the polyester compositions of the invention. Thus, in one embodiment, there is provided a beverage bottle made from PET suitable for holding water. In another embodiment, there is provided a

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heat-set beverage bottle suitable for holding beverages which are hot-filled into the bottle. In yet another embodiment, the bottle is suitable for holding carbonated soft drinks. Further, in yet another embodiment, the bottle is suitable for holding alcoholic beverages.

5

The titanium nitride particles used according to the invention may affect the reheat rate, UV light extinction (the UV light that is absorbed and/or scattered), brightness and color of the molded articles (whether preforms or finished bottles such as stretch blow-molded bottles, or extrusion blow
10 molded bottles), and provide improved resistance of the contents to the effects of UV light. Any one or more of these performance characteristics may be adjusted by varying the amount of the particles used, or by changing the particle size, particle shape, or the particle size distribution.

15

The invention also provides processes for making polyester preforms or injection-molded bottles that comprise feeding a liquid or solid bulk polyester and a liquid, molten or solid polyester concentrate composition to a machine for manufacturing the preform or bottle, the concentrate
20 being as described elsewhere. According to the invention, not only may the concentrate be added at the stage for making preforms or injection-molded bottles, but in other embodiments, there are provided processes for the manufacture of polyester compositions that comprise adding a concentrate polyester composition to a melt phase for the manufacture
25 of virgin polyester polymers, the concentrate comprising titanium nitride particles and at least 65 wt.% of a polyester polymer. Alternatively, the suspension of titanium nitride particles may be added to recycled PET to form the concentrate.

30

The polyester compositions according to the invention may have a good reheat rate with acceptable or even improved visual appearance properties, and improved UV-blocking properties. The resulting

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polymers may also have excellent solid stating stability, if such process is used in the polyester manufacturing process.

5 In yet another embodiment of the invention, there is thus provided a polyester beverage bottle made from a preform, wherein the preform has a RIT of 5°C or more, and an L* value of 60 or more.

10 In each of the described embodiments, there are also provided additional embodiments encompassing the processes for the manufacture of each, and the preforms and articles, and in particular bottles, blow-molded from the preforms, as well as their compositions containing titanium nitride particles.

15 The polyester compositions of this invention may be any thermoplastic polymers, optionally containing any number of ingredients in any amounts, provided that the polyester component of the polymer is present in an amount of at least 30 wt.%, or at least 50 wt.%, or at least 80 wt.%, or even 90 wt.% or more, based on the weight of the polymer, the backbone of the polymer typically including repeating terephthalate or naphthalate units.

25 Examples of suitable polyester polymers include one or more of: PET, polyethylene naphthalate (PEN), poly(1,4-cyclo-hexylenedimethylene) terephthalate (PCT), poly(ethylene-co-1,4-cyclohexylenedimethylene terephthalate) (PETG), copoly(1,4-cyclohexylene dimethylene/ethylene terephthalate) (PCTG), poly(1,4-cyclohexylene dimethylene terephthalate-co-isophthalate) (PCTA), poly(ethylene terephthalate-co-isophthalate) (PETA) and their blends or their copolymers. The form of the polyester composition is not limited, and includes a melt in the manufacturing process or in the molten state after polymerization, such as may be found in an injection molding machine, and in the form of a liquid, pellets, preforms, and/or bottles. Polyester pellets may be

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isolated as a solid at 25°C and 1 atm in order for ease of transport and processing. The shape of the polyester pellet is not limited, and is typified by regular or irregular shaped discrete particles and may be distinguished from a sheet, film, or fiber.

5

Examples of suitable polyesters include those described in U.S. Pat. No. 4,359,570, incorporated herein by reference in its entirety.

10

It should also be understood that as used herein, the term polyester is intended to include polyester derivatives, including, but not limited to, polyether esters, polyester amides, and polyetherester amides.

15

Therefore, for simplicity, throughout the specification and claims, the terms polyester, polyether ester, polyester amide, and polyetherester amide may be used interchangeably and are typically referred to as polyester, but it is understood that the particular polyester species is dependant on the starting materials, i.e., polyester precursor reactants and/or components.

20

The location of the titanium nitride particles within the polyester compositions is not limited. The titanium nitride particles may be disposed anywhere on or within the polyester polymer, pellet, preform, or bottle. Preferably, the polyester polymer in the form of a pellet forms a continuous phase. By being distributed "within" the continuous phase we mean that the titanium nitride particles are found at least within a

25

portion of a cross-sectional cut of the pellet. The titanium nitride particles may be distributed within the polyester polymer randomly, distributed within discrete regions, or distributed only within a portion of the polymer. In a specific embodiment, the titanium nitride particles are disposed randomly throughout the polyester polymer composition as by way of adding the suspension of titanium nitride particles to a melt, or by mixing the suspension of titanium nitride particles with a solid polyester composition followed by melting and mixing.

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5 The titanium nitride particles may be added in an amount so as to achieve a twenty-ounce bottle preform RIT of at least 3°C, or at least 5°C, or at least 10°C, while maintaining acceptable preform color/appearance properties.

10 Suitable amounts of titanium nitride particles in the polyester compositions (other than polyester concentrate compositions as discussed elsewhere), preforms, and containers, may thus range from about 0.5 ppm to about 500 ppm, based on the weight of the polymer in the polyester compositions, or as already described herein. The amount of the titanium nitride particles used may depend on the type, quality, and quantity of the carrier and the titanium nitride particles used, the particle size, surface area, morphology of the particle, and the level of
15 desired reheat rate improvement, or color improvement, or UV-blocking effect, as the case may be.

20 The particle size may be measured with a laser diffraction type particle size distribution meter, or scanning or transmission electron microscopy methods, or size exclusion chromatography. Alternatively, the particle size can be correlated by a percentage of particles screened through a mesh.

25 In various other embodiments, there are provided polyester compositions, whether in the form of a melt, pellets, sheets, preforms, and/or bottles, comprising at least 0.5 ppm, or at least 50 ppm, or at least 100 ppm titanium nitride particles, having a d_{50} particle size of less than 100 μm , or less than 50 μm , or less than 1 μm or less, wherein the polyester compositions have a preform L^* value of 70 or more, or 79 or
30 more, or even 80 or more, and an RIT up to 10°C, or at least 5°C, or at least 3°C.

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According to various embodiments of the invention, the suspension of titanium nitride particles may be added at any point during polymerization, which includes to the esterification zone, to the polycondensation zone comprised of the prepolymer zone and the finishing zone, to or prior to the pelletizing zone, and at any point
5 between or among these zones. The suspension of titanium nitride particles may also be added to solid-stated pellets as they are exiting the solid-stating reactor. Furthermore, the suspension of titanium nitride particles may be added to the PET pellets in combination with other
10 feeds to the injection molding machine, or may be fed separately to the injection molding machine. For clarification, the suspension of titanium nitride particles may be added in the melt phase or to an injection molding machine without solidifying and isolating the polyester composition into pellets. Thus, the suspension of particles can also be
15 added in a melt-to-mold process at any point in the process for making the preforms. In each instance at a point of addition, the titanium nitride particles may be added as a suspension, or the suspension first used to form a polymer concentrate, and can be added to virgin or recycled PET, or added as a polymer concentrate using virgin or recycled PET as the
20 PET polymer carrier.

In other embodiments, the invention relates to processes for the manufacture of polyester compositions containing the suspension of titanium nitride particles, such as polyalkylene terephthalate or
25 naphthalate polymers made by transesterifying a dialkyl terephthalate or dialkyl naphthalate or by directly esterifying terephthalic acid or naphthalene dicarboxylic acid.

Thus, there are provided processes for making polyalkylene
30 terephthalate or naphthalate polymer compositions by transesterifying a dialkyl terephthalate or naphthalate or directly esterifying a terephthalic acid or naphthalene dicarboxylic acid with a diol, adding the suspension

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of titanium nitride particles to the melt phase for the production of a polyalkylene terephthalate or naphthalate after the prepolymer zone, or to polyalkylene terephthalate or naphthalate solids, or to an injection molding machine for the manufacture of bottle preforms.

5

Each of these process embodiments, along with a description of the polyester polymers, is now explained in further detail.

10 The polyester polymer may be PET, PEN, or copolymers or mixtures, thereof. A preferred polyester polymer is polyethylene terephthalate. As used herein, a polyalkylene terephthalate polymer or polyalkylene naphthalate polymer means a polymer having polyalkylene terephthalate units or polyalkylene naphthalate units in an amount of at least 60 mole% based on the total moles of units in the polymer, respectively.

15 Thus, the polymer may contain ethylene terephthalate or naphthalate units in an amount of at least 85 mole%, or at least 90 mole%, or at least 92 mole%, or at least 96 mole%, as measured by the mole% of ingredients in the finished polymer. Thus, a polyethylene terephthalate polymer may comprise a copolyester of ethylene terephthalate units and

20 other units derived from an alkylene glycol or aryl glycol with an aliphatic or aryl dicarboxylic acid.

While reference is made in certain instances to polyethylene terephthalate, it is to be understood that the polymer may also be a

25 polyalkylene naphthalate polymer.

Polyethylene terephthalate can be manufactured by reacting a diacid or diester component comprising at least 60 mole % terephthalic acid or C₁ - C₄ dialkylterephthalate, or at least 70 mole %, or at least 85 mole %, or

30 at least 90 mole %, and for many applications at least 95 mole%, and a diol component comprising at least 60 mole % ethylene glycol, or at least 70 mole %, or at least 85 mole %, or at least 90 mole %, and for

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many applications, at least 95 mole %. It is preferable that the diacid component is terephthalic acid and the diol component is ethylene glycol. The mole percentage for all the diacid component(s) totals 100 mole %, and the mole percentage for all the diol component(s) totals 100 mole %.

The polyester pellet compositions may include admixtures of polyalkylene terephthalates, PEN, or mixtures thereof, along with other thermoplastic polymers, such as polycarbonates and polyamides. It is preferred in many instances that the polyester composition comprise a majority of a polyalkylene terephthalate polymers or PEN polymers, or in an amount of at least 80 wt.%, or at least 95 wt.%, based on the weight of polymers (excluding fillers, compounds, inorganic compounds or particles, fibers, impact modifiers, or other polymers which may form a discontinuous phase). In addition to units derived from terephthalic acid, the acid component of the present polyester may be modified with, or replaced by, units derived from one or more other dicarboxylic acids, such as aromatic dicarboxylic acids preferably having from 8 to 14 carbon atoms, aliphatic dicarboxylic acids preferably having 4 to 12 carbon atoms, or cycloaliphatic dicarboxylic acids preferably having 8 to 12 carbon atoms.

Examples of dicarboxylic acid units useful for the acid component are units from phthalic acid, isophthalic acid, naphthalene-2,6-dicarboxylic acid, cyclohexanedicarboxylic acid, cyclohexanediacetic acid, diphenyl-4,4'-dicarboxylic acid, succinic acid, glutaric acid, adipic acid, azelaic acid, sebacic acid, and the like, with isophthalic acid, naphthalene-2,6-dicarboxylic acid, and cyclohexanedicarboxylic acid being preferable.

It should be understood that use of the corresponding acid anhydrides, esters, and acid chlorides of these acids is included in the term "dicarboxylic acid".

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In addition to units derived from ethylene glycol, the diol component of the present polyester may be modified with, or replaced by, units from additional diols including cycloaliphatic diols preferably having 6 to 20
5 carbon atoms and aliphatic diols preferably having 2 to 20 carbon atoms. Examples of such diols include diethylene glycol (DEG); triethylene glycol; 1,4-cyclohexanedimethanol; propane-1,3-diol; butane-1,4-diol; pentane-1,5-diol; hexane-1,6-diol; 3-methylpentanediol- (2,4); 2-methylpentanediol-(1,4); 2,2,4-trimethylpentane-diol-(1,3); 2,5-
10 ethylhexanediol-(1,3); 2,2-diethyl propane-diol-(1, 3); hexanediol-(1,3); 1,4-di-(hydroxyethoxy)-benzene; 2,2-bis-(4-hydroxycyclohexyl)-propane; 2,4- dihydroxy-1,1,3,3-tetramethyl-cyclobutane; 2,2-bis-(3-hydroxyethoxyphenyl)-propane; and 2,2-bis-(4-hydroxypropoxyphenyl)-propane.

15 The polyester compositions of the invention may be prepared by conventional polymerization procedures well-known in the art sufficient to effect esterification and polycondensation. Polyester melt phase manufacturing processes include direct condensation of a dicarboxylic
20 acid with a diol optionally in the presence of esterification catalysts in the esterification zone, followed by polycondensation in the prepolymer and finishing zones in the presence of a polycondensation catalyst; or else ester interchange usually in the presence of a transesterification catalyst in the esterification zone, followed by prepolymerization and finishing in
25 the presence of a polycondensation catalyst, and each may optionally be subsequently solid-stated according to known methods. After melt phase and/or solid-state polycondensation the polyester polymer compositions typically have an intrinsic viscosity (It.V.) ranging from 0.55 dL/g to about 0.70 dL/g as precursor pellets, and an It.V. ranging from
30 about 0.70 dL/g to about 1.15 dL/g for solid stated pellets.

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Alternatively, the polyester composition may be prepared entirely in the melt phase, by continuing melt-phase polycondensation such that the polyester polymer compositions made in this manner have an lt.v. of at least 1.0 dL/g, or at least 1.1 dL/g, or at least 1.2 dL/g.

5

To further illustrate, a mixture of one or more dicarboxylic acids, preferably aromatic dicarboxylic acids, or ester forming derivatives thereof, and one or more diols, are continuously fed to an esterification reactor operated at a temperature of between about 200°C and 300°C, typically between 240°C and 290°C, and at a pressure of about 1 psig up to about 70 psig. The residence time of the reactants typically ranges from between about one and five hours. Normally, the dicarboxylic acid is directly esterified with diol(s) at elevated pressure and at a temperature of about 240°C to about 270°C. The esterification reaction is continued until a degree of esterification of at least 60% is achieved, but more typically until a degree of esterification of at least 85% is achieved to make the desired monomer. The esterification monomer reaction is typically uncatalyzed in the direct esterification process and catalyzed in transesterification processes. Polycondensation catalysts may optionally be added in the esterification zone along with esterification/transesterification catalysts.

Typical esterification/transesterification catalysts which may be used include titanium alkoxides, dibutyl tin dilaurate, used separately or in combination, optionally with zinc, manganese, or magnesium acetates or benzoates and/or other such catalyst materials as are well known to those skilled in the art. Phosphorus-containing compounds and cobalt compounds may also be present in the esterification zone. The resulting products formed in the esterification zone include bis(2-hydroxyethyl) terephthalate (BHET) monomer, low molecular weight oligomers, DEG, and water as the condensation by-product, along with other trace impurities formed by the reaction of the catalyst and other compounds

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such as colorants or the phosphorus-containing compounds. The relative amounts of BHET and oligomeric species will vary depending on whether the process is a direct esterification process, in which case the amount of oligomeric species are significant and even present as the
5 major species, or a transesterification process, in which case the relative quantity of BHET predominates over the oligomeric species. The water is removed as the esterification reaction proceeds and excess ethylene glycol is removed to provide favorable equilibrium conditions. The esterification zone typically produces the monomer and oligomer
10 mixture, if any, continuously in a series of one or more reactors. Alternatively, the monomer and oligomer mixture could be produced in one or more batch reactors.

It is understood, however, that in a process for making PEN, the reaction
15 mixture will contain monomeric species such as bis(2-hydroxyethyl) naphthalate and its corresponding oligomers. Once the ester monomer is made to the desired degree of esterification, it is transported from the esterification reactors in the esterification zone to the polycondensation zone comprised of a prepolymer zone and a finishing zone.

20 Polycondensation reactions are initiated and continued in the melt phase in a prepolymerization zone and finished in the melt phase in a finishing zone, after which the melt may be solidified into precursor solids in the form of chips, pellets, or any other shape. For convenience, solids are
25 referred to as pellets, but it is understood that a pellet can have any shape, structure, or consistency. If desired, the polycondensation reaction may be continued by solid-stating the precursor pellets in a solid-stating zone.

30 Although reference is made to a prepolymer zone and a finishing zone, it is to be understood that each zone may comprise a series of one or more distinct reaction vessels operating at different conditions, or the

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zones may be combined into one reaction vessel using one or more sub-stages operating at different conditions in a single reactor. That is, the prepolymer stage can involve the use of one or more reactors operated continuously, one or more batch reactors or even one or more reaction

5 steps or sub-stages performed in a single reactor vessel. In some reactor designs, the prepolymerization zone represents the first half of polycondensation in terms of reaction time, while the finishing zone represents the second half of polycondensation. While other reactor

10 designs may adjust the residence time between the prepolymerization zone to the finishing zone at about a 2:1 ratio, a common distinction in all designs between the prepolymerization zone and the finishing zone is that the latter zone operates at a higher temperature, lower pressure, and a higher surface renewal rate than the operating conditions in the prepolymerization zone. Generally, each of the prepolymerization and

15 the finishing zones comprise one or a series of more than one reaction vessel, and the prepolymerization and finishing reactors are sequenced in a series as part of a continuous process for the manufacture of the polyester polymer.

20 In the prepolymerization zone, also known in the industry as the low polymerizer, the low molecular weight monomers and minor amounts of oligomers are polymerized via polycondensation to form polyethylene terephthalate polyester (or PEN polyester) in the presence of a catalyst. If the catalyst was not added in the monomer esterification stage, the

25 catalyst is added at this stage to catalyze the reaction between the monomers and low molecular weight oligomers to form prepolymer and split off the diol as a by-product. If a polycondensation catalyst was added to the esterification zone, it is typically blended with the diol and fed into the esterification reactor as the diol feed. Other compounds

30 such as phosphorus-containing compounds, cobalt compounds, and colorants can also be added in the prepolymerization zone. These

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compounds may, however, be added in the finishing zone instead of or in addition to the prepolymerization zone.

5 In a typical DMT-based process, those skilled in the art recognize that other catalyst material and points of adding the catalyst material and other ingredients vary from a typical direct esterification process.

10 Typical polycondensation catalysts include the compounds of antimony, titanium, germanium, zinc and tin in an amount ranging from 0.1 ppm to 1,000 ppm based on the weight of resulting polyester polymer. A common polymerization catalyst added to the prepolymerization zone is an antimony-based polymerization catalyst. Suitable antimony-based catalysts include antimony (III) and antimony (V) compounds recognized in the art, and in particular, diol-soluble antimony (III) and antimony (V)
15 compounds with antimony (III) being most commonly used. Other suitable compounds include those antimony compounds that react with, but are not necessarily soluble in, the diols, with examples of such compounds including antimony (III) oxide. Specific examples of suitable antimony catalysts include antimony (III) oxide and antimony (III)
20 acetate, antimony (III) glycolates, antimony (III) ethyleneglycoxide and mixtures thereof, with antimony (III) oxide being preferred. The preferred amount of antimony catalyst added is that effective to provide a level of between about 75 ppm and about 400 ppm of antimony by weight of the resulting polyester.

25

This prepolymer polycondensation stage generally employs a series of two or more vessels and is operated at a temperature of between about 250°C and 305° C for between about one and four hours. During this stage, the It.V. of the monomers and oligomers is typically increased up
30 to about no more than 0.35 dL/g. The diol byproduct is removed from the prepolymer melt using an applied vacuum ranging from 15 torr to 70 torr to drive the reaction to completion. In this regard, the polymer melt

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is typically agitated to promote the escape of the diol from the polymer melt and to assist the highly viscous polymer melt in moving through the polymerization vessels. As the polymer melt is fed into successive vessels, the molecular weight and thus the intrinsic viscosity of the polymer melt increases. The temperature of each vessel is generally increased and the pressure decreased to allow for a greater degree of polymerization in each successive vessel. However, to facilitate removal of glycols, water, alcohols, aldehydes, and other reaction products, the reactors are typically run under a vacuum or purged with an inert gas. Inert gas is any gas which does not cause unwanted reaction or product characteristics at reaction conditions. Suitable gases include, but are not limited to, carbon dioxide, argon, helium, and nitrogen.

Once an It.V. of typically no greater than 0.35 dL/g, or no greater than 0.40 dL/g, or no greater than 0.45 dL/g, is obtained, the prepolymer is fed from the prepolymer zone to a finishing zone where the second half of polycondensation is continued in one or more finishing vessels ramped up to higher temperatures than present in the prepolymerization zone, to a value within a range of from 280°C to 305°C until the It.V. of the melt is increased from the It.V. of the melt in the prepolymerization zone (typically 0.30 dL/g but usually not more than 0.35 dL/g) to an It.V. in the range of from about 0.50 dL/g to about 0.70 dL/g. The final vessel, generally known in the industry as the "high polymerizer," "finisher," or "polycondenser," is operated at a pressure lower than used in the prepolymerization zone, typically within a range of between about 0.8 torr and 4.0 torr, or from about 0.5 torr to about 4.0 torr. Although the finishing zone typically involves the same basic chemistry as the prepolymer zone, the fact that the size of the molecules, and thus the viscosity, differs, means that the reaction conditions also differ. However, like the prepolymer reactor, each of the finishing vessel(s) is connected to a flash vessel and each is typically agitated to facilitate the removal of ethylene glycol.

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Alternatively, if a melt-phase-only polycondensation process is employed in the absence of a solid-stating step, the finisher is operated under similar temperatures and pressures, except that the It.V. of the melt is
5 increased in the finisher to an It.V. in the range of from about 0.70 dL/g up to about 1.0 dL/g, or up to 1.1 dL/g, or up to 1.2 dL/g.

The residence time in the polycondensation vessels and the feed rate of the ethylene glycol and terephthalic acid into the esterification zone in a
10 continuous process is determined in part based on the target molecular weight of the polyethylene terephthalate polyester. Because the molecular weight can be readily determined based on the intrinsic viscosity of the polymer melt, the intrinsic viscosity of the polymer melt is generally used to determine polymerization conditions, such as
15 temperature, pressure, the feed rate of the reactants, and the residence time within the polycondensation vessels.

Once the desired It.V. is obtained in the finisher, the melt is fed to a pelletization zone where it is filtered and extruded into the desired form.
20 The polyester polymers of the present invention are filtered to remove particulates over a designated size, followed by extrusion in the melt phase to form polymer sheets, filaments, or pellets. Although this zone is termed a "pelletization zone", it is understood that this zone is not limited to solidifying the melt into the shape of pellets, but includes
25 solidification into any desired shape. Preferably, the polymer melt is extruded immediately after polycondensation. After extrusion, the polymers are quenched, preferably by spraying with water or immersing in a water trough, to promote solidification. The solidified condensation polymers are cut into any desired shape, including pellets.

30 Alternatively, once the polyester polymer is manufactured in the melt phase polymerization, it may be solidified. The method for solidifying the

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polyester polymer from the melt phase process is not limited. For example, molten polyester polymer from the melt phase may be directed through a die, or merely cut, or both directed through a die followed by cutting the molten polymer. A gear pump may be used as the motive
5 force to drive the molten polyester polymer through the die. Instead of using a gear pump, the molten polyester polymer may be fed into a single or twin screw extruder and extruded through a die, optionally at a temperature of 190°C or more at the extruder nozzle. Once through the die, the polyester polymer may be drawn into strands, contacted with a
10 cool fluid, and cut into pellets, or the polymer may be pelletized at the die head, optionally underwater. The polyester polymer melt optionally filtered to remove particulates over a designated size before being cut. Any conventional hot pelletization or dicing method and apparatus can be used, including but not limited to dicing, strand pelletizing and strand
15 (forced conveyance) pelletizing, pastillators, water ring pelletizers, hot face pelletizers, underwater pelletizers, and centrifuged pelletizers.

The polyester polymer of the invention may be partially crystallized to produce semi-crystalline particles. The method and apparatus used to
20 crystallize the polyester polymer is not limited, and includes thermal crystallization in a gas or liquid. The crystallization may occur in a mechanically agitated vessel; a fluidized bed; a bed agitated by fluid movement; an un-agitated vessel or pipe; crystallized in a liquid medium above the glass transition temperature (T_g) of the polyester polymer,
25 preferably at 140°C to 190°C; or any other means known in the art. Also, the polymer may be strain crystallized. The polymer may also be fed to a crystallizer at a polymer temperature below its T_g (from the glass), or it may be fed to a crystallizer at a polymer temperature above its T_g . For example, molten polymer from the melt phase polymerization
30 reactor may be fed through a die plate and cut underwater, and then immediately fed to an underwater thermal crystallization reactor where the polymer is crystallized underwater. Alternatively, the molten polymer

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may be cut, allowed to cool to below its T_g , and then fed to an underwater thermal crystallization apparatus or any other suitable crystallization apparatus. Or, the molten polymer may be cut in any conventional manner, allowed to cool to below its T_g , optionally stored,
5 and then crystallized. Optionally, the crystallized polyester may be solid stated according to known methods.

As known to those of ordinary skill in the art, the pellets formed from the condensation polymers, in some circumstances, may be subjected to a
10 solid-stating zone wherein the solids are first crystallized followed by solid-state polymerization (SSP) to further increase the It.V. of the polyester composition solids from the It.V exiting the melt phase to the desired It.V. useful for the intended end use. Typically, the It.V. of solid
15 stated polyester solids ranges from 0.70 dL/g to 1.15 dL/g. In a typical SSP process, the crystallized pellets are subjected to a countercurrent flow of nitrogen gas heated to 180°C to 220°C, over a period of time as needed to increase the It.V. to the desired target.

Thereafter, polyester polymer solids, whether solid stated or not, are re-
20 melted and re-extruded to form items such as containers (e.g., beverage bottles), filaments, films, or other applications. At this stage, the pellets are typically fed into an injection molding machine suitable for making preforms which are stretch blow molded into bottles.

25 As noted, the suspension of titanium nitride particles may be added at any point in the melt phase or thereafter, such as to the esterification zone, to the prepolymerization zone, to the finishing zone, or to the pelletizing zone, or at any point between each of these zones, such as to metering devices, pipes, and mixers. The suspension can also be
30 added to the pellets in a solid stating zone within the solid stating zone or as the pellets exit the solid-stating reactor. Furthermore, the suspension may be added to the pellets in combination with other feeds

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to the injection molding machine or fed separately to the injection molding machine.

5 If the suspension of titanium nitride particles is added to the melt phase, it is desirable to use particles having a small enough particle size to pass through the filters in the melt phase, and in particular the pelletization zone. In this way, the particles will not clog up the filters as seen by an increase in gear pump pressure needed to drive the melt through the filters. However, if desired, the suspension of titanium nitride particles
10 can be added after the pelletization zone filter and before or to the extruder of the injection molding machine.

In addition to adding the suspension of titanium nitride particles to virgin polymer, whether to make a concentrate, or as a dispersion to the melt
15 phase after the prepolymerization reactors or to an injection molding zone, the suspension may also be added to post-consumer recycle (PCR) polymer. PCR containing the suspension of titanium nitride particles may be added to virgin bulk polymers by solid/solid blending or by feeding both solids to an extruder. Alternatively, PCR polymers
20 containing the particles are advantageously added to the melt phase for making virgin polymer between the prepolymerization zone and the finishing zone. The It.V. of the virgin melt phase after the prepolymerization zone is sufficiently high at that point to enable the PCR to be melt blended with the virgin melt. Alternatively, PCR may be
25 added to the finisher. In either case, the PCR added to the virgin melt phase may contain the titanium nitride particles.

Other components can be added to the compositions of the present invention to enhance the performance properties of the polyester
30 polymers. For example, crystallization aids, impact modifiers, surface lubricants, denesting agents, compounds, antioxidants, ultraviolet light absorbing agents, catalyst deactivators, colorants, nucleating agents,

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acetaldehyde reducing compounds, other reheat rate enhancing aids, sticky bottle additives such as talc, and fillers and the like can be included. The polymer may also contain small amounts of branching agents such as trifunctional or tetrafunctional comonomers such as
5 trimellitic anhydride, trimethylol propane, pyromellitic dianhydride, pentaerythritol, and other polyester forming polyacids or diols generally known in the art. All of these additives and many others and their use are well known in the art and do not require extensive discussion. Any of these compounds can be used in the present composition.

10

Examples of other reheat rate enhancing additives that may be used in combination with titanium nitride particles include carbon black, antimony, tin, copper, silver, gold, palladium, platinum, black iron oxide, and the like, as well as near infrared absorbing dyes, including, but not
15 limited to, those disclosed in U.S. Pat. No. 6,197,851, incorporated herein by reference.

The compositions of the present invention optionally may contain one or more additional UV-absorbing compounds. One example includes UV-
20 absorbing compounds which are covalently bound to the polyester molecule as either a comonomer, a side group, or an end group. Suitable UV-absorbing compounds are thermally stable at polyester processing temperatures, absorb in the range of from about 320 nm to about 380 nm, and migrate minimally from the polymer. The UV-
25 absorbing compounds preferably provide less than about 20%, more preferably less than about 10%, transmittance of UV light having a wavelength of 370 nm through a bottle wall or sample that is 0.012 inches thick. Suitable chemically reactive UV absorbing compounds may include, for example, substituted methine compounds.

30

Suitable compounds, their methods of manufacture and incorporation into polyesters include those disclosed in U.S. Pat. No. 4,617,374, the

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disclosure of which is incorporated herein by reference. Other suitable UV-absorbing materials include benzophenone, benzotriazole, triazine, benzoxazinone derivatives. These UV-absorbing compound(s) may be present in amounts between about 1 ppm to about 5,000 ppm by weight, preferably from about 2 ppm to about 1,500 ppm, and more preferably between about 10 ppm and about 1000 ppm by weight. Dimers of the UV absorbing compounds may also be used. Mixtures of two or more UV absorbing compounds may be used. Moreover, because the UV absorbing compounds are reacted with or copolymerized into the backbone of the polymer, the resulting polymers display improved processability including reduced loss of the UV absorbing compound due to plateout and/or volatilization and the like.

The polyester compositions of the present invention are suitable for forming a variety of shaped articles, including films, sheets, tubes, preforms, molded articles, containers and the like. Suitable processes for forming the articles are known and include extrusion, extrusion blow molding, melt casting, injection molding, stretch blow molding, thermoforming, and the like.

The polyesters of this invention may also, optionally, contain color stabilizers, such as certain cobalt compounds. These cobalt compounds can be added as cobalt acetates or cobalt alcoholates (cobalt salts or higher alcohols). They can be added as solutions in ethylene glycol. Polyester resins containing high amounts of the cobalt additives can be prepared as a masterbatch for extruder addition. The addition of the cobalt additives as color toners is a process used to further minimize or eliminate the yellow color, measured as b^* , of the resin. Other cobalt compounds such as cobalt aluminate, cobalt benzoate, cobalt chloride and the like may also be used as color stabilizers. It is also possible to add certain diethylene glycol (DEG) inhibitors to reduce or prevent the formation of DEG in the final resin product. Preferably, a specific type of

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DEG inhibitor would comprise a sodium acetate-containing composition to reduce formation of DEG during the esterification and polycondensation of the applicable diol with the dicarboxylic acid or hydroxyalkyl, or hydroxyalkoxy substituted carboxylic acid. It is also
5 possible to add stress crack inhibitors to improve stress crack resistance of bottles, or sheeting, produced from this resin.

With regard to the type of polyester which can be utilized, any high clarity, neutral hue polyester, copolyester, etc., in the form of a resin,
10 powder, sheet, etc., can be utilized to which it is desired to improve the reheat time or the heat-up time of the resin. Thus, polyesters made from either the dimethyl terephthalate or the terephthalic acid route or various homologues thereof as well known to those skilled in the art along with conventional catalysts in conventional amounts and utilizing
15 conventional processes can be utilized according to the present invention. Moreover, the type of polyester can be made according to melt polymerization, solid state polymerization, and the like. Moreover, the present invention can be utilized for making high clarity, low haze powdered coatings. An example of a preferred type of high clarity
20 polyester resin is set forth herein below wherein the polyester resin is produced utilizing specific amounts of antimony catalysts, low amounts of phosphorus and a bluing agent which can be a cobalt compound.

As noted above, the polyester may be produced in a conventional
25 manner as from the reacting of a dicarboxylic acid having from 2 to 40 carbon atoms with polyhydric alcohols such as glycols or diols containing from 2 to about 20 carbon atoms. The dicarboxylic acids can be an alkyl having from 2 to 20 carbon atoms, or an aryl, or alkyl substituted aryl containing from 8 to 16 carbon atoms. An alkyl diester
30 having from 4 to 20 carbon atoms or an alkyl substituted aryl diester having from 10 to 20 carbon atoms can also be utilized. Desirably, the diols can contain from 2 to 8 carbon atoms and preferably is ethylene

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glycol. Moreover, glycol ethers having from 4 to 12 carbon atoms may also be used. Generally, most of the commonly produced polyesters are made from either dimethyl terephthalate or terephthalic acid with ethylene glycol. When powdered resin coatings are made, neopentyl
5 glycol is often used in substantial amounts.

Specific areas of use of the polyester include situations wherein preforms exist which then are heated to form a final product, for example, as in the use of preforms which are blow-molded to form a
10 bottle, for example, a beverage bottle, and the like. Another use is in preformed trays, preformed cups, and the like, which are heated and drawn to form the final product. Yet another use relates to polyester yarn which is forced through a plurality of spinnerets having an infrared quench collar thereabout. Additionally, the present invention is
15 applicable to highly transparent, clear and yet low haze powdered coatings wherein a desired transparent film or the like is desired. Because of the improved UV-blocking effect of the inventive compositions, a further use is in injection-molded bottles, such as those intended for juice packaging. Similarly, when used as a bluing agent,
20 the titanium nitride particles of the invention provide packaging having improved color, regardless of whether improved reheat is a necessary effect for the packaging application.

This invention can be further illustrated by the following examples of
25 preferred embodiments, 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 1-32 demonstrate the suitability of *commercial* titanium nitride particles and titanium carbonitride to improve the reheat of polyester compositions in which the particles are dispersed.

Experimental

The following nanometer-size particles used in the examples were purchased from Nanostructured & Amorphous Materials, Inc. (Houston, TX):

1. Nanometer-size titanium nitride (TiN) particles. The samples had an average particle size of 20 nm with a relatively narrow particle size distribution. The particles had a stated purity of > 97%, a specific surface area of 120 m²/g, a bulk density of 0.08 g/cm³, and a true density of 5.22 g/cm³. The particles had a spherical morphology. Two types of nanometer size TiN particles were obtained, i.e., "JY", type and "KE" type. The two nanometer-scale titanium nitride particles are referred to herein as 20nm-TiN(JY) and 20nm-TiN(KE). The average particle size of the two samples was confirmed by transmission electron microscopy. Average particle size values of both samples, as expressed by d₅₀, were around 20nm.
 2. Titanium carbonitride (empirical formula approximately TiC_{0.5}N_{0.5}) nanometer size particles. The particles had a stated average particle size of 50-80nm. The bulk density was 0.23g/cm³, and true density was 5.08 g/cm³.
- The micron-scale titanium nitride (TiN) particles used in the examples were purchased from Aldrich, and had a reported d₅₀ of less than 3 μm.

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The d_{50} as estimated using a scanning electron microscope was about 1.5 μm .

5 In the examples, the reheat of a given polyester composition was measured as a twenty-ounce bottle preform Reheat Improvement Temperature (RIT). In order to determine the RIT of each composition, all preforms were run through the oven bank of a Sidel SBO2/3 blow molding unit in a consistent manner. The lamp settings for the Sidel blow molding machine are shown in Table 1. The reheat time was 38
10 seconds, and the power output to the quartz infrared heaters was set at 64%. A series of fifteen preforms was passed in front of the quartz infrared heaters and the average preform surface temperature of the middle five preforms was measured. As mentioned earlier, in the examples, the reheat rate of a given composition was measured by
15 preform reheat improvement temperature. The preform reheat improvement temperature was calculated by comparing the difference in preform surface temperature of the target samples with that of the virgin polymer. The higher the RIT value, the higher the reheat rate of the composition.

20

The concentration of the aforementioned additive particles in the samples was determined by Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) using a Perkin-Elmer Optima 2000 instrument.

25

Bottles used for the UV-VIS measurements were blown using the Sidel SBO2/3 blow molding unit as already described. These bottles were blown at a preform surface temperature of 110°C to ensure consistent material distribution in the sidewall. Bottle sidewall thickness was all
30 around 0.012 inches. Samples for the UV-VIS measurements were cut from a similar location of different bottles for comparison purposes. The UV-VIS transmission rate measurements were performed using HP8453

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Ultraviolet-Visible Diode Array Spectrometer. The tests were performed from a wavelength ranging from 200nm to 800nm.

Color measurements were performed using a HunterLab UltraScan XE
 5 (Hunter Associates Laboratory, Inc., Reston VA), which employs
 diffuse/8° (illumination/view angle) sphere optical geometry. The color
 scale employed was the CIE LAB scale with D65 illuminant and 10°
 observer specified. Preforms with a mean outer diameter of 0.846
 inches and a wall thickness of 0.154 inches were measured in regular
 10 transmission mode using ASTM D1746, "Standard Test Method for
 Transparency of Plastic Sheeting." Preforms were held in place in the
 instrument using a preform holder, available from HunterLab, and
 triplicate measurements were averaged, whereby the sample was
 rotated 90° about its center axis between each measurement.

15

Bottle sidewall haze was measured using a BYK-Gardner (Silver Spring, MD) haze-guard plus according to ASTM D 1003-00 on sections of the bottle sidewalls with a sidewall thickness of 0.012 inches.

20 Color in transmission at any thickness can be recalculated according to the following:

$$T_h = T_o 10^{-\beta h}$$

$$\beta = \frac{\log_{10} \left(\frac{T_o}{T_d} \right)}{d}$$

25 Where

T_h = transmittance at target thickness

T_o = transmittance without absorption

β = Absorption coefficient

T_d = transmittance measured for sample

h = target thickness

d = thickness of sample

Examples 1-5

- 5 The base polymer used in Examples 1-5 was a commercial grade PET Voridian™ CM01 Polymer, which is a PET copolymer containing no titanium nitride or titanium carbonitride. Prior to compounding, the CM01 polymer was dried at 150°C for 8 hrs. The particles were added into virgin CM01 polymer during melt compounding. First, concentrates
- 10 (containing on the order of 500 ppm particles) were made using a one-inch single-screw extruder with saxton and pineapple mixing head. The extruder was also equipped with pelletization capability. The concentrate was then crystallized using a tumbling crystallizer at 170°C for 1 hour. The crystallized concentrate was then let down into CM01
- 15 virgin polymer with the final concentration of titanium nitride in CM01 ranging from 2 ppm to 50 ppm. During the compounding process, CM01 virgin polymer was used to purge the extruder barrel several times to ensure no cross contamination between different batches. Finally, the CM01 polymers with different levels of titanium nitride particles were
- 20 injection molded into twenty-ounce bottle preforms using a BOY (22D) injection molding machine operated under the following injection molding conditions: melt temperature 270°C, mold temperature 3°C, cycle time 30s, screw speed 110rpm, and cooling time 12s.
- 25 Table 2 shows the correlation between the concentration of 20nm-TiN(JY) and the preform reheat improvement temperature (RIT), from which one can see that 10ppm 20nm-TiN(JY) was suitable to achieve an RIT of 10.5°C. The data also suggest that RIT increased roughly by 1°C to 2°C for every 1ppm increase of 20nm-TiN(JY).

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TABLE 2. Impact of 20nm-TiN (JY) on twenty-ounce bottle preform reheat improvement temperature (RIT), intrinsic viscosity (ItV), and color.

Ex.	System	d50 of TiN (nm)	Measured TiN concentration (ppm)	Preform ItV (dL/g)	Preform RIT (°C)	Preform L*	Preform a*	Preform b*
1	CM01	NA	0	0.78	0	83.3	-0.5	2.5
2	CM01+20nm-TiN(JY)	20	2	0.78	3.3	80.3	-0.9	1.5
3	CM01+20nm-TiN(JY)	20	4	0.77	5.7	79.1	-1.1	0.9
4	CM01+20nm-TiN(JY)	20	10	0.76	10.5	71.9	-1.9	-0.8
5	CM01+ micron-size TiN	1,500	41	0.76	4.1	79.9	-0.7	2.2

5

The data also show that 20nm-TiN(JY) particles led to satisfactory preform color values. Titanium nitride led to a lower (compared to control sample) b* value in the virgin polymer, indicating its blue tinting power. It is evident that b* decreased significantly with the addition of 20nm-TiN (JY) particles: the preform b* decreased roughly 0.3 units at every 1ppm increase of 20nm-TiN (JY). Therefore, with the addition of 20nm-TiN (JY) at 10 ppm, the b* value decreased by 132%, indicating a significant negative b* shift, or bluing effect. The visual observation of the difference in b* was also quite striking.

Thus, the titanium nitride particles with nanometer-scale particle size were effective as a reheat additive as well as a bluing agent.

20

The impact of titanium nitride particles on preform ItV is also shown in Table 2, from which one can see that no significant preform ItV change resulted from the addition of 20nm-TiN(JY).

25

Examples 6-10

The base polymer used in Examples 6-10 was also commercial grade PET Vordian™ CM01 Polymer, and the samples were prepared as already described above. In these examples, the nano-scale TiN

30

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particles used were 20nm KE type of TiN, i.e. 20nm-TiN(KE). Table 3 shows that the bluing effect from the 20nm-TiN(KE) was even greater than that from the 20nm-TiN(JY). At 11ppm loading of 20nm-TiN(KE), the preform b* drop was 5.9 units. These examples also show that bottle sidewall haze was only minimally impacted with the addition of 20nm-TiN(KE).

TABLE 3. Impact of 20nm-TiN(KE) on twenty-ounce bottle preform reheat improvement temperature (RIT), intrinsic viscosity (ItV) and color.

Ex.	d50 of 20nm-TiN (KE) (nm)	20nm-TiN (KE) conc.(ppm)	Preform RIT (°C)	Preform L*	Preform a*	Preform b*	Preform ItV (dL/g)	Bottle sidewall haze
6	NA	0	0	83.3	-0.5	2.5	0.77	0.85
7	20	5	10	75.5	-1.2	-0.4	0.76	0.91
8	20	11	19	66.0	-1.5	-3.4	0.77	1.12
9	20	22	24	59.5	-1.7	-5.4	0.76	1.23
10	20	33	31	47.4	-1.8	-8.5	0.76	1.71

On the other hand, with the addition of micron-scale TiN, such as the 1,500 nm particles seen in Table 2 (ex. 5), the bluing effect was less significant.

Examples 11-19

In this set of examples, two PET copolymers were used, i.e., Vordian Aqua PET WA314 intended for water bottle packaging, and carbonated soft drink grade resin, CB12, both available from Eastman Chemical Company, Kingsport, Tennessee. These resins were evaluated as blends with MXD-6 at 3.0 wt% plus various levels of 20nm-TiN (JY), and then as blends with PET only, WA314, plus various levels of 20nm-TiN (JY).

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Blends were prepared by drying the PET at 150°C for 8 hrs. MXD-6 grade 6007 was obtained from Mitsubishi and was not dried as it is shipped in foil-lined bags already dried. The pellet/pellet blends were prepared after drying and just before injection molding of the preforms using a cement-type mixer with baffles. Immediately after blends were homogenized in the mixer, they were placed in the hopper of the injection molding machine with a hot air purge. The blends were subsequently molded into twenty ounce preforms, 25 grams. The preform color was measured using the method already described.

Preform acetaldehyde (AA) concentration was measured according to ASTM F.2013.

The data for each set of blends is set out in Table 4, from which it can be seen that the addition of 3% MXD-6, grade 6007, caused the color of WA314 to drop 8 L* units and the b* to decrease 6.5 units. This b* change was unexpected, as usually the blend shifts to the yellow side; however, we believe the increased haze from the PET/polyamide blend confounded the color measurement to give a misleading b* value. With the addition of titanium nitride, the b* continued to shift to the blue side while the L* dropped at a rate of 1 unit per 1ppm of 20nm-TiN (JY). The acetaldehyde (AA) was affected by the polyamide, such that it dropped more than 58% in the blend of PET/MXD-6, as compared to the WA314 control. The addition of titanium nitride appeared to drop the AA slightly more, from 2.36 to 1.89, or about a 66.5% reduction.

TABLE 4. Impact of concentration level of 20nm-TiN (JY) on compositions including a polyamide in WA314.

Ex.	Conc. of MXD-6/ Conc. of 20nm-TiN (JY) in WA314	Preform L*	Preform a*	Preform b*	Bottle sidewall haze	Preform AA (ppm)
11	0 - 0	85.7	-0.2	1.5	0.45	5.65
12	3.0% - 0ppm	77.7	-1.0	-5.0	5.69	2.36
13	3.0% - 5ppm	72.0	-1.6	-6.4	5.96	2.12
14	3.0% - 10ppm	66.9	-2.2	-8.0	6.92	1.90
15	3.0% - 20ppm	59.2	-2.8	-8.6	7.24	1.89

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When looking at WA314 blended with TiN only (Table 5), it can be seen that again 20nm-TiN (JY) dropped the L* about 1 unit per 1ppm and moved b* about 1.5 units per 5ppm's TiN, toward the blue side (lower b*). The AA did not change significantly, nor did the haze increase as it usually does with most reheat-enhancing additives.

TABLE 5. WA314 preforms containing 20nm-TiN (JY).

Ex.	Conc. of 20nm-TiN in WA314 (ppm)	Preform L*	Preform a*	Preform b*	Bottle sidewall haze	Preform AA (ppm)
16	0	86.0	-0.3	1.6	0.47	4.47
17	5	79.8	-1.0	-0.1	0.57	4.32
18	10	75.1	-1.6	-1.5	0.78	4.61
19	20	68.2	-2.5	-3.2	0.99	4.42

Examples 20-24

When looking at the blends of CB12 with MXD-6 and 20nm-TiN (JY) in Table 6, prepared as above, it can be seen that preform L* dropped about 5 units when the MXD-6 was added while the haze was increased by about 6 units. The further addition of 20nm-TiN (JY) did not change the haze value significantly. However, there was a slight trend in AA reduction with increasing 20nm-TiN. L* was again lowered about 1 unit per 1 ppm of 20nm-TiN(JY). The b* decreased about 0.257 units, on average, per 1 ppm TiN.

TABLE 6. Impact of concentration level of 20nm-TiN (JY) on preform color, bottle sidewall haze and preform AA for a blend of CB12 with 3wt% MXD-6.

Ex.	Conc. of MXD-6/ 20nm-TiN (JY) in CB12	Preform L*	Preform a*	Preform b*	Bottle sidewall haze	Preform AA (ppm)
20	0	71.0	-1.4	4.5	1.62	9.39
21	3.0% - 0ppm	65.6	-3.0	2.7	7.71	3.96
22	3.0% - 5ppm	63.6	-2.9	2.3	6.13	4.46
23	3.0%-10ppm	55.3	-4.0	-0.2	7.45	3.71
24	3.0%-20ppm	48.6	-4.4	-2.1	7.83	3.51

Examples 25-26

- 5 The base polymer used in examples 25-26 was commercial grade PET Voridian™ CM01 Polymer. The samples were prepared as already described. UV light radiation experiment: 20 ounce bottles made with virgin CM01, and a sample with 77 ppm 20nm-TiN (JY) in CM01, were blown at the same preform surface temperature and were tested under
- 10 UV light. The UV light lamp used was a model UVL-28, obtained from UVP, Inc. (UPLAND, CA). It held two 8 watt bulbs that emit light from 340 to 400nm with a peak emission at 365nm. The lamp had a filter that filtered light with wavelengths above 400 nm. The beverage used was a juice drink containing FD&C Red#40. Testing was done to see if the
- 15 addition of TiN to CM01 would increase the UV protection provided by the polymer. All samples were tested in a consistent manner.

Table 7 shows the 370nm-UV transmission rate of each of the samples, from which one can see at 79.4ppm loading of TiN, the UV transmission

20 rate at 370nm decreased 22%. The sample thickness was approximately 0.012 inches.

TABLE 7. Comparison of the 370 nm UV light transmission rates.

Ex.	System	TiN concentration (ppm)	370nm transmission rate (%)
25	CM01 control	0	78.7
26	CM01+20nm-TiN (JY)	79.4	61.4

25

Examples 27-32

- 30 Table 8 shows that the addition of $\text{TiC}_{0.5}\text{N}_{0.5}$ also led to an improvement in reheat rates. The base polymer used in examples 27-32 was commercial grade PET Voridian™ CM01 Polymer. The addition of

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6.4ppm $\text{TiC}_{0.5}\text{N}_{0.5}$ led to an RIT of 7°C with an L^* value of 76.2. Good preform appearance properties were also achieved at reasonable reheat improvement temperatures, e.g. RIT=7°C.

5 **TABLE 8.** Impact of titanium carbonitride ($\text{TiC}_{0.5}\text{N}_{0.5}$) on twenty-ounce bottle preform reheat improvement temperature (RIT), intrinsic viscosity (ItV) and color.

Ex.	Concentration of $\text{TiC}_{0.5}\text{N}_{0.5}$ in CM01 (ppm)	Syetem	Preform RIT (°C)	Preform L^*	Preform a^*	Preform b^*	Preform ItV (dL/g)	Bottle sidewall haze
27	0	CM01 control	0	83.3	-0.5	2.5	0.77	0.85
28	6.4	CM01+ $\text{TiC}_{0.5}\text{N}_{0.5}$ (50-80nm)	7	76.2	-0.3	4.6	0.77	1.04
29	9.9	CM01+ $\text{TiC}_{0.5}\text{N}_{0.5}$ (50-80nm)	14	70.4	0.0	5.8	0.76	1.11
30	24.1	CM01+ $\text{TiC}_{0.5}\text{N}_{0.5}$ (50-80nm)	23	56.1	0.7	8.3	0.76	1.32
31	29.2	CM01+ $\text{TiC}_{0.5}\text{N}_{0.5}$ (50-80nm)	29	45.6	1.3	9.8	0.76	1.53
32	41.9	CM01+ $\text{TiC}_{0.5}\text{N}_{0.5}$ (50-80nm)	32	38.0	1.6	10.2	0.76	1.90

10 Example 33 (Prophetic)

Titanium dioxide particles, for example having an average particle diameter of about 60 nm, are reacted with a nitrogen-containing gas, such as ammonia, at a temperature of about 850°C, for a period of about 4 hours, to obtain titanium nitride particles which are slightly larger in size than the titanium dioxide particles used to form them. The particles formed are quenched in ethylene glycol at a temperature of about 25°C to form a suspension, and the suspension thereafter added to a polyester polymerization process to obtain a polyester having about 20 ppm titanium nitride particles therein. The polyester exhibits improved reheat properties, and may also exhibit a bluer tint, compared to a similar polyester lacking titanium nitride particles.

Example 34 (Prophetic)

25 Titanium dioxide particles, for example having an average particle diameter from about 10 nm to about 60 nm, or from 20 nm to 40 nm, are reacted with a nitrogen-containing gas, such as ammonia, at a

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temperature of about 850°C, for a period of about 4 hours, to obtain titanium nitride particles which are slightly larger in size than the titanium dioxide particles used to form them. The particles formed are quenched in ethylene glycol at a temperature of about 25°C to form a suspension, and the suspension thereafter added to a polyester polymerization process to obtain a polyester having about 20 ppm titanium nitride particles therein. The polyester exhibits improved reheat properties, and may also exhibit a bluer tint and UV blocking effect, compared to a similar polyester lacking titanium nitride particles.

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We claim:

1. A process for producing a polyester composition, comprising:
heating titanium oxide particles in a nitrogen-containing gas at a
temperature sufficient to obtain titanium nitride particles;
5 suspending the titanium nitride particles in a carrier to obtain a
suspension of titanium nitride particles; and
introducing the suspension of titanium nitride particles to a polyester
polymerization process to obtain a polyester composition having the
titanium nitride particles dispersed therein.
10
2. The process of claim 1, wherein the nitrogen-containing gas
comprises one or more of: N₂, trimethylamine, triethylamine, or ammonia.
3. The process of claim 1, wherein the nitrogen-containing gas
15 comprises ammonia.
4. The process of claim 1, wherein the temperature is from about
700°C to about 1,500°C.
- 20 5. The process of claim 1, wherein the titanium oxide particles
comprise titanium dioxide particles.
6. The process of claim 1, wherein the titanium dioxide particles are
in one or more of the following crystalline forms: anatase, brookite, or rutile.
25
7. The process of claim 1, wherein the titanium oxide particles have
a median particle size from about 0.5 nm to about 1,000 nm.
8. The process of claim 1, wherein the titanium oxide particles have
30 a median particle size from about 0.5 nm to about 500 nm.

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9. The process of claim 1, wherein the titanium oxide particles have a median particle size from 1 nm to 100 nm.

5 10. The process of claim 1, wherein the titanium oxide particles have a median particle size from 1 nm to 50 nm.

11. The process of claim 1, wherein the carrier comprises one or more of: ethylene glycol, a fatty acid ester, an ethoxylated fatty acid ester, a
10 paraffin oil, a polyvalent alcohol, a polyvalent amine, a silicone oil, a hydrogenated castor oil, a hydrogenated ricinus oil, a stearic ester of pentaerythritol, soybean oil, or an ethoxylated alcohol.

12. The process of claim 1, wherein the titanium nitride particles
15 have a median particle size from about 0.5 nm to about 1,000 nm.

13. The process of claim 1, wherein the titanium oxide particles have a median particle size from about 0.5 nm to about 500 nm.

20 14. The process of claim 1, wherein the titanium oxide particles have a median particle size from 1 nm to 100 nm.

15. The process of claim 1, wherein the titanium oxide particles have a median particle size from 1 nm to 50 nm.

25

16. The process of claim 1, wherein the titanium nitride particles are dispersed in the polyester composition in an amount from about 0.5 ppm to about 1,000 ppm, with respect to the total weight of the polyester composition.

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17. The process of claim 1, wherein the titanium nitride particles are dispersed in the polyester composition in an amount from 5 ppm to 50 ppm, with respect to the total weight of the polyester composition.

5 18. The process of claim 1, wherein the polyester composition comprises polyethylene terephthalate.

19. The process of claim 1, further comprising forming the polyester composition into the form of a beverage bottle preform.

10

20. The process of claim 1, further comprising forming the polyester composition into the form of a beverage bottle.

15 21. The process of claim 1, further comprising forming the polyester composition into the form of a molded article.

22. The process of claim 1, wherein the polyester composition comprises a polyester polymer as a continuous phase, and wherein the titanium nitride particles are dispersed within the continuous phase.

20

23. The process of claim 19, wherein the titanium nitride particles have a median particle size from 1 nm to 1,000 nm, and provide the beverage bottle preform with a reheat improvement temperature (RIT) of at least 5°C while maintaining a preform L* value of 70 or more, and a b* value from about minus 0.8 to about plus 2.5.

25

24. The process of claim 1, wherein the polyester composition obtained demonstrates a reduction in the percent of UV transmission of at least 10% at a wavelength of 370nm; as measured at a sample thickness of

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about 0.012 inches, when compared with a polyester composition lacking the titanium nitride particles,.

25. The process of claim 1, wherein the titanium nitride particles
5 comprise particles coated with titanium nitride.

26. The process of claim 1, wherein the titanium nitride particles
comprise a titanium nitride having an empirical formula from about $\text{TiN}_{0.42}$ to
about $\text{TiN}_{1.16}$.
10

27. The process of claim 1, wherein the titanium nitride particles
comprise titanium nitride in an amount of at least about 90 wt.%, with
respect to the total weight of the titanium nitride particles.

28. The process of claim 1, wherein the titanium nitride particles
15 further comprise titanium carbide.

29. The process of claim 19, wherein the beverage bottle preform
has a reheat improvement temperature greater than 5°C.
20

30. The process of claim 1, wherein the polyester polymerization
process comprises the following steps:

a) an esterification step comprising transesterifying a dicarboxylic
acid diester with a diol, or directly esterifying a dicarboxylic acid with a diol,
25 to obtain one or more of a polyester monomer or a polyester oligomer;

b) a polycondensation step comprising reacting the one or more of a
polyester monomer or a polyester oligomer in a polycondensation reaction
in the presence of a polycondensation catalyst to produce a molten
polyester polymer having an lt.V. from about 0.50 dL/g to about 1.1 dL/g;

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c) a particulation step in which the molten polyester polymer is solidified into particles; and

d) an optional solid-stating step in which the solid polymer is polymerized to an It.V. from about 0.70 dL/g to about 1.2 dL/g;

5 and wherein the suspension of titanium nitride particles is introduced into the polyester polymerization process before, during, or after any of the preceding steps.

10 31. The process according to claim 30, wherein the polyester polymerization process further comprises a forming step, following the solid-stating step, the forming step comprising melting and extruding the resulting solid polymer to obtain a formed item having the titanium nitride particles dispersed therein.

15 32. The process according to claim 31, wherein the suspension of titanium nitride particles is dispersed in a thermoplastic polymer to form a thermoplastic concentrate in which the titanium nitride particles are present in an amount from about 100 ppm to about 5,000 ppm, with respect to the weight of the thermoplastic concentrate, and the thermoplastic concentrate
20 is thereafter introduced into the polyester polymerization process prior to or during the forming step.

25 33. The process according to claim 30, wherein the titanium nitride particles have a median particle size from about 1 nm to about 100 nm.

34. The process according to claim 30, wherein the suspension of titanium nitride particles is added to the polyester polymerization process prior to or during the polycondensation step.

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35. The process according to claim 30, wherein the suspension of titanium nitride particles is added to the polyester polymerization process prior to or during the esterification step.

5 36. The process according to claim 30, wherein the dicarboxylic acid comprises terephthalic acid.

37. The process according to claim 30, wherein the dicarboxylic acid diester comprises dimethyl terephthalate.

10

38. The process according to claim 30, wherein the diol comprises ethylene glycol.

39. The process of claim 32, wherein the thermoplastic concentrate
15 is added to the molten polyester polymer when the molten polyester polymer has an It.V. which is within +/- 0.2 It.V. units of the It.V. of the thermoplastic concentrate.

40. A process for producing a polyester composition, comprising:
20 heating titanium oxide particles in a nitrogen-containing gas to a temperature sufficient to convert a portion of the titanium oxide particles to titanium nitride particles;

suspending the titanium oxide particles and the titanium nitride particles in a carrier to obtain a suspension of titanium oxide particles and
25 titanium nitride particles; and

introducing the suspension of titanium oxide particles and titanium nitride particles to a polyester polymerization process to obtain a polyester composition having the titanium oxide particles and the titanium nitride particles dispersed therein.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2007/009914

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08K3/10 C08K3/28 C08L67/02

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)
C08L C08K

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

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

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2005/095516 A (COLORMATRIX EUROP LTD [GB]; JARVIS ANTHONY [GB]; FROST MARK [GB]) 13 October 2005 (2005-10-13)	1-40
Y	claims 1,3,7-11,28-30,35-38,40-48 page 1, lines 1-18 page 20, line 14 - page 21, line 2 -----	1-40
Y	JINGGUO LI, LIAN GAO, JING SUN, QINGHONG ZHANG, JINGKUN GUO, DONGDHENG YAN: "Synthesis of Nanocrystalline Titanium Nitride Powders by direct Nitridation of Titanium Oxide" J. AM. CERAM. SOC., vol. 84, no. 12, 2001, pages 3045-3047, XP002447498 column 2, paragraphs 1,3 ----- -/--	1-40

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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- *&* document member of the same patent family

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INTERNATIONAL SEARCH REPORT

International application No
PCT/US2007/009914

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
E	WO 2007/064312 A (EASTMAN CHEM CO [US]) 7 June 2007 (2007-06-07) claims 27-55 -----	1-40

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2007/009914

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