Abstract: Disclosed are polytrimethylene terephthalate-based flame retardant compositions and fibrous articles produced therefrom. The flame retardant compositions comprise (a) 74 weight % to 99.4 weight % of polytrimethylene terephthalate; (b) 0.5 weight % to 10 weight % of a flame retardant, which is a phosphorous containing polyester of Formula 1, wherein n is an integer ranging from 22 to 150; (c) 0.1 weight % to 6 weight % of alumina oxide nanoparticles; and (d) 0 to 10 weight % of an optional additive; wherein the weight percent is based on the total weight of the flame retardant composition.
FIELD OF THE INVENTION

This invention relates to polytrimethylene terephthalate-based flame retardant compositions, particularly relates to polytrimethylene terephthalate-based flame retardant compositions comprising phosphorous containing polyester flame retardants and inorganic nanoparticles. The invention also relates to articles comprising or prepared from the present flame retardant compositions, especially to fibrous articles.

BACKGROUND OF THE INVENTION

Polytrimethylene terephthalate (commonly referred to as "PTT", "PPT" or "3GT") is generally prepared by the condensation polymerization of 1,3-propanediol and terephthalic acid or 1,3-propanediol and terephthalate ester, and is a new class of aromatic polyester after polyethylene terephthalate (commonly abbreviated to "PET") and polybutylene terephthalate (commonly abbreviated to "PBT"). PTT resin has better performance in mechanical properties, weather resistance, heat aging resistance and hydrolysis resistance as compared to that of PET and PBT.

PTT fibers combines the softness of nylon fibers, the fluffiness of acrylic fibers and the stain resistance of PBT fibers; meanwhile, it has better color fastness than nylon fibers, and avoids the pilling shortcoming of acrylic fibers, and it also has better hand feel, good inherent elasticity and dyeability at room temperature. Since PTT resin has the excellent performance, it is commonly used in applications such as textile, upholstery, and engineering plastics, especially carpets. However, in some environment, the inherent flame retardancy of PTT resin is insufficient, as a result, it limits the applications of PTT resin in some area.

There are three major methods to improve the flame retardancy of PTT: one method is the post-treatment, in which PTT fibers or fabrics are impregnated with flame retardants to form flame retardant PTT fibers or fabrics, the disadvantage of this method is that flame retardancy cannot be sustained, and the appearance of the fibers or fabrics may be negatively affected, this method is also not suitable for engineering plastics; another method is copolymerization, i.e., introducing the flame retardant as commoner into the PTT macromolecular chains to obtain a flame retardant PTT resin, the PTT resin prepared by this method has sustainable flame retardancy, but also has other inherent properties changed at the same time; yet another method is blending, i.e., blending the flame retardant with PTT resin to obtain flame retardant composition, which is subsequently
molded or spun into flame retardant fibers or fabrics. While the PPT resin prepared by blending has advantages such as simple process and low cost than the PPT resin prepared by copolymerization, the added flame retardants must be uniformly dispersed in the resin matrix without migration, frosting, etc., so as to avoid the flame retardancy of PTT blends decreases or diminishes.

There are broad studies on adding halogenated flame retardants to polyester, however, halogenated flame retardants cause environmental pollution during manufacturing, recycling and disposing, and generate toxic and harmful gases during burning, therefore, halogenated flame retardants are gradually replaced by halogen-free flame retardants. Halogen-free flame retardants, especially phosphorus containing flame retardants have been widely used in polyesters, especially in polyester fibers. Phosphorus containing flame retardants include reactive type and additive type. When introduced into polyester molecular chains, the reactive type of phosphorus containing flame retardants generally alter the thermal property of the resulting flame retardant polyester and subsequently cause spinning difficulty; moreover, its processing cannot be done on the existing manufacture platform, and requires adjusting equipment or process parameters, thus increases the production cost.

Patent application CN101532189A discloses flame retardant PTT fibers and preparation method thereof, which includes a copolymerization method to incorporate flame retardant phosphorus containing monomers (e.g., 2-carboxyethyl alkyl phosphonic acid, 2-phenyl carboxyethyl phosphinic acid and the like) into the molecular chains of PTT polyester, meanwhile, adding inorganic nanoparticles selected from silicon oxide, calcium carbonate, magnesium carbonate and barium sulfate into the copolymerization reactants to obtain the flame retardant PTT polyesters.

Patent application CN101709137A discloses a phosphorus containing flame retardant polyethylene terephthalate copolyester/nanocomposition and preparation method thereof, which includes a copolymerization method to add flame retardant phosphorus containing monomers (e.g., BHET, BHPPO, CEMPP, DDP and the like) to the molecular chains of PTT polyester, simultaneously, adding inorganic nanoparticles selected from barium sulfate, silicon oxide, titanium oxide, zinc oxide and the like to obtain flame retardant PTT polyesters. This patent application also relates to the aforementioned reactive type of phosphorus containing flame retardant.

Prior art also discloses blending flame retardants and polyester resin to obtain compositions with improved flame retardancy (i.e., the aforementioned additive type flame retardant), for example, patent application JP2006-144184A discloses a flame retardant polyester composition for artificial hair, that the composition is the blends of a polyester (e.g., PET) and a flame retardant polyester copolymer. The flame retardant polyester
copolymers is prepared by copolymerization terephthalic acid, alkylene glycols and phosphorus or bromine containing compounds.

Patent application JP2007-112875A discloses a flame retardant polyester resin composition which is prepared by melt mixing 100 parts by weight of polyesters, 10-80 parts by weight of organic phosphorus flame retardants and 10-100 parts by weight of inorganic compounds. The main application of flame retardant polyester resin composition is the molded parts of automobiles, household appliances, electronics, etc., thus inorganic compounds (e.g. mica, talc, etc.) are introduced to increase the mechanical strength and rigidity, and the amount of inorganic compounds is at least 10 parts by weight. The organic phosphorus containing flame retardant is a homopolymer of Formula A:

\[
\text{H(OCH}_2\text{CH}_2\text{OCCHCH}_2\text{C)}_n\text{OCH}_2\text{CH}_2\text{OH}
\]

wherein, \(n\) is an integer in the range of 2-20.

Currently, there still are needs for PTT compositions that not only have improved flame retardancy and are environmentally friendly, and the applications of such compositions include, not limited to engineering plastic, but also fibrous articles such as textiles, upholstery and carpets.

**SUMMARY OF THE INVENTION**

The inventors of the present invention found that flame retardant compositions obtained by blending phosphorous containing polyester of Formula 1 and PTT provided improved flame retardancy. In particular, the inventors found that adding a small amount of aluminum oxide nanoparticles to the blends of PTT and the phosphorous containing polyester of Formula 1 (b) synergistically improves the flame retardancy of the phosphorous containing polyester of Formula 1 (b).

Based on the above findings, the present invention provides a flame retardant composition comprising:

(a) about 74 weight % to about 99.4 weight % of polytrimethylene terephthalate;
(b) about 0.5 weight % to about 10 weight % of a flame retardant, which is phosphorous containing polyester of Formula 1:

In one embodiment, in the flame retardant composition of the present invention, the polytrimethylene terephthalate (a) is a polytrimethylene terephthalate homopolymer, a polytrimethylene terephthalate copolymer, or blends thereof, wherein the polytrimethylene terephthalate copolymer contains at least 70 mol % of trimethylene terephthalate as the major copolymerized unit.

In one embodiment, in the flame retardant composition of the present invention, the amount of the polytrimethylene terephthalate (a) is about 74 weight % to about 99.4 weight %, or about 85 weight % to about 95 weight %, based on the total weight of the flame retardant composition.

In one embodiment, in the flame retardant composition of the present invention, the average number molecular weight of the flame retardant (b), i.e., the phosphorus containing polyester of Formula 1, is from 9,000 to about 50,000.

In one embodiment, in the flame retardant composition of the present invention, the amount of the flame retardant (b) is about 0.5 weight % to about 10 weight %, or about 1 weight % to about 6 weight %, based on the total weight of the flame retardant composition.

In one embodiment, in the flame retardant composition of the invention, the primary particle size of the alumina oxide nanoparticles (c) is about 100 nm or less, or from about 1
nm to about 80 nm, or from about 10 nm to about 70 nm, or from about 20 nm to about 50 nm.

In one embodiment, in the flame retardant composition of the present invention, the amount of the aluminum oxide nanoparticles (c) is from about 0.1 weight % to about 6 weight %, or from about 0.2 weight % to about 4 weight %, or from about 0.3 weight % to about 2 weight %, based on the total weight of the flame retardant composition.

In one embodiment, in the flame retardant composition of the present invention, the optional additive (d) is selected from the group consisting of antioxidants, colorants including dyes and pigments, hydrolysis resistsants, lubricants, nucleating agents, coupling agents, thermal stabilizers, anti-static agents and ultraviolet light stabilizers.

In one embodiment, in the flame retardant composition of the present invention, the amount of the optional additive (d) is typically from 0 to about 10 weight %, or from about 0.01 weight % to about 6 weight %, or from about 0.1 weight % to about 2 weight %, based on the total weight of the flame retardant composition.

The invention also relates to an article comprising or produced from the flame retardant compositions mentioned above, especially to a fibrous article, wherein the fibrous article is filaments, fibers, staple fibers, yarns, fabrics, or carpets.

**DETAILS OF THE INVENTION**

All publications, patent applications, patents and other references mentioned herein, if not otherwise indicated, are explicitly incorporated by reference herein in their entirety for all purposes as if fully set forth.

Unless otherwise defined, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this invention belongs. In case of conflict, the present specification, including definitions, will control.

Unless stated otherwise, all percentages, parts, ratios, etc., are by weight.

"mol %" refers to mole percent.

When an amount, concentration, or other value or parameter is given as either a range, preferred range or a list of upper preferable values and lower preferable values, this is to be understood as specifically disclosing all ranges formed from any pair of any upper range limit or preferred value and any lower range limit or preferred value, regardless of whether ranges are separately disclosed. Where a range of numerical values is recited herein, unless otherwise stated, the range is intended to include the endpoints thereof, and all integers and fractions within the range.

As used herein, the term "produced from" is synonymous to "comprising". As used herein, the terms "includes", "including", "comprises", "comprising", "has", "having",
"contains" or "containing", or any other variation thereof, are intended to cover a non-exclusive inclusion. For example, a composition, process, method, article, or apparatus that comprises a list of elements is not necessarily limited to only those elements but may include other elements not expressly listed or inherent to such composition, process, method, article, or apparatus. Further, unless expressly stated to the contrary, "or" refers to an inclusive "or" and not to an exclusive "or". For example, a condition A "or" B is satisfied by any one of the following: A is true (or present) and B is false (or not present), A is false (or not present) and B is true (or present), and both A and B are true (or present).

Also, the indefinite articles "a" and "an" preceding an element or component of the invention are intended to be nonrestrictive regarding the number of instances (i.e. occurrences) of the element or component. Therefore "a" or "an" should be read to include one or at least one, and the singular word form of the element or component also includes the plural unless the number is obviously meant to be singular.

The materials, methods, and examples herein are illustrative only and, except as specifically stated, are not intended to be limiting. Although methods and materials similar or equivalent to those described herein can be used in the practice or testing of the present invention, suitable methods and materials are described herein.

When the term "about" is used in describing a value or an end-point of a range, the disclosure should be understood to include the specific value or end-point referred to.

The flame retardant compositions of the present invention are described in detail hereinunder.

(a) PTT

Suitable PTT resin for the present invention is a PTT homopolymer, a PTT copolymer or blends thereof. The preferred PTT resin is a PTT homopolymer.

The term "homopolymer" refers to a polymer derived from polymerization of one species of repeating unit. In the present invention, "PTT homopolymer" refers to the polymer prepared by the condensation polymerization of 1,3-propanediol and terephthalic acid or terephthalic acid equivalent, wherein "terephthalic acid equivalent" refers to the compound having essentially the same properties as terephthalic acid in the reactions with diol. For purposes of this invention, terephthalic acid equivalents include esters of terephthalic acid (e.g., dimethyl terephthalate) and derivatives of ester precursor of other (e.g., acid halides and acid anhydrides). Generally, terephthalic acid equivalent is terephthalic acid and dimethyl terephthalate are preferred.

The term "copolymer" refers to polymers copolymerized from two or more comonomers, i.e., polymers comprising two or more species of repeating units. In the present invention, "PTT copolymer" preferably contains 70 mol% or more, or 80 mol% or more, or 90 mol% or more, or 95 mol% or more of polytrimethylene terephthalate, and the
rest are the derivatives from the monomers excluding terephthalic acid and 1,3-propanediol (such as glycol, butanediol, etc.).

The term "blends" means a mixture of two or more components. In the present invention, "PTT blends" can be prepared by blending PTT homopolymers or PTT copolymers; the PPT blends preferably contain about 80 weight % or more, or about 90 weight % or more, or about 95 weight % or more of PTT homopolymers or PTT copolymers, based on the total weight of the PTT blends.

The methods suitable for preparing the PTT homopolymer, PTT copolymer or PTT blends are well known to persons skilled in the art, for examples, the method disclosed in U.S. Patent Application Publication No. US6281325 (Bl).

Suitable PTT resin for the present invention is commercially available, Sorona® from DuPont, for example, in accordance with matting agent content, there are various classes including bright, semi-bright, semi-dull and dull, and each class further includes several types of PTT resins having different intrinsic viscosity (IV).

In the flame retardant composition of the present invention, the amount of PTT resin (a) is from about 74 weight % to about 99.4 weight %, or from about 85 weight % to about 95 weight %, based on the total weight of the flame retardant composition.

(b) Flame Retardant

The flame retardant (b) employed in the present invention is a phosphorus containing polyester of Formula 1:

![Formula 1](image)

wherein

n is an integer ranging from 22 to 150.

When used as spinning materials, suitable flame retardant (b) of the present invention, i.e., a phosphorus containing polyester of Formula 1, should be in molten state at the typical spinning temperature of PTT resin, so that the resultant compositions do not block the spinning die at the spinning temperature. In addition, the phosphorus containing
polyester of Formula 1 of the present invention should not degrade at the typical spinning temperature of PTT. Typical spinning temperature of PTT is between 240 °C and 290 °C.

In view of flame retardancy, there is no particular limitation on the molecular weight of the phosphorus containing polyester of Formula 1 (b), as the phosphorus content does not vary much (about 7.8-8.3 %) as the n value increases, therefore, when applying the phosphorus containing polyester of Formula 1 (b), it only needs to adjust the amount. However, considering the desired migration, frosting and thermal stability of the blend of the phosphorus containing polyester Formula 1 (b) and PTT (a), the average number molecular weight of the phosphorus containing polyester of Formula 1 (b) preferably is at least about 9,000; or about 9,500; or about 10,000. On the other hand, considering the accessibility and the melting temperature, the average number molecular weight of the phosphorus containing polyester of Formula 1 (b) preferably is no more than about 50,000; or 40,000; or 30,000; or 20,000. The average number molecular weight of the phosphorus containing polyester of Formula 1 (b) can be measured by gel permeation chromatography (GPC), see US2006/025824A1.

In one embodiment, in the flame retardant composition of the invention, the average number molecular weight of the flame retardant (b), i.e. the phosphorus containing polyester of Formula 1, is from about 9,000 to about 50,000; or from about 9,500 to about 40,000; or from about 10,000 to about 30,000.

Suitable flame retardant (b), i.e. the phosphorus containing polyester of Formula 1, can be synthesized by methods known to one skilled in the art, for example, the condensation polymerization method disclosed in Patent Application JP2007-112875A, which is obtained by reacting directly 9,10-dihydro-9-oxa-10- phosphaphenanthrene-10-oxide (DOPO, CAS No. 35848-25-5), itaconic acid (CAS No. 2170-03-8), ethylene glycol and suitable catalyst. Additionally, one can adopt the condensation polymerization method disclosed in Patent Application US2006/025824A1, wherein the phosphorus containing diol (i.e., a compound of Formula 2), which is prepared in advance from DOPO, itaconic acid and ethylene glycol, reacts with suitable catalyst at high temperature, under reduced pressure to obtain phosphorus containing polyester homopolymers having various average number molecular weight by adjusting the reaction duration.
Alternatively, the phosphorus containing polyester of Formula 1 is also commercially available, for example, the phosphorus containing homopolymer under trade name of ME-P8 from Sanko Co. Ltd., Japan.

In the flame retardant composition of the present invention, the amount of the phosphorus containing polyester of Formula 1 (b) is from about 0.5 weight % to about 10 weight %, or from about 1 weight % to about 6 weight %, based on the total weight of the flame retardant composition.

(c) Alumina Oxide Nanoparticles

In the present specification and/or claims, the term "nanoparticles" is broadly defined as the particles with at least one dimension smaller than 1 \( \mu \)m. The shape of the nanoparticles can be sphere, needle, rod, plate, or other irregular shape.

When the nanoparticles are non-sphere, the ratio between the length of the largest dimension and the length of the smallest dimension is defined as aspect ratio.

As the alumina oxide nanoparticles (c) employed in the present invention are within the aforementioned definitions, there is no special limitation for the shape, size, and particle distribution curve shown as unimodal or bimodal.

Alumina oxide nanoparticles (c) of the present invention are typically spherical or nearly spherical shape. Although just for illustration, the primary particle size (i.e., non-agglomeration state) of the alumina oxide nanoparticles (c) employed in the present invention is about 100 nm or less, or from about 1 nm to about 80 nm, or from about 10 nm to about 70 nm, or from about 20 nm to about 50 nm.

Alumina oxide nanoparticles (c) of the present invention can form agglomerates, which have a size of from about 50 nm to about 300 nm, depending on the dispersion degree of the alumina oxide nanoparticles (c) in the polymer matrix.

The size of the nanoparticles and the dispersion of them in the polymer matrix can be determined by for example, confocal laser scanning electron microscope (SEM).

Suitable alumina oxide nanoparticles (c) are commercially available; for examples, Hangzhou Wan Jing New Material Co., Ltd. provides alumina oxide nanoparticles under trade name of nano alumina oxide that have various size and surface treatment.

In the flame retardant composition of the present invention, the amount of alumina oxide nanoparticles (c) is from about 0.1 weight % to about 6 weight %, or from about 0.2 weight % to about 4 weight %, or from about 0.3 weight % to about 2 weight %, based on the total weight of the flame retardant composition.

(d) Optional Additive

The flame retardant compositions of the present invention may optionally include additives selected from the group consisting of antioxidants, colorants (including dyes and pigments), hydrolysis resistant, lubricants, nucleating agents, coupling agents, thermal stabilizers, anti-static agents and ultraviolet light stabilizers. There is no particular limitation for the additives in the present invention, persons skilled in the art can select and add the commonly used additives according to the application and actual need.

Examples of the above additives are list below, however, persons skilled in the art should understand that suitable additives include, but are not limited to, the following examples.

The antioxidants, for example, are hindered phenol antioxidants. The colorants are usually dry powders to impart color to the compositions or articles (e.g., fibers), which may be inorganic or organic, natural or synthetic; generally, the colorants are inert (for example, charge neutral and do not react with the polymer). The hydrolysis resistant are carbodiimide hydrolysis resistant. The lubricants, for example, are TAF lubricants. The nucleating agent may be inorganic or organic, such as nano silicon oxide, organic carboxylate salt, organic phosphonate salts, etc. The coupling agents, for example, are silane or titanate coupling agents. The heat stabilizers, for example, are large molecules hindered amines, phosphate and copper halides. The ultraviolet light stabilizers, for example, are benzotriazole ultraviolet absorbers or benzophenone ultraviolet absorbers. The anti-static agents include five common types of anti-static agents, i.e., amine derivative, quaternary ammonium salts, sulfuric acid esters, phosphate esters and polyethylene glycol derivatives.
In the flame retardant composition of the present invention, the amount of the optional additive (d) is generally form 0 to about 10 weight %, or from about 0.01 weight % to about 6 weight %, or from about 0.1 weight % to about 2 weight %, based on the total weight of the flame retardant composition, so long as they do not detract from the basic and novel characteristics of the flame retardant compositions and do not significantly adversely affect the performance of the flame retardant compositions.

Preparation and Application of the Flame Retardant Compositions

The flame retardant compositions of the present invention may be prepared by general blend techniques known in the art, the components (a)-(c) and the optional additives (d) are typically in powder or granule form at room temperature, the blended compositions can be obtained by combining the components (a)-(c) and the optional additive (d) using various methods, e.g., heating and mixing at molten state simultaneously, pre-mixing (such as dry mixing) before heating, or mixing after heating separately. Mixing and heating described above can be processed in the equipments known in the art such as extruder or other mixer, etc. In one embodiment, the components (a)-(c) and optional additives (d) in powder or granular form are blended at the melt temperature, extruded and comminuted into pellets or other suitable shapes. The term "pellets" is used generically in this regard, although sometimes called "chips", "flakes", etc.

In one preferred embodiment of the present invention, the flame retardant composition is prepared by melt blending the components (a)-(c) and optional additive (d). In addition, the flame retardant compositions of the present invention can be produced into molded articles by conventional molding apparatus; or can be spun into as-spun yarn, and then drawn into filaments by re-melting the pellets prepared therefrom, or spun directly using the conventional spinning apparatus known to one skilled in the art.

The blending temperatures should be higher than the melting point of each component, but lower than the lowest decomposition temperature of each component, and must be adjusted according to the PTT resin (a), component (b), component (c) and/or component (d) of the flame retardant composition. The blending temperature is generally from about 180°C to about 290°C, preferably at least about 220°C, and more preferably up to about 280°C, depending on each component of the present invention.

The component (b), component (c) and/or component (d) can be uniformly dispersed in the PTT resin matrix of component (a) through melt blending, and the structure of the resulting flame retardant composition of the present invention can be determined by electron microscope such as transmission electron microscopy (TEM) and scanning electron microscope (SEM).
The PTT-based flame retardant composition of the present invention can be produced into fibrous articles, films, molded articles and other shaped articles of various shape and forms. For purposes of the present invention, the term "fibrous articles" includes, but are not limited to, filaments, fibers, staple fibers, yarns, fabrics, carpets or other textile products, and are for applications such as garments, home furnishings, carpets, and other consumer products.

The flame retardant compositions of the present invention can be produced into filaments with various shape and fineness, the filaments can be produced into fibers or yarns through steps comprising doubling, twisting and stranding, or be cut into staple fibers. The filaments, fibers, staple fibers and yarns can be produced into fabrics, carpets, and other textile products. The fibrous articles of the present invention may be knitted, woven or nonwoven. Nonwoven fabric of the present invention is a web or matt of fibers or staple fibers which are bound by the application of heat, entanglement, and/or pressure.

A filament may be round or in other shape such as octalobal, delta, sunburst (also known as sol), scalloped oval, trilobal, tetra-channel (also known as quatra-channel), scalloped ribbon, ribbon, starburst, etc. The filament may be solid, hollow, or multi-hollow, and are preferably solid. The general size of a suitable filament for most applications such as fabrics and carpets is at least about 0.5 dpf (denier per filament), and up to about 35 dpf. The monofilament may be thicker and is from about 10 dpf to about 2000 dpf.

Use of the PTT-based flame retardant compositions of the present invention is preferably for fibrous articles, include filaments, fibers, staple fibers, yarns, fabrics, and carpets.

In one embodiment, use of the flame retardant composition of the present invention is for fibrous articles, films or molded articles. In another embodiment, use of the flame retardant composition of the present invention is for fibrous articles, wherein the fibrous articles include filaments, fibers, staple fibers, yarns, fabrics, or carpets.

PTT-based flame retardant compositions are obtained by blending PTT with the phosphorous containing polyester of Formula 1 (b) and alumina oxide nanoparticles (c). Additionally, the flame retardant compositions of the present invention can be successfully spun into filaments without blocking the spinning die, i.e., good spinability because the phosphorous containing polyester of Formula 1 (b) and alumina oxide nanoparticles (c) were uniformly dispersed in the PTT matrix. Furthermore, the mechanical properties of the fibrous articles produced from the flame retardant compositions are not significantly adversely affected. When compared to PTT fibrous articles without flame retardant, the mechanical properties of the fibrous articles produced from the inventive flame retardant compositions are not significantly worsen, sometimes are even improved.
EXAMPLES

The present invention is exemplarily described in the following examples, however, the scope of the present invention is not limited to the following examples.

Materials

(a) PTT: polytrimethylene terephthalate under trade name of Sorona® semidull grade with intrinsic viscosity (IV) of 1.02 dL/g was obtained from E. I. DuPont de Nemours and Company (DuPont).

(b) ME-P8: phosphorus containing polyester of Formula 1, CAS No. 403614-60-8, was purchased from Sanko Co. Ltd., Japan, the number average molecular weight was about 10,000, and the phosphorus content is 7.8-8.2%.

(c) Alumina oxide nanoparticles: purchased from Hangzhou Wan Jing New Material Co. Ltd., trade name: nano alumina oxide, surface treated with 2% silane coupling agent, particle size was 30-50 nm as measured by TEM.

(d) IRGANOX® 1010: antioxidant, tetrakis(methylene-3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate)methane (CAS No. 6683-19-8), a phenolic antioxidant, purchased from BASF.

Preparation of Flame Retardant Compositions and Test Specimens

1. Melt Blending

The PTT pellets were dried at 120 °C for about 8 hours in a forced air-circulating oven prior to melt blending.

The ingredients of each example and comparative example (according to Table 1) were fed batchwise to a twin screw extruder (Coperion Co. Ltd., ZSK-26 MC) to obtain the corresponding flame retardant composition as pellets. For the extruder of 10 heating blocks configuration, the temperature of the extruder was set to be 180/240/240/240/240/240/240/240/240/240/240/240°C with a die temperature of 230 °C, the screw speed was at 300 rpm with a throughput of 20 Kg/hour. The batch size of each example is about 4.0 Kg (molded articles) or 10 Kg (fibrous articles); moreover, 0.2% of antioxidant was additionally added based on the total weight of each batch.

2. Preparation of Molded Articles

The extruded pellets were dried to a moisture level of less than 40 ppm prior to molding. For flame retardancy testing, test specimen according to GB/T 2406.2-2009 was molded on a Sumitomo 100 Ton molding machine with a screw diameter of 32 mm and a
nozzle diameter of 5 mm. The barrel temperature was set to be 240 °C, and the molding temperature was 80 °C.

The test specimen for mechanical property tests had the basic dumbbell shape, 150 mm long, with the center section 10 mm wide by 4 mm thick by 80 mm long.

The test specimen for flame retardant property tests (LOI) had the rectangle shape with 10 mm wide by 4 mm thick by 80 mm long.

3. Preparation of Fibrous Articles

The extruded pellets were dried in an oven at 120 °C for 8 hours prior to melt spinning, then the dried pellets were metered to a single screw extruder (Fuji E0200), then at suitable temperature (250 °C-270 °C), to a Fuji melt-spinning tester (Model ABE) at the speed of 27 mL/min to obtain the fibers; the Fuji melt-spinning tester was equipped with a 36 hole spinneret pack, with a diameter of 100 mm, each hole has a diameter of 0.3 mm and a L/D ratio of 2. The spun fibers were drawn in a drawing twisting machine (Suzhou Tefa Electromechanical Technology Development Co. Ltd., VC403-01 11) using a hot roller temperature of 65 °C, a hot plate temperature of 135 °C, a drawing speed of 800 meter/min, and the draw ratio was about 1.8, and finally rolled into partially oriented yarns (POY).

The pellets of other Examples and Comparative Examples were all melt spun with same parameters to evaluate the spinability of the respective flame retardant compositions. In addition, the mechanical properties of the as-prepared fibers were tested to evaluate their tenacity and elongation at break.

The as-prepared fibers were knitted into a stocking with a needle pitch of 0.08 mm by a stock knitting machine made by Wuxi Zhenrong Electric Co., Ltd. with model No. of KU482, and then cut open into a rectangular shape with size of 150 mm x 58 mm to evaluate the flame retardancy of the fabrics according to GB/T 5454-1997 for fabrics limiting oxygen index (LOI) test requirements.

**Flame Retardancy Test**

Limiting Oxygen Index (LOI) test was used to evaluate the flame retardancy of the flame retardant compositions. The basic testing and mechanism of LOI test include: placing the test specimen in a transparent cylinder with an upward flowing mixture of nitrogen and oxygen inside, igniting the top of the test specimen to observe the burning, and comparing the continuous burning duration and the burned length with the criteria in relevant standard. A series of tests were done under various oxygen concentrations, and the minimum oxygen concentration needed for burning was recorded.
1. LOI test of molded article: in the present invention, LOI of molded article was tested according to the standard of GB/T 2406.2-2009, and the test equipment was from Textile Research Institute, Shandong Province (Model JF-3LSY-605 automatic oxygen index tester), the testing steps are as follows:

   Igniting the top of the test specimen of molded article in no more than 30 seconds, if the test specimen cannot be ignited, it indicates that the oxygen concentration is too low. Keep increasing the oxygen concentration until the test specimen is ignited, and observing the burning duration and the burned length. If burning duration is more than 180 seconds, or the burned length is greater than 50 mm, it indicates the oxygen concentration used in the test is the minimum oxygen concentration needed for igniting the test specimen.

2. LOI test of textile: LOI of the rectangular fabric is test according to the standard of GB/T 5454-1997, and the test equipment is purchased from Textile Research Institute, Shandong Province (Model JF-3LSY-605 automatic oxygen index tester), the testing steps are as follows:

   Igniting the top of the test specimen of fabric sample in 10-15 seconds, if the test specimen cannot be ignited, it indicates that the oxygen concentration is too low. If the test specimen can be ignited, recording its after-glow duration, sustained burning duration and burned length. If the after-glow duration, or the sustained burning duration, or the total of the after-glow duration and the sustained burning is more than 2 minutes, or the burned length is greater than 40 mm, it indicates the oxygen concentration used in the test is the minimum oxygen concentration needed for igniting the test specimen.

   **Tenacity and Elongation at Break Test**

   Preparation of fibrous test specimen: the fibers prepared through the above spinning process and parameters were measured on an electronic single fiber tensile strength tester (Shimadzu, Japan, AG-XPLUS) at 25 °C and 65 % relative humidity, to obtain the tenacity and elongation at break results. The reported data was the average of 20 measurements.

   The flame retardant compositions of Comparative Examples 1-8 and Examples 1-6 were prepared according to the manner described above, and produced into test specimens (molded specimens) for LOI tests, the test results are shown in Table 1, wherein the LOI result was the average of 2-4 measurements of flame retardant compositions of repeated batches.
Table 1: Formulation of Flame Retardant Compositions and the LOI test results

<table>
<thead>
<tr>
<th>Samples No.</th>
<th>Component and Content*</th>
<th>LOI</th>
</tr>
</thead>
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<td>PTT (a) (weight %)</td>
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<td>Comparative Example 1</td>
<td>100</td>
<td>23.0</td>
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<td>Comparative Example 2</td>
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*The weight percent of each component, 0.2 weight % of antioxidants which was added during melt blending is excluded.

From the results of Table 1, the following are evident.

From Comparative Examples 2-6, it can be seen that when blended with the phosphorous containing polyester of Formula 1 (b) (e.g., ME-P8) only, the flame retardancy of the compositions (e.g., LOI is 23.0 and 27.5) increased as the amount of the phosphorous containing polyester of Formula 1 (e.g., 1 weight % and 10 weight %). From Comparative Examples 7-8, it can be seen that when blended with alumina oxide...
nanoparticles (c) only, the amount of alumina oxide nanoparticles (c) (e.g., 0.5 weight % and 2 weight %) has little effect on the flame retardancy of the compositions (e.g., LOI is 23.0 and 23.5).

From Examples 1-6, it can be seen that when blended with the phosphorous containing polyester of Formula 1 (b) and alumina oxide nanoparticles (c) together, in case of same content of the phosphorous containing polyester of Formula 1 (b), addition of a small amount of alumina oxide nanoparticles (c) provided significant flame retardancy improvement, that means that alumina oxide nanoparticles (c) synergistically improves the flame retardancy of the phosphorous containing polyester of Formula 1 (b).

The fibers produced from the flame retardant compositions of Comparative Example 9 and Examples 7 and 8 were all knitted into fibrous articles according to the manner described above, and the LOT test results are shown in Table 2.

Table 2: Flame Retardancy of Fibrous Articles

<table>
<thead>
<tr>
<th>Samples No.</th>
<th>Component and Content*</th>
<th>LOI</th>
</tr>
</thead>
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<tr>
<td></td>
<td>PTT (a) (weight %)</td>
<td>Phosphorous containing polyester of Formula 1 (b) (weight %)</td>
</tr>
<tr>
<td>Comparative</td>
<td>100</td>
<td>-</td>
</tr>
<tr>
<td>Example 9</td>
<td></td>
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</tr>
<tr>
<td>Example 7</td>
<td>98.5</td>
<td>1</td>
</tr>
<tr>
<td>Example 8</td>
<td>96.5</td>
<td>3</td>
</tr>
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</table>

*The weight percent of each component, 0.2 weight % of antioxidants which was added during melt blending is excluded.

From Table 2, it can be seen that the fabrics produced from the fibers comprising the PTT-based flame retardant compositions of the present invention showed significant improvement in flame retardancy.

The tenacity and elongation at break of the fibers produced from the flame retardant compositions of Comparative Example 9 and Examples 7 and 8 were measured, and the results are shown in Table 3.

Table 3: Mechanical Property of Fibers

<table>
<thead>
<tr>
<th>Samples No.</th>
<th>Tenacity (cN / dtex)</th>
<th>Elongation at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Comparative</td>
<td>2.16</td>
<td>138.6</td>
</tr>
<tr>
<td>Example 7</td>
<td>2.32</td>
<td>140.9</td>
</tr>
<tr>
<td>Example 8</td>
<td>1.84</td>
<td>132.5</td>
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</table>
The results of Table 3 indicate that although the mechanical strength of the fibers produced from the flame retardant compositions of the present invention is slightly reduced (e.g., Example 8), but is still in the acceptable range, or even is increased (e.g., Example 7).

The invention has been described in details in the specification in conjunction with specific embodiments, however, many variations and modifications are apparent to those skilled in the art without departing from the spirit of the present invention. All such variations and modifications are believed to be within the scope as defined by the claims of the present application.
CLAIMS

What is claimed is:
1. A flame retardant composition comprising:
   (a) 74 weight % to 99.4 weight % of polytrimethylene terephthalate;
   (b) 0.5 weight % to 10 weight % of a flame retardant, which is a phosphorous containing polyester of Formula 1:

   ![Chemical Structure](image)

   1

   (c) 0.1 weight % to 6 weight % of alumina oxide nanoparticles; and
   (d) 0 to 10 weight % of an optional additive;

   wherein
   
   n is an integer ranging from 22 to 150; and
   
   the weight percent is based on the total weight of the flame retardant composition.

2. The flame retardant composition of claim 1, wherein the polytrimethylene terephthalate (a) is a polytrimethylene terephthalate homopolymer, a polytrimethylene terephthalate copolymer, or blends thereof, wherein the polytrimethylene terephthalate copolymer contains at least 70 mol % of trimethylene terephthalate as the major copolymerized unit.

3. The flame retardant composition of claim 1, wherein the phosphorous containing polyester of Formula 1 (b) has an average number molecular weight of from 9,000 to 50,000.

4. The flame retardant composition of claim 1, wherein the amount of the phosphorous containing polyester of Formula 1 (b) is from 1 weight % to 6 weight %, and the weight percent is based on the total weight of the flame retardant composition.

5. The flame retardant composition of claim 1, wherein the primary particle size of the alumina oxide nanoparticles (c) is 100 nm or less.
6. The flame retardant composition of claim 1, wherein the amount of the alumina oxide nanoparticles (c) is from 0.2 weight % to 4 weight %, and the weight percent is based on the total weight of the flame retardant composition.

7. The flame retardant composition of claim 1, wherein the optional additive (d) is selected from the group consisting of antioxidants, colorants including dyes and pigments, hydrolysis resistsants, lubricants, nucleating agents, coupling agents, thermal stabilizers, anti-static agents and ultraviolet light stabilizers.

8. An article, which comprises the flame retardant composition of claim 1 or is prepared from the flame retardant composition of claim 1, wherein the article includes a fibrous article, a film, or a molded article.

9. The article of claim 8, wherein the article is a fibrous article.

10. The article of claim 9, wherein the fibrous article is filaments, fibers, staple fibers, yarns, fabrics, or carpets.
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

INV. C09K21/14 C08G63/692 C08L67/02 C08K3/22 D06M15/07

ADD.

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)
C09K C08G C08K D06M D01F

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 practicable, search terms used)
EPO-Internal , WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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<td>JP 2007 112875 A (KANEKA CORP) 10 May 2007 (2007-05-10) cited in the application paragraph [0064]; table 1</td>
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X Further documents are listed in the continuation of Box C. K See patent family annex.

* Special categories of cited documents :
  "A" document defining the general state of the art which is not considered to be of particular relevance
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  "O" document referring to an oral disclosure, use, exhibition or other means
  "P" document published prior to the international filing date but later than the priority date claimed
  "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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  "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
  "Z" document member of the same patent family

Date of the actual completion of the international search
22 May 2014

Date of mailing of the international search report
30/05/2014

Name and mailing address of the ISA/
European Patent Office, P.B. 5818 Patentlaan 2
NL-2280 HV Rijswijk
Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016

Authorised officer
Kappen, Sascha
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Form PCT/DA/210 (continuation of second sheet) (Apr. 2005)
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