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(54) Title: POLYMER FIBER CONTAINING FLAME RETARDANT, PROCESS FOR PRODUCING THE SAME, AND MA-
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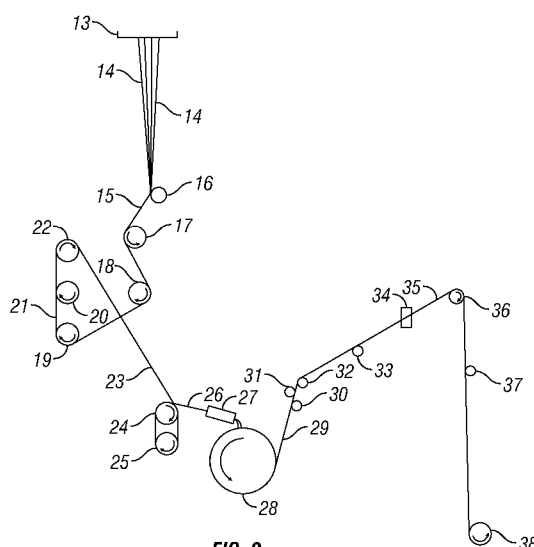


FIG. 2

(57) Abstract: A flame retardant polymer fiber, a process for making such a fiber, and a material containing such fibers are pro-
vided. The flame retardant polymer fiber is a high tenacity fiber formed of a poly(trimethylene terephthalate) co-polymer containing
a trimethylene terephthalate monomer and a phosphorous containing flame retardant monomer. The flame retardant PTT co-polymer
fiber is produced by a process in which the trimethylene terephthalate monomer or its precursors and the phosphorous containing
flame retardant monomer or its precursors are combined to form the PTT co-polymer in one or more pre-polymerization and poly-
merization steps, and the PTT co-polymer is spun into a fiber. Materials including such flame retardant PTT co-polymer fibers, e.g.
Carpets and textiles, are also provided.

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**POLYMER FIBER CONTAINING FLAME RETARDANT, PROCESS FOR
PRODUCING THE SAME, AND MATERIAL CONTAINING SUCH FIBERS**

Field of the Invention:

5 The present invention is directed to a polymer fiber containing a flame retardant, a process for producing the fiber, and materials containing the fiber. More particularly, the present invention is directed to a polymer fiber containing a flame retardant co-polymer component, a process for producing the same, and a material containing such fibers.

Background of the Invention

10 Flame retardants are frequently added to or incorporated in polymers to provide flame retardant properties to the polymers. The flame retardant polymers may then be spun into fibers that may be used in applications in which resistance to flammability is desirable, for example, in textile or carpet applications.

 A large variety of compounds have been used to provide flame retardancy to
15 polymers. For example, numerous classes of phosphorous containing compounds, halogen containing compounds, and nitrogen containing compounds have been utilized as flame retardants in polymers. Classes of halogen containing compounds that have been used as flame retardants in polymers include polyhalogenated hydrocarbons. Classes of
20 phosphorous containing compounds that have been used as flame retardants in polymers include inorganic phosphorous compounds such as red phosphorous, monomeric organic phosphorous compounds, orthophosphoric esters or condensates thereof, phosphoric ester amides, phosphonitrilic compounds, phosphine oxides (e.g. triphenylphosphine oxides), and metal salts of phosphinic, phosphoric, and phosphonic acids. The metal salts of
25 phosphinic acids (metal salt phosphinates) that have been utilized as flame retardants in polymers comprise a large variety of compounds themselves, including monomeric, oligomeric, and polymeric species with one, two, three, or four phosphinate groups per coordination center including metals selected from beryllium, magnesium, calcium, strontium, barium, titanium, zirconium, vanadium, antimony, bismuth, chromium, molybdenum, tungsten, manganese, iron, ruthenium, cobalt, rhodium, iridium, nickel,
30 platinum, palladium, copper, silver, zinc, cadmium, mercury, aluminum, tin, and lead.

 Such flame retardant compounds have been used in a wide variety of polymers. For example, phosphorous containing compounds have been used as flame retardants in polymers such as polymers of mono- and di-olefins such as polypropylene,

polyisobutylene, polyisoprene, and polybutadiene; aromatic homopolymers and copolymers derived from vinyl aromatic monomers such as styrene, vinyl naphthalene, and p-vinyltoluene; hydrogenated aromatic polymers such as polycyclohexylethylene; halogen containing polymers such as polychloroprene and polyvinylchloride; polymers derived
5 from α,β -unsaturated acids and derivatives thereof such as polyacrylates and polyacrylonitriles; polyamides such as poly(ϵ -caproamide) sold as NYLON-6 and poly(hexamethylene adipamide) sold as NYLON-6,6; polysulfones; and polyesters such as polyethylene terephthalate (PET) and polybutylene terephthalate (PBT).

Poly(trimethylene terephthalate) ("PTT") is a polyester that has recently been
10 commercially developed as a result of the recent availability of commercial quantities of 1,3-propanediol, a requisite compound for forming PTT. PTT has an array of desirable characteristics when used in fiber applications relative to other polymers used in fiber applications such as polyamides, polypropylenes, and its polyester counterparts PET and PBT, such as soft touch, good stain resistance, and resilience and shape recovery due to its
15 spring-like molecular structure.

It is desirable to provide PTT fibers with flame retardant properties by incorporating a flame retardant in PTT fibers. Incorporation of a flame retardant in a PTT fiber, however, has proven difficult since PTT fibers containing effective amounts of flame retardants are prone to breakage during spinning of the fiber due to the presence of the
20 flame retardant in the PTT. As a result, a PTT fiber having a high tenacity, for example a tenacity of at least 1.5 gram per denier (g/d), and an effective amount of flame retardant has proven elusive. A PTT fiber having a high tenacity is necessary to produce quality yarns, carpets, and textiles from the PTT fiber. It would be useful to have a PTT fiber containing a highly effective flame retardant in which the fiber has a tenacity of at least 1.5
25 g/d, where the fiber has reduced flame retardant induced breakage when melt spun relative to presently available PTT fibers containing flame retardants.

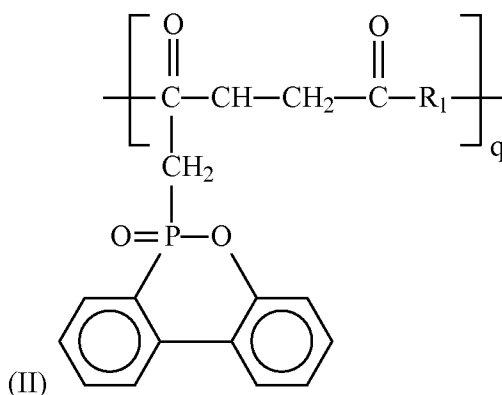
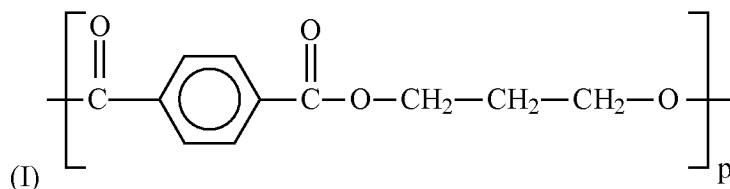
U.S. Patent Nos. 4,180,495; 4,208,321; and 4,208,322 provide poly(metal phosphinate) flame retardants that may be added to polyester resins, polyamide resins, or polyester-polyamide resins. Among several other applications, the resins may be spun into
30 fibers and thereafter be made into fabric and clothing. One of the polyester resins to which such flame retardants may be added is PTT. The list of poly(metal phosphinate) flame retardants that may be added to the polyester, polyamide, or polyester-polyamide resins is extensive, and includes the metal salts of phosphinic acids (metal salt phosphinates) listed

above—e.g. monomeric, oligomeric, and polymeric species with one, two, three, or four phosphinate groups per coordination center including metals selected from beryllium, magnesium, calcium, strontium, barium, titanium, zirconium, vanadium, antimony, bismuth, chromium, molybdenum, tungsten, manganese, iron, ruthenium, cobalt, rhodium, iridium, nickel, platinum, palladium, copper, silver, zinc, cadmium, mercury, aluminum, tin, and lead. The poly(metal phosphinate) flame retardants may be utilized in the polymers in an amount from 0.25 to 30 parts by weight per 100 parts by weight of polymer resin. These references, however, do not provide a PTT fiber having a high tenacity, e.g. a tenacity of at least 1.5 g/d, containing an effective amount of flame retardant since they do not provide a PTT fiber that is not prone to breakage in melt spinning due to the presence of the flame retardant in the PTT when the flame retardant is present in amounts sufficient to effectively reduce the flammability of the fiber.

Co-polymers comprising a polyester and a flame retardant monomer are also known. Synthesis and Characterization of Copolyesters Containing the Phosphorous Linking Pendent Groups, *J. App. Polymer Sci.*, Vol. 72, 109-122 (1999) provides a flame retardant poly(ethylene terephthalate)-co-poly(ethylene 9,10-dihydro-10[2,3-di-(hydroxy carbonyl)propyl]-10-phosphaphenanthrene-10-oxide) [PET-co-PEDDP] co-polymer. The flame retardant PET-co-PEDDP co-polymer provides improved flame retardant characteristics relative to a PET homopolyester. The PET-co-PEDDP co-polymer, however, has a significantly decreased tensile strength relative to the PET homopolyester, where inclusion of 0.7 wt.% of phosphorous (from the flame retardant) in the co-polymer reduces that tensile strength by a third, and increasing levels of phosphorous from the flame retardant further decrease the tensile strength of the co-polymer. The tensile strength of a polymer is related to its tenacity, as both are measures of tensile stress—therefore, the PET-co-PEDDP co-polymer would be expected to have a significantly lower tenacity than a PET homopolyester since the co-polymer has significantly decreased tensile strength relative to the homopolyester.

Summary of the Invention

In one aspect, the invention is directed to a flame retardant polyester fiber comprised of a polymer formed of from 50 mol% to 99.9 mol% of a trimethylene terephthalate component of formula (I) and from 0.1 mol% to 50 mol% of a phosphorous containing component of formula (II)



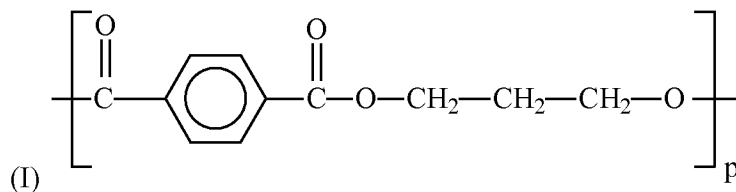
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where p is from 1 to 2500, q is from 1 to 1250, and R_1 is an alkyl alcohol residuum having from 1 to 5 carbon atoms, an alkyl acid residuum having from 1 to 5 carbon atoms, an alkyl ester residuum having from 1 to 5 carbon atoms, or an oxygen atom;

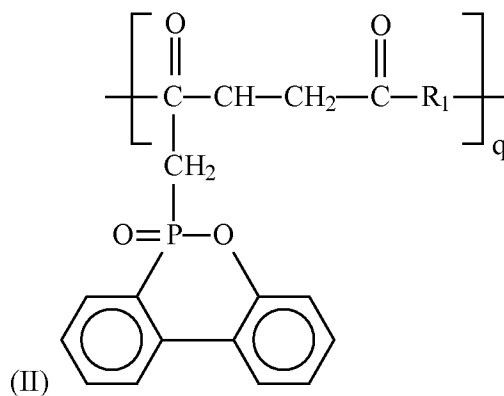
where the fiber has a tenacity of at least 1.5 g/d.

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In another aspect, the invention is directed to a material comprising a plurality of fibers wherein at least 5% of the fibers are comprised of a polymer comprised of from 50 mol% to 99.9 mol% of a trimethylene terephthalate component of formula (I) and from 0.1 mol% to 50 mol% of a phosphorous containing component of formula (II)



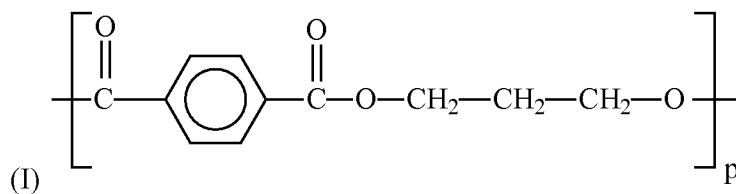
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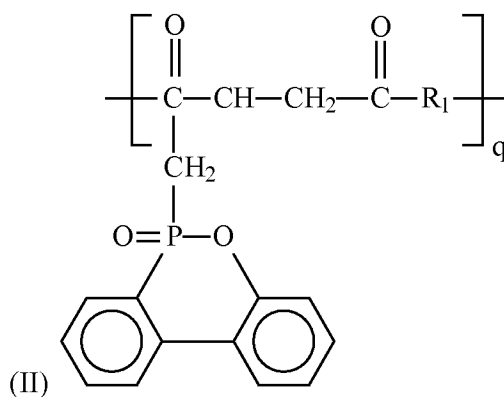
where p is from 1 to 2500, q is from 1 to 1250, and R₁ is an alkyl alcohol residuum having from 1 to 5 carbon atoms, an alkyl acid residuum having from 1 to 5 carbon atoms, an alkyl ester residuum having from 1 to 5 carbon atoms, or an oxygen atom.

In another aspect, the invention is directed to a process for producing a flame retardant polyester fiber, comprising:

providing a flame retardant poly(trimethylene terephthalate) co-polymer comprising from 50 mol% to 99.9 mol% of a trimethylene terephthalate component of formula (I) and from 0.1 mol% to 50 mol% of a phosphorous containing component of formula (II)



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where p is from 1 to 2500, q is from 1 to 1250, and R₁ is an alkyl alcohol residuum having from 1 to 5 carbon atoms, an alkyl acid residuum having from 1 to 5 carbon atoms, an alkyl ester residuum having from 1 to 5 carbon atoms, or an oxygen atom;

heating the poly(trimethylene terephthalate) co-polymer to a temperature of from
5 240°C to 280°C to melt the co-polymer; and
passing the molten poly(trimethylene terephthalate) co-polymer through a spinneret to form a fiber.

Brief Description of the Drawings

Advantages of the present invention will become apparent to those skilled in the art
10 with the benefit of the following detailed description and upon reference to the accompanying drawings in which:

FIG. 1 is a schematic of a process for producing a fiber of the present invention incorporated into a yarn.

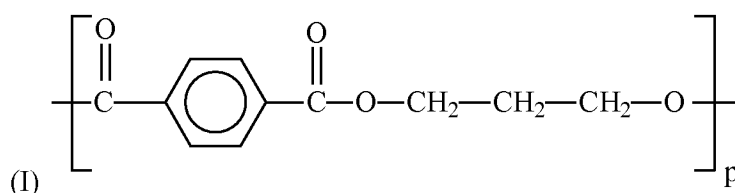
FIG. 2 is a schematic of a process for producing a fiber of the present invention as a
15 bulk continuous filament.

Detailed Description of the Invention

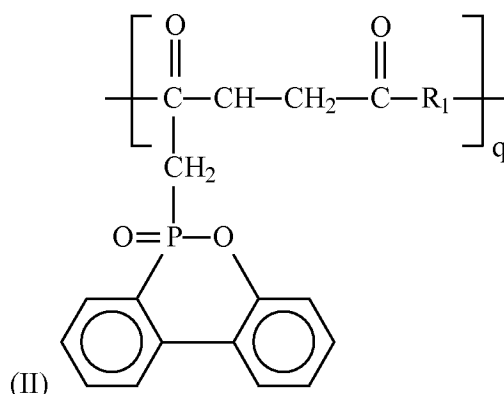
The present invention provides a flame retardant polymer fiber comprised of a poly(trimethylene terephthalate) co-polymer containing a flame retardant phosphorous component and trimethylene terephthalate as monomers in the co-polymer. Surprisingly
20 the co-polymer fiber does not have significantly reduced tenacity relative to a PTT homopolymer fiber when the phosphorous containing component is included in the co-polymer fiber in an amount sufficient to provide effective flame retardancy to the fiber. The PTT co-polymer fiber of the present invention may exhibit a tenacity of at least 1.5 grams/denier (hereinafter "g/d"), or at least 1.6 g/d, or at least 1.7 g/d. The flame retardant
25 PTT co-polymer fiber's maintenance of a relatively high tenacity as compared with a PTT homopolymer was unexpected since analogous (e.g. containing the same or substantially similar flame retardant monomer) flame retardant poly(ethylene terephthalate) (PET) co-polymers exhibit a substantial decrease of tensile strength relative to a PET homopolymer. Tensile strength and tenacity are each measures of tensile stress, so a significant decrease
30 in tensile strength in the flame retardant PET co-polymer relative to a PET homopolymer would be expected to correlate to a similar decrease in tenacity in an analogous flame retardant PTT co-polymer relative to a PTT homopolymer.

The high tenacity flame retardant PTT co-polymer fiber of the present invention has sufficient strength to be formed into flame retardant yarns that may be used to produce flame retardant materials such as carpets and textiles. Unlike PTT polymers combined with flame retardant additives, the flame retardant PTT co-polymer fiber of the invention has a flame retardant component incorporated into the polymer itself so the flame retardancy of the polymer is uniformly distributed in the fiber, and the flame retardant is not subject to being gradually removed from the fiber. Further, the high tenacity flame retardant PTT co-polymer fiber may be spun without significant fiber breakage due to either the low tenacity/tensile stress of the fiber or due to particulate flame retardant additives.

The flame retardant PTT co-polymer fiber of the present invention is comprised of a PTT containing co-polymer comprising at least 50 mol%, or at least 80 mol%, or at least 95 mol%, or at least 97 mol%, or from 50 mol % to 99.9 mol %, or from 70 mol % to 99.5 mol %, or from 80 mol % to 95 mol % of a trimethylene terephthalate monomer, shown as Formula (I)

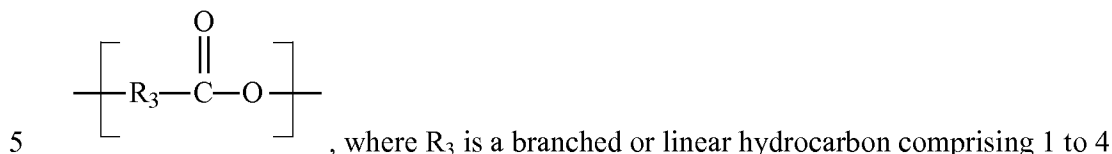


and greater than 0 mol% but at most 50 mol%, or at most 30 mol%, or at most 20 mol%, or at most 10 mol%, or from 0.1 mol % to 50 mol %, or from 0.5 mol % to 30 mol %, or from 5 mol % to 20 mol % of a phosphorous containing monomer of formula (II).



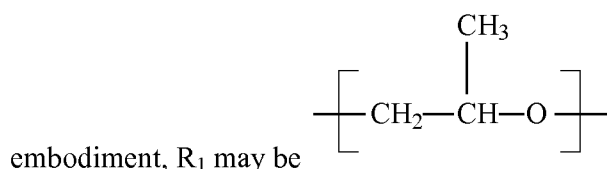
In formula (I), p may be from 1 to 2500, and preferably is from 4 to 250. In formula (II), q may be from 1 to 1250, or from 1 to 10, and preferably is from 1 to 5. In formula (II), R₁ may be an alkyl alcohol residuum having from 1 to 5 carbon atoms, an alkyl acid residuum

having from 1 to 5 carbon atoms, an alkyl ester residuum having from 1 to 5 carbon atoms, or an oxygen atom. An alkyl alcohol residuum, as used herein, has the structure of $-\text{[R}_2\text{-O]}-$, where R_2 is a branched or linear hydrocarbon comprising 1 to 5 carbon atoms. An alkyl acid residuum and an alkyl ester residuum, as used herein, may have the structure of



carbon atoms. In one embodiment, R_1 may be

$-\text{[CH}_2\text{-CH}_2\text{-CH}_2\text{-O]}-$. In another embodiment, R_1 may be $-\text{[CH}_2\text{-CH}_2\text{-O]}-$. In another



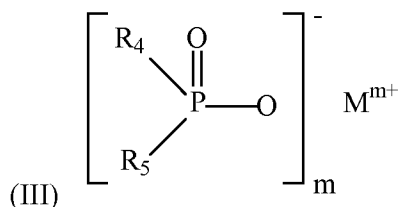
The flame retardant PTT containing co-polymer fiber of the present invention may also contain minor amounts of monomers other than the trimethylene terephthalate component of formula (I) and the phosphorous containing component of formula (II). Such monomers include, but are not limited to, esterification products of one or more diols selected from the group consisting of ethylene glycol, 1,3-propanediol, 1,4-butanediol, 1,4-butenediol, and 1,4 cyclohexanedimethanol with a dicarboxylic acid selected from the group consisting of oxalic acid, succinic acid, phthalic acid, 2,6-naphthalenedicarboxylic acid, 5-sodiumsulfoisophthalic acid, isophthalic acid, adipic acid, terephthalic acid (except with 1,3-propanediol, which would form a trimethylene terephthalate monomer), and mixtures thereof; or transesterification products of one or more of the diols listed above with one or more esters of one or more of the dicarboxylic acids listed above. The PTT containing co-polymer fiber may contain up to 25 mol % of these monomers, or may contain at most 15 mol %, or at most 10 mol %, or at most 5 mol % of these monomers. The flame retardant PTT containing co-polymer fiber of the present invention may also contain no monomers other than the trimethylene terephthalate component of formula (I) and the phosphorous containing component of formula (II).

Other polymers may be included in minor amounts in the flame retardant PTT containing co-polymer fiber of the present invention along with the flame retardant PTT containing co-polymer. Polymers that may also be included in the flame retardant PTT containing co-polymer fiber include polysulfones, polyesters such as poly(ethylene

terephthalate), poly(butylene terephthalate), poly(ethylene naphthalate) and poly(trimethylene naphthalate), and polyamides such as poly(ϵ -caproamide) (NYLON-6) and poly(hexamethylene adipamide)(NYLON-6,6). The polymers that may be included in the fiber of the present invention with the flame retardant PTT containing co-polymer do not exceed 25 wt.%, or 15 wt. %, or 10 wt. %, or 5 wt. % of the composition. In an embodiment of the composition of the invention, the flame retardant PTT containing co-polymer may be present in the fiber in a weight ratio to other polymers of at least 3:1, or at least 4:1, or at least 5:1, or at least 6:1. In an embodiment, no other polymer is present in the flame retardant PTT containing co-polymer fiber other than the PTT containing co-polymer itself.

The flame retardant PTT co-polymer fiber of the present invention has a tenacity of at least 1.5 g/d. In an embodiment of the fiber of the present invention, the fiber may have a tenacity of at least 1.6 g/d, or at least 1.7 g/d. Tenacity, for purposes of the present invention, is measured with a Statimat ME tester with a load cell of 100 newtons. A pretension force of 0.05 g/d is applied to the fiber/yarn with a gauge length of 110 mm, and the tenacity is measured at a cross-head speed of 300 mm/min. The test is repeated ten times on segments of a selected yarn or fiber, and the average value of the ten measurements is defined as the tenacity of the yarn or fiber for purposes of the present invention.

The flame retardant PTT co-polymer fiber of the invention may contain dispersed therein minor amounts of a flame retardant component that does not have a melting point equal to or below 280°C, which is defined for purposes of the present invention as a "non-fusible flame retardant component". The non-fusible flame retardant component, if present, does not have a melting point equal to or below 280°C, although the non-fusible flame retardant component may, but does not necessarily, have a melting point above 280°C since the non-fusible flame retardant component may decompose rather than melt at temperatures above 280°C. Such non-fusible flame retardants may include: phosphinate metal salts of the formula (III) that do not melt at or below a temperature of 280°C



where R_4 and R_5 may be identical or different, and are C_1 - C_{18} alkyl, linear or branched, and/or aryl, M is Mg, Ca, Al, Sb, Ge, Ti, Fe, Zr, Ce, Bi, Sr, Mn, Li, Na, or K, and m is from 1 to 4; other phosphorous containing compounds that are non-fusible at a temperature of equal to or below 280°C , including inorganic phosphorous compounds such as red phosphorous; monomeric organic phosphorous compounds; orthophosphoric esters or condensates thereof; phosphoric ester amides; phosphonitrilic compounds; phosphine oxides (e.g. triphenylphosphine oxides); metal salts of phosphoric and phosphonic acids; diphosphinic salts; nitrogen containing compounds such as benzoguanamine compounds, ammonium polyphosphate, and melamine compounds such as melamine borate, melamine oxalate, melamine phosphate, melamine pyrophosphate, polymeric melamine phosphate, and melamine cyanurate; and polyhalogenated hydrocarbons.

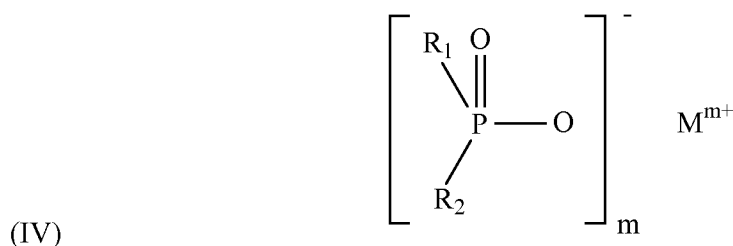
If present, the non-fusible flame retardant component in the fiber is present as a minor component of the flame retardant PTT co-polymer fiber so that the non-fusible flame retardant will not negatively affect the melt spinning of the fiber by inducing breakage in the fiber as it is spun. The non-fusible flame retardant component may comprise from 0 wt.% to 5 wt.%, or from 0 wt.% to 2.5 wt.%, or from 0 wt.% to 1 wt.% of the flame retardant PTT co-polymer fiber.

If present, the non-fusible flame retardant component in the fiber may be particulate. The particle size of the non-fusible flame retardant component of the fiber of the invention may range up to a mean particle size of $150\ \mu\text{m}$. In an embodiment, the mean particle size of the non-fusible flame retardant component may be at most $10\ \mu\text{m}$, or the non-fusible flame retardant may contain nanoparticles and may have a mean particle size of at most $1\ \mu\text{m}$. Smaller mean particle size of the non-fusible flame retardant in the fiber provides at least two benefits: 1) a more homogeneous dispersion of the particulate flame retardant in the fiber; and 2) reduced breakage in melt spinning the fibers as a result of few or no large particulates in the polymer melt as it is spun into the fiber.

In an embodiment, the flame retardant PTT co-polymer fiber of the present invention may contain dispersed therein minor amounts of a flame retardant component

that has a melting point equal to or below 280°C, which is defined for purposes of the present invention as a "fusible flame retardant component". The fusible flame retardant component may be at least one flame retardant fusible phosphinate metal salt having a melting point of equal to or below 280°C, or below 270°C, or below 250°C, or below 230°C, or below 200°C, or below 180°C.

The flame retardant fusible phosphinate metal salt(s) may be any phosphinate metal salt having the structure shown in formula (IV) and having a melting point equal to or below 280°C, or below 270°C, or below 250°C, or below 230°C, or below 200°C, or below 180°C.



In formula (IV), R₁ and R₂ may be identical or different, and are C₁-C₁₈ alkyl, linear or branched, and/or aryl, M is Mg, Ca, Al, Sb, Ge, Ti, Fe, Zr, Ce, Bi, Sr, Mn, Li, Na, or K, and m is from 1 to 4. The flame retardant fusible phosphinate metal salt must have a melting point equal to or below 280°C, or below 270°C, or below 250°C, or below 230°C, or below 200°C, or below 180°C so that it may be melted and dispersed in the PTT co-polymer at a temperature that will not substantially degrade the co-polymer.

In a preferred embodiment, the flame retardant fusible phosphinate metal salt is a zinc phosphinate having a melting point equal to or below 280°C, or below 270°C, or below 250°C, or below 230°C, or below 200°C, or below 180°C and having the structure of formula (IV) where R₁ and R₂ are identical or different and are hydrogen, C₁-C₁₈ alkyl, linear or branched, and/or aryl, M is zinc, and m is 2. In one embodiment the zinc phosphinate has a melting point of equal to or below 280°C, or below 270°C, or below 250°C, or below 230°C, or below 200°C, or below 180°C and is of the formula (IV), where R₁ and R₂ are identical or different and are methyl, ethyl, isopropyl, n-propyl, t-butyl, n-butyl, or phenyl, M is zinc, and m is 2. In a preferred embodiment, the zinc phosphinate is selected from the group consisting of zinc diethylphosphinate, zinc dimethylphosphinate,

zinc methylethylphosphinate, zinc diphenylphosphinate, zinc ethylbutylphosphinate, and zinc dibutylphosphinate. In a most preferred embodiment, the zinc phosphinate is zinc diethylphosphinate.

If present, the fusible flame retardant component is present as a minor component
5 of the flame retardant PTT co-polymer fiber. The fusible flame retardant component may comprise from 0 wt.% to 5 wt.%, or from 0 wt.% to 2.5 wt.%, or from 0 wt.% to 1 wt.% of the flame retardant PTT co-polymer fiber. In an embodiment, the flame retardant PTT co-polymer fiber may contain minor amounts of both a fusible flame retardant component and a non-fusible flame retardant component. If both a fusible flame retardant component and
10 a non-fusible flame retardant component are present in the flame retardant PTT co-polymer fiber, the combined fusible and non-fusible flame retardant components may comprise up to 5 wt.%, or up to 2.5 wt. %, or up to 1 wt. % of the flame retardant PTT co-polymer fiber.

In an embodiment of the invention, the flame retardant PTT co-polymer fiber may contain a filler. "Filler" as the term is used herein is defined as "a particulate or fibrous
15 material having no flame retardant activity". Too much filler may negatively affect the melt spinning of the fiber of the present invention by inducing breakage in the fiber as it is spun, therefore, the fiber may contain from 0 wt.% to 5 wt.% filler, or may contain from 0 wt.% to 3 wt.% filler. In an embodiment of the fiber of the present invention, a filler may be included in the fiber as a delusterant. A preferred filler for inclusion in the fiber as a
20 delusterant is titanium dioxide. Other examples of filler materials that may be included in the fiber include fibrous materials such as glass fiber, asbestos fiber, carbon fiber, silica fiber, fibrous woolastonite, silica-alumina fiber, zirconia fiber, potassium titanate fiber, metal fibers, and organic fibers with melting points above 300°C; and particulate or amorphous materials such as carbon black, white carbon, silicon carbide, silica, powder of
25 quartz, glass beads, glass powder, milled fiber, silicates such as calcium silicate, aluminum silicate, clay, and diatomites, metal oxides such as iron oxide, zinc oxide, and alumina, metal carbonates such as calcium carbonate and magnesium carbonate, metal sulfates such as calcium sulfate and barium sulfate, and metal powders.

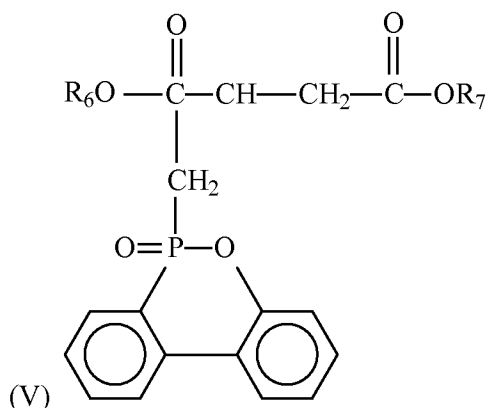
In an embodiment, the flame retardant PTT co-polymer fiber of the present
30 invention may contain one or more modifying agents to provide selected properties to the fiber. "Modifying agent", as the term is used herein, is defined as a material useful to modify the physical, chemical, color, or electrical characteristics of the flame retardant PTT co-polymer fiber, excluding the filler materials and non-fusible flame retardants

discussed above. Modifying agents may include conventional antioxidants, lubricants, dyes and other colorants, UV absorbers, and antistatic agents.

The flame retardant PTT co-polymer fiber of the present invention may be undrawn, partially oriented, or fully oriented depending on the conditions used to produce the fiber. An undrawn fiber of the present invention is defined herein as a fiber comprising a PTT co-polymer as described above having an elongation to break of at least 120 %. The undrawn fiber may have a birefringence of less than 0.3 or less than 0.2. A partially oriented fiber of the present invention is defined herein as a fiber comprising a PTT co-polymer as described above having an elongation to break of from 50 % up to 120 %. The partially oriented fiber may have a birefringence of from 0.3 up to 0.9. A fully oriented fiber of the present invention is defined herein as a fiber comprising a PTT co-polymer as described above having an elongation to break of up to 50%. The fully oriented fiber may have a birefringence of greater than 0.9.

The flame retardant PTT co-polymer fiber of the present invention has fiber-like dimensions, namely, that the length of the fiber is much greater than the width or diameter of the fiber. The fiber has a length of at least 100 times the width of the fiber, and, in one embodiment, has a length of at least 1000 times the width of the fiber. In one embodiment the fiber may be a filament, e.g. a fiber of extreme length. In one embodiment the fiber is a bulk continuous filament in which the filament has been textured, e.g. by jet air texturing, to provide the filament with bulk. In another embodiment, the fiber may be a staple fiber having a length of from 0.5 cm to 15 cm (0.2 in. to 6 in.).

In one aspect, the present invention is directed to a process for producing the fiber of the present invention. In an embodiment, the fiber may be produced by co-polymerizing a trimethylene terephthalate containing material and a phosphorous containing compound of formula (V)



where R₆ and R₇ may be the same or different and are a hydrogen atom, an alkyl hydrocarbon group having from 1 to 5 carbons, or an alkyl alcohol group having from 1 to 5 carbons and one or more alcohol substituents to form a flame retardant PTT containing polymer (the PTT co-polymer) having an intrinsic viscosity of at least 0.7 dl/g, then
5 passing the PTT co-polymer in a molten phase through a spinneret to form the fiber.

In an embodiment, the trimethylene terephthalate containing material and the phosphorous containing compound of formula (V) may be contacted at a temperature of from 230°C to 280°C and a pressure of from 0.01 kPa to 5 kPa (0.1 mbar to 50 mbar) to co-polymerize the trimethylene terephthalate containing material and the phosphorous
10 containing compound. In an embodiment, the amounts of the trimethylene terephthalate containing material and the phosphorous containing compound of formula (V) utilized in the co-polymerization may be selected to provide a mole ratio of trimethylene terephthalate to phosphorous containing compound of from 1:1 to 999:1.

In an embodiment, the flame retardant PTT containing polymer for use in forming
15 the fiber may be produced by 1) reacting terephthalic acid with 1,3-propanediol to form a trimethylene terephthalate containing material which may comprise trimethylene terephthalate and/or an oligomer thereof (the esterification step); and 2) co-polymerizing the trimethylene terephthalate containing material with a phosphorous containing compound of formula (V) (the co-polymerization step).

20 In the esterification step, the pressure may be adjusted to and maintained in a range of from 70 kPa to 550 kPa (0.7 bar to 5.5 bar) and the temperature may be adjusted to and maintained in the range of from 230°C to 280°C, or from 240°C to 270°C. In an embodiment of the process, the instantaneous concentration of unreacted 1,3-propanediol in the reaction mass in the esterification step may be kept low to minimize formation of
25 dipropyleneglycol by regulation of the reactant feeds—e.g. 1,3-propanediol and terephthalic acid may be regulated such that they are added to the reaction mass in a molar ratio of 1.15:1 to 2.5:1 to minimize formation of dipropylene glycol—and the reaction pressure may be kept low, e.g. less than 300 kPa absolute (3 bar absolute), to remove excess unreacted 1,3-propanediol from the reaction medium in the reaction overhead gases.

30 In an embodiment, minor amounts of other compounds may be included in the esterification step that may be incorporated into the trimethylene terephthalate containing material. For example, compounds such as ethylene glycol, 1,4 butanediol, 1,4-butanediol, 1,4-cyclohexanedimethanol, oxalic acid, succinic acid, phthalic acid, 2,6-

naphthalenedicarboxylic acid, 5-sodiumsulfoisophthalic acid, isophthalic acid, and/or adipic acid may be included in the esterification step. Such compounds may be included in amounts that they comprise, along with any other such compounds utilized in the co-polymerization step, at most 25 mol%, or at most 15 mol%, or at most 10 mol%, or at most 5 mol% of the final PTT containing co-polymer composition to be spun into fiber.

An esterification catalyst may be used to promote the esterification reaction. Esterification catalysts useful for promoting the esterification reaction include titanium and zirconium compounds, including titanium alkoxides and derivatives thereof such as tetra(2-ethylhexyl)titanate, tetrastearyl titanate, diisopropoxy-bis(acetylacetonato)titanium, tributyl monacetyltitanate, triisopropyl monoacetyltitanate; di-n-butoxy-bis(triethanolaminoato)titanium, tetrabenzoic acid titanate, and titanium tetrabutoxide; titanium complex salts such as alkali titanium oxalates and malonates, potassium hexafluorotitanate and titanium complexes with hydroxycarboxylic acids such as tartaric acid, citric acid, or lactic acid, catalysts such as titanium dioxide/silicon dioxide co-precipitate and hydrated alkaline-containing titanium dioxide; and the corresponding zirconium compounds. Catalysts of other metals, such as antimony, tin, and zinc, may also be used. A preferred catalyst for use in promoting the esterification reaction is titanium tetrabutoxide. The esterification catalyst may be provided to the esterification reaction mass in an amount effective to catalyze the esterification, and may be provided in an amount in the range of 5 to 250 ppm (metal), or in the range of 10 ppm to 100 ppm (metal), based on the weight of the final PTT containing co-polymer composition to be spun into fiber.

The esterification may be carried out in stages in a single or multiple vessels at one or more temperatures and/or pressures with one or more catalysts or catalyst amounts present in each stage. For example, a two-stage esterification step may include a first stage carried out in a first esterification vessel at or a little above atmospheric pressure in the presence of 5 to 50 ppm titanium catalyst and a second stage carried out in a second esterification vessel at or below atmospheric pressure with an additional 20 to 150 ppm of titanium catalyst added, where both stages are conducted at a temperature of from 230°C to 280°C, or from 240°C to 270°C. The first esterification stage may be conducted until a selected amount of terephthalic acid is consumed, for example, at least 80%, or at least 85%, or at least 90%, or at least 95%, or from 85% to 95%. The second esterification stage may also be conducted until a selected amount of terephthalic acid is consumed, for

example, at least 97%, or at least 98%, or at least 99%. In a continuous process, the esterification steps may be carried out in separate reaction vessels.

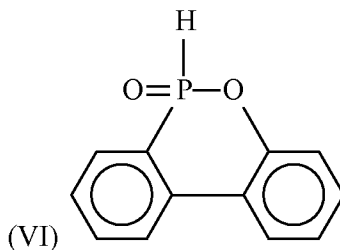
The conditions of the esterification may be selected to produce a low molecular weight oligomeric esterification product containing trimethylene terephthalate monomers.

- 5 The oligomeric trimethylene terephthalate containing material may have an intrinsic viscosity of less than 0.2 dl/g, or from 0.05 to 0.15 dl/g (corresponding to a degree of polymerization of 3 to 10, e.g. the value of p of formula (I) above is from 3 to 10).

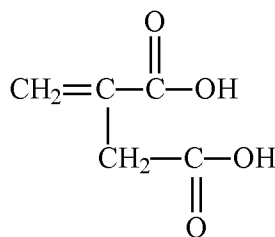
- In the co-polymerization step, the trimethylene terephthalate containing material produced in the esterification step may be contacted and mixed with the phosphorous containing compound of formula (V) under conditions effective to induce co-polymerization of the trimethylene terephthalate containing material and the phosphorous containing compound. The co-polymerization step may comprise several steps, for example: a pre-polycondensation step in which the reaction mixture containing the trimethylene terephthalate containing material and the phosphorous containing compound of formula (V) may be processed under selected temperature and pressure conditions to produce a product having an intrinsic viscosity of from 0.15 to 0.4 dl/g (corresponding to a degree of polymerization of 10 to 30, e.g., the sum of the values of p of formula (I) and q of formula (II) is from 10 to 30); a melt polycondensation step in which the reaction mixture comprising the product of the pre-polycondensation step or alternatively, the trimethylene terephthalate containing material from the esterification step and the phosphorous containing compound of formula (V), may be processed under selected temperature and pressure conditions to produce a melt co-polymer product having an intrinsic viscosity of at least 0.25 dl/g or least 0.7 dl/g, or at least 0.8 dl/g, or at least 0.9 dl/g; and a solid state polymerization step in which the melt co-polymer may be solidified, optionally dried and annealed, heated, and charged to a solid state polymerization reactor for further polycondensation to raise the intrinsic viscosity of the co-polymer. The co-polymerization step may optionally contain fewer than the three steps specified above, for example, an all melt PTT co-polymer may be produced by omitting the solid state polymerization step, where the pre-polycondensation step and the melt polycondensation step produce a melt co-polymer having a intrinsic viscosity of at least 0.7 dl/g, or at least 0.8 dl/g, or at least 0.9 dl/g.
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The phosphorous containing compound of formula (V) where R₆ and R₇ are both hydrogen atoms may be produced by reacting equimolar amounts of 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide, shown as formula (VI),

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with itaconic acid, shown as formula (VII),



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at a temperature of from 120°C to 200°C or from 140°C to 180°C for a period effective to convert at least a majority, or at least 75%, or at least 85%, or at least 90% of the reactants to the phosphorous compound of formula (V) where R₆ and R₇ are hydrogen atoms, which may be a period of at least 15 minutes, or at least 30 minutes, or at least 60 minutes, or at least 90 minutes. In an embodiment, the preparation of the phosphorous compound of formula (V) may be conducted under an inert atmosphere, for example under a nitrogen atmosphere. Where R₆ and/or R₇ of the phosphorous compound of formula (V) are an alkyl hydrocarbon group having from 1 to 5 carbons, the phosphorous compound of formula (V) having R₆ and R₇ hydrogen atoms may be reacted with an alkyl alcohol to produce the desired phosphorous compound, where the molar ratio of the alkyl alcohol to the phosphorous compound may range from 0.5:1 to 2.5:1, or from 1:1 to 2:1. Where R₆ and/or R₇ of the phosphorous compound of formula (V) are an alkyl alcohol group having 1 to 5 carbon atoms and having one or more alcohol substituents, the phosphorous compound of formula (V) having R₆ and R₇ hydrogen atoms may be reacted with an alkyl

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diol or polyol to produce the desired phosphorous compound, where the molar ratio of the alkyl diol or polyol to the phosphorous compound may range from 0.5:1 to 2.5:1, or from 1:1 to 2:1. The phosphorous compound having R₆ and R₇ hydrogen atoms and the alkyl alcohol, diol, or polyol may be reacted at a temperature of from 75°C to 200°C, or from 100°C to 150°C for a period of time effective to replace the R₆ and/or R₇ hydrogen atom with the alkyl group, or alkyl alcohol, diol, or polyol group. In an alternative embodiment, the alkyl alcohol, diol, or polyol may be added to the reaction mixture of the 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide and itaconic acid in an amount from equimolar to two times the respective molar amounts of each of the other reactants.

10 In an embodiment of the process, minor amounts of other compounds may be included in the co-polymerization step that may be incorporated into the PTT co-polymer product to be used to form the fiber. For example, compounds such as ethylene glycol, 1,4-butanediol, 1,4-butenediol, 1,4-cyclohexanedimethanol, oxalic acid, succinic acid, phthalic acid, 2,6-naphthalenedicarboxylic acid, 5-sodiumsulfoisophthalic acid, isophthalic acid, 15 and/or adipic acid may be included in the co-polymerization step. Such compounds may be included in amounts that they comprise, in combination with any such compounds utilized in the esterification step, at most 25 mol%, or at most 15 mol%, or at most 10 mol%, or at most 5 mol% of the final PTT co-polymer composition to be spun into fiber.

The relative amounts of the 1,3-propanediol and terephthalic acid components used to form the trimethylene terephthalate containing material in the esterification step and the phosphorous containing compound of formula (V) in the co-polymerization reaction step are selected so that trimethylene terephthalate in the esterification product may be present in the mixture in an amount of at least 50 mol%, or at least 70 mol%, or at least 90 mol%, or at least 95 mol%, or at least 99 mol% of the total moles of reactants in the 20 copolymerization step, and the phosphorous containing compound may be present in the co-polymerization reaction mixture in an amount greater than 0 mol% up to 50 mol% of the total moles of reactants in the copolymerization step, or up to 30 mol%, or up to 10 mol%, or up to 5 mol%, or up to 1 mol% of the total moles of reactants in the 25 copolymerization step. In an embodiment, trimethylene terephthalate may be present in the mixture for co-polymerization an amount of from 50 mol% to 99.9 mol%, or from 70 mol% to 99 mol% of the total moles of reactants in the copolymerization step and the phosphorous containing compound may be present in the mixture in an amount of from greater than 0 mol % to 50 mol%, or from 0.1 mol% to 30 mol%, or from 0.5 mol% to 10 30

mol% of the total moles of reactants in the copolymerization step. Alternatively, trimethylene terephthalate may be present in the mixture for copolymerization in an amount of at least 20 wt.%, or at least 25 wt.%, or at least 30 wt.% up to 99.9 wt.%, or up to 99.5 wt.%, or up to 99 wt.% of the total weight of the reactants, and the phosphorous compound of formula (V) may be present in the mixture in an amount of at least 0.1 wt.%, or at least 0.3 wt.%, or at least 1 wt.%, or at least 2 wt.%, up to 80 wt.%, or up to 75 wt.%, or up to 50 wt.% of the total weight of the reactants.

In an embodiment, it may be preferable to maximize the poly(trimethylene terephthalate) character of the co-polymer by maximizing the trimethylene terephthalate monomer of formula (I) content and minimizing the phosphorous containing component of formula (II) content in the co-polymer. This may be useful to provide a polymer having characteristics similar to a poly(trimethylene terephthalate) homopolymer yet having improved flame retardance relative to a PTT homopolymer. In this embodiment, the minimum amount of the phosphorous containing compound of formula (V) required to provide a desired degree of flame retardancy is included in the co-polymerization step. For example, at most 5 mol%, or at most 4 mol%, or at most 3 mol%, or at most 2 mol%, or from 0.25 mol% to 3 mol%, or from 0.5 mol% to 2 mol% of the phosphorous containing compound of formula (V), relative to the total moles of reactants, may be included in the mixture for co-polymerization to provide a PTT co-polymer having flame retardancy with a minimal amount of the phosphorous containing component of formula (II) monomer. Alternatively, at most 5 wt.%, or at most 4 wt.%, or at most 3 wt.%, or from 0.5 wt.% to 4 wt.%, or from 1 wt.% to 3 wt.% of the phosphorous containing compound of formula (V), based on the total weight of the reactants, may be included in the mixture for co-polymerization to provide a PTT co-polymer having flame retardancy with a minimal amount of the phosphorous containing component monomer.

The co-polymerization may comprise an optional pre-polycondensation step which is useful to obtain a high intrinsic viscosity PTT melt co-polymer, particularly in the absence of subsequent a solid-state polymerization step. In the pre-polycondensation step, the trimethylene terephthalate containing material from the esterification step and the phosphorous containing compound of formula (V) may be mixed and reacted where the reaction pressure may be reduced to less than 20 kPa (200 mbar), or less than 10 kPa (100 mbar), or from 0.2 kPa to 20 kPa (2 mbar to 200 mbar), or from 0.5 kPa to 10 kPa (5 mbar to 100 mbar) and the temperature may be from 230°C to 280°C, or from 240°C to 275°C,

or from 250°C to 270°C. The pre-polycondensation step of the co-polymerization may be carried out at two or more vacuum stages, where each stage may have a successively lower pressure. For example, a two-stage pre-polycondensation may be effected in which the phosphorous containing compound of formula (V) and the trimethylene terephthalate
5 containing material from the esterification step are mixed at an initial pressure of from 5 kPa to 20 kPa (50 mbar to 200 mbar) and then mixed at a second pressure of from 0.2 kPa to 2 kPa (2 mbar to 20 mbar) while being held at a temperature of from 230°C to 280°C, preferably from 250°C to 270°C. The pre-polycondensation step may be conducted until the pre-polycondensation reaction product has the desired intrinsic viscosity, which may be
10 for at least 10 minutes, or at least 25 minutes, or at least 30 minutes, and up to 4 hours, or up to 3 hours, or up to 2 hours, or from 10 minutes to 4 hours, or from 25 minutes to 3 hours, or from 30 minutes to 2 hours.

The pre-polycondensation step of the co-polymerization may be carried out in the presence of a pre-polycondensation catalyst. The pre-polycondensation catalyst is
15 preferably a titanium or zirconium catalyst selected from the titanium and zirconium catalysts discussed above in relation to the esterification step due to the high activity of these metals. The pre-polycondensation catalyst may be provided to the pre-polycondensation reaction mass in an amount effective to catalyze the reaction, and may be provided in an amount in the range of 5 to 250 ppm (metal), or in the range of 10 ppm to
20 100 ppm (metal), based on the weight of the final co-polymer. In an embodiment, at least a portion or all of the pre-polycondensation catalyst may be the catalyst used in the esterification reaction and included in the pre-polycondensation reaction in the esterification product mixture.

The co-polymerization includes a polycondensation step which may produce a PTT
25 melt co-polymer having an intrinsic viscosity of at least 0.4 dl/g or at least 0.7 dl/g, or at least 0.8 dl/g, or at least 0.9 dl/g. In the polycondensation step, the pre-polycondensation step product, or alternatively the trimethylene terephthalate containing material from the esterification step and the phosphorous containing compound of formula (V), may be mixed and reacted where the reaction pressure may be reduced to 0.02 kPa to 0.25 kPa (0.2
30 mbar to 2.5 mbar) and the temperature may be from 240°C to 275°C, or from 250°C to 270°C. The polycondensation step may be carried out for a period of time effective to provide a PTT melt co-polymer having the desired intrinsic viscosity, which is at least 0.4 dl/g where a subsequent solid state polymerization step is effected or at least 0.7 dl/g in an

all melt process without a subsequent solid state polymerization step. In general, the polycondensation step may require from 1 to 6 hours, with shorter reaction times preferred to minimize the formation of color bodies.

The polycondensation step of the co-polymerization includes a polycondensation catalyst, preferably a titanium or zirconium compound, such as those discussed above in relation to the esterification step because of the high activity of these metals. A preferred polycondensation catalyst is titanium butoxide. The polycondensation catalyst may be provided to the polycondensation reaction mass in an amount effective to catalyze the reaction, and may be provided in an amount in the range of 5 to 250 ppm (metal), or in the range of 10 ppm to 100 ppm (metal), based on the weight of the final co-polymer. In an embodiment, at least a portion or all of the polycondensation catalyst may be the catalyst used in the pre-polycondensation reaction and/or the esterification reaction and included in the polycondensation reaction in the pre-polycondensation product mixture and/or the esterification product mixture.

The polycondensation step is most suitably carried out in a high surface area generation reactor capable of large vapor mass transfer, such as a cage-type, basket, perforated disk, disk ring, or twin screw reactor. Optimum results are achievable in the process from the use of a cage-type reactor or a disk ring reactor, which promote the continuous formation of large film surfaces in the reaction product and facilitate evaporation of excess 1,3-propanediol and polymerization by-products.

The polycondensation step may optionally include the addition to the reaction mixture of stabilizers, coloring agents, fillers, and other additives for polymer property modification. Specific additives include coloring agents such as cobalt acetate or organic dyes; stabilizers such as hindered phenols; branching agents such as polyfunctional carboxylic acids, polyfunctional acid anhydrides, and polyfunctional alcohols; and particulate fillers including delustering agents such as titanium dioxide, fibrous materials such as glass fiber, asbestos fiber, carbon fiber, silica fiber, fibrous woolastonite, silica-alumina fiber, zirconia fiber, potassium titanate fiber, metal fibers, and organic fibers with melting points above 300°C, and particulate or amorphous materials such as carbon black, white carbon, silicon carbide, silica, powder of quartz, glass beads, glass powder, milled fiber, silicates such as calcium silicate, aluminum silicate, clay, and diatomites, metal oxides such as iron oxide, zinc oxide, and alumina, metal carbonates such as calcium carbonate and magnesium carbonate, metal sulfates such as calcium sulfate and barium

sulfate, and metal powders. To limit particulate induced breakage of the fiber to be spun from the polycondensed PTT co-polymer, particulate additives, such as fillers, may be included in the polycondensation step in a limited amount of from 0 wt. % to 5 wt.% of the PTT co-polymer composition, more preferably from 0 wt.% to 3 wt.% of the PTT co-polymer composition.

Optionally, in an "all-melt" process, upon completion of the polycondensation (i.e. upon achieving the desired intrinsic viscosity in the polycondensation mixture), the polycondensation product may be cooled to produce the flame retardant PTT co-polymer. The polycondensation product may be cooled, solidified, and pelletized using a strand pelletizer, an underwater pelletizer, or a drop forming device.

The co-polymerization may comprise an optional solid-state polymerization step which is useful to obtain a high intrinsic viscosity PTT co-polymer, particularly in the absence of pre-polycondensation step. The polycondensation product may be cooled, solidified, and pelletized using a strand pelletizer, and underwater pelletizer, or a drop forming device. The resulting PTT co-polymer pellets may then be fed into a crystallizer/preheater in which the pellets are rapidly preheated to a solid-state reaction temperature which is between 150°C and up to 1°C below the melting temperature of the PTT co-polymer. The PTT co-polymer pellets may be pre-heated for a period of time typically of from 5 to 60 minutes or from 10 to 30 minutes.

The crystallizer/preheater may be a fluid bed or an agitated heat exchanger. Suitable types of fluid beds include standard (stationary) fluid beds, vibrating fluid beds, and pulsating fluid beds. Multiple heating zones may be used to narrow the residence time distribution of the PTT co-polymer pellets as well as to improve energy efficiency. In a single-zone crystallizer/pre-heater, the temperature of the direct heat transfer medium (i.e. hot nitrogen or hot air in a fluid bed) or the heat transfer surface (of an agitated heat exchanger) is at least as high as the intended solid-state reactor temperature. Thus the PTT co-polymer is exposed to the reaction temperature as soon as it is charged into the single-zone crystallizer/preheater. In a multiple-zone crystallizer/preheater, the heat transfer medium or heat transfer surface temperature of the first zone may be lower or no lower than the solid state reactor temperature. Thus the PTT co-polymer may be exposed to the solid-state reaction temperature in the first or later zones of the multiple-zone crystallizer/preheater.

The preheated pellets may then be discharged from the crystallizer/preheater into a solid-state reactor. Inside the solid state reactor, solid state polycondensation takes place as the PTT co-polymer pellets move downward by gravitational force in contact with a stream of inert gas, typically nitrogen, which flows upwardly to sweep away reaction by-products such as 1,3-propanediol, water, allyl alcohol, acrolein, and cyclic dimer. The nitrogen flow rate may be from 0.11 to 0.45 kg/min per kg of PTT co-polymer (0.25 to 1.0 pound per pound of PTT co-polymer). The nitrogen may be heated or unheated before entering the reactor. The exhaust nitrogen may be purified and recycled after exiting the reactor.

The PTT co-polymer pellets may be discharged as solid-stated product from the bottom of the solid-state reactor, after having acquired the desired intrinsic viscosity. The solid-stated product may be cooled to below 65 °C in a product cooler, which may be a fluid bed or an agitated heat exchanger. The solid-stated PTT co-polymer product may be cooled in an atmosphere of nitrogen or air.

In an embodiment in which the co-polymerization includes a solid-state polymerization step, the esterification and copolymerization steps may be conducted so that a pre-polycondensation step is not required. The esterification step may be conducted as described above, where the esterification step is conducted under a super-atmospheric pressure of from 205 kPa to 550 kPa absolute (2.05 bar to 5.5 bar absolute) in the absence of an esterification catalyst to produce the trimethylene terephthalate containing material. The co-polymerization may be conducted utilizing a polycondensation step and a solid-state polymerization step, where the polycondensation step includes the addition of from 10 to 400 ppm of a polycondensation catalyst based on the weight of the co-polymer, as described above, under reaction conditions for polycondensation as described above, except that the polycondensate product needs only have an intrinsic viscosity of at least 0.25 dl/g. The polycondensate PTT co-polymer product may then be solid-state polymerized as described above to produce a PTT co-polymer having an intrinsic viscosity sufficient to be spun into a fiber, e.g. at least 0.7 dl/g, or at least 0.8 dl/g, or at least 0.9 dl/g.

In a preferred embodiment, the co-polymerization does not require a solid-state polymerization step, and a PTT co-polymer having an intrinsic viscosity sufficient to be spun into fiber (e.g. at least 0.7 dl/g, or at least 0.8 dl/g, or at least 0.9 dl/g) may be produced using an all-melt process in which the esterification, pre-polycondensation step

and the polycondensation step, as described above, are sufficient to produce the PTT co-polymer with the required intrinsic viscosity.

In an alternative embodiment, dimethylterephthalate (DMT) may be substituted for terephthalic acid in the esterification step (which becomes a transesterification step upon the substitution). The process of producing a PTT co-polymer using DMT in place of terephthalic acid in a transesterification step may be performed in a similar manner as the process utilizing terephthalic acid in the esterification step as described above, except that DMT is substituted for terephthalic acid. The transesterification generates an alcohol, specifically methanol, which is distilled off as a byproduct under the transesterification reaction conditions.

In another embodiment, the flame retardant PTT co-polymer composition may be produced by forming the phosphorous containing compound of formula (V) from 9,10-dihydro-9-*oxa*-10-phosphaphenanthrene-10-oxide, itaconic acid, and, optionally selected alkyl alcohols, alkyl diols, and/or alkyl polyols as described above, and including the phosphorous containing compound of formula (V) in the esterification or transesterification step described above, followed by the co-polymerization step as described above. Optionally, in this embodiment, addition of the phosphorous containing compound of formula (V) may be excluded from the co-polymerization step provided sufficient amounts of the phosphorous compound are added in the esterification or transesterification step to provide the PTT co-polymer composition with sufficient flame retardancy. Sufficient amounts of the phosphorous compound required in the process to provide an effective degree of flame retardancy to the PTT co-polymer composition are described above. The amounts of 1,3-propanediol, a compound selected from the group consisting of terephthalic acid, dimethylterephthalate, and mixtures thereof, and the phosphorous containing compound are also selected to provide the flame retardant PTT co-polymer composition with from 50 mol% to 99.9 mol% of the trimethylene terephthalate monomer of formula (I) in the PTT co-polymer.

In another embodiment, 9,10-dihydro-9-*oxa*-10-phosphaphenanthrene-10-oxide, itaconic acid, and, optionally selected alkyl alcohols, alkyl diols, and/or alkyl polyols as described above, may be directly included in the esterification or transesterification step of 1,3-propanediol and terephthalic acid or dimethylterephthalate as described above. In this embodiment, a phosphorous containing compound of formula (V) need not be added in either the esterification or transesterification step or in the copolymerization step, however,

optionally, a phosphorous containing compound of formula (V) may be added in either of these steps. The amounts of 1,3-propandiol and terephthalic acid or dimethylterephthalate in the esterification mixture relative to each other are described above in the description of the esterification step. The 9,10-dihydro-9-*oxa*-10-phosphaphenanthrene-10-oxide and
5 itaconic acid may be added in equimolar amounts relative to each other in the esterification reaction. The amounts of 9,10-dihydro-9-*oxa*-10-phosphaphenanthrene-10-oxide and itaconic acid relative to 1,3-propanediol and terephthalic acid or dimethylterephthalate in the esterification reaction mixture may be selected to provide a final PTT co-polymer composition comprising at least 50 mol%, or at least 70 mol%, or at least 90 mol%, or at
10 least 95 mol%, or at least 99 mol% trimethylene terephthalate monomer of formula (I) above.

In an embodiment of the process of the present invention, a supplementary polymer may be mixed with the flame retardant PTT co-polymer to form a flame retardant PTT containing co-polymer composition to be spun into a fiber. The flame retardant PTT co-
15 polymer and supplementary polymer may be mixed at a temperature of from 180°C to 280°C where the temperature is selected so that flame retardant PTT co-polymer and the supplementary polymer each have a melting point below the selected temperature. The supplementary polymer may be mixed with the flame retardant PTT co-polymer in an amount of up to 25 wt.%, or up to 15 wt.%, or up to 10 wt.%, or up to 5 wt.% of the
20 mixture of the flame retardant PTT co-polymer and supplementary polymer. In one embodiment, the supplementary polymer is selected from the group consisting of polyamides, polysulfones, and polyesters. In an embodiment, the supplementary polymer may be NYLON-6, NYLON-6,6, poly(ethylene terephthalate), poly(butylene terephthalate), poly(ethylene naphthalate), poly(trimethylene naphthalate), or mixtures
25 thereof.

In an embodiment of the process of the present invention, a non-fusible flame retardant that does not have a melting point below 280°C may be incorporated in the flame retardant PTT containing co-polymer to be spun into fiber to provide additional flame retardancy to the fiber, if desired. Such non-fusible flame retardants may include:
30 polyhalogenated hydrocarbon compounds; phosphinate metal salts of the formula (III) above that do not melt or decompose at or below a temperature of 280°C; other phosphorous containing compounds that are non-fusible at a temperature of equal to or below 280°C, including inorganic phosphorous compounds such as red phosphorous;

monomeric organic phosphorous compounds; orthophosphoric esters or condensates thereof; phosphoric ester amides; phosphonitrilic compounds; phosphine oxides (e.g. triphenylphosphine oxides); metal salts of phosphoric and phosphonic acids; diphosphinic salts; and nitrogen containing compounds such as benzoguanamine compounds,
5 ammonium polyphosphate, and melamine compounds such as melamine borate, melamine oxalate, melamine phosphate, melamine pyrophosphate, polymeric melamine phosphate, and melamine cyanurate. In an embodiment of the process of the present invention, a non-fusible flame retardant may be incorporated in the flame retardant PTT containing co-polymer composition by heating the co-polymer composition to a temperature above the
10 melting point of the co-polymer composition but below 280°C and mixing the non-fusible flame retardant in the molten co-polymer.

If a non-fusible flame retardant is mixed in the flame retardant PTT containing co-polymer composition, the non-fusible flame retardant component in the composition is added in a minor amount such that the non-fusible flame retardant component may
15 comprise from 0 wt.% to 5 wt.%, or from 0 wt.% to 2.5 wt.%, or from 0 wt.% to 1 wt.% of the total weight of the flame retardant PTT containing composition (including any other polymers, fillers, or modifying agents mixed with the flame retardant PTT co-polymer) and the non-fusible flame retardant. Further, if a non-fusible flame retardant is mixed in the flame retardant PTT containing co-polymer composition, the non-fusible flame retardant
20 component mixed in the composition may be particulate. The particle size of the non-fusible flame retardant component in the composition may range up to a mean particle size of 150 µm. In an embodiment, the mean particle size of the non-fusible flame retardant component may be at most 10 µm, or the non-fusible flame retardant may contain nanoparticles and may have a mean particle size of at most 1 µm.

25 In an embodiment of the process of the present invention, a fusible flame retardant that has a melting point equal to or less than 280°C may be incorporated into the flame retardant PTT containing co-polymer to be spun into fiber to provide additional flame retardancy to the fiber, if desired. Such fusible flame retardants are described above. The fusible flame retardant may be incorporated into the flame retardant PTT co-polymer
30 composition by heating the fusible flame retardant and the flame retardant PTT co-polymer, separately or together, to a temperature above the melting points of the fusible flame retardant and the flame retardant PTT co-polymer, then mixing the molten fusible

flame retardant and molten flame retardant PTT co-polymer to disperse the fusible flame retardant in the PTT co-copolymer.

If a fusible flame retardant is mixed in the flame retardant PTT co-polymer composition, the fusible flame retardant component may be added in a minor amount such that the fusible flame retardant may comprise from 0 wt.% to 5 wt.%, or from 0.1 wt.% to 2.5 wt.%, or from 0.1 wt.% to 1 wt.% of the total weight of the flame retardant PTT co-polymer composition (including any other polymers, fillers, reinforcing agents, modifying agents, and non-fusible flame retardant components) mixed with the flame retardant PTT co-polymer) and the fusible flame retardant.

In an embodiment of the process of the present invention, a filler may be mixed into the flame retardant PTT containing co-polymer composition to be spun into a fiber.

"Filler" as the term is used herein is defined as "a particulate or fibrous material having no flame retardant activity". Examples of filler materials that may be utilized in the process of the present invention include fibrous materials such as glass fiber, asbestos fiber, carbon

fiber, silica fiber, fibrous woolastonite, silica-alumina fiber, zirconia fiber, potassium titanate fiber, metal fibers, and organic fibers with melting points above 300°C, carbon black, white carbon, silicon carbide, silica, powder of quartz, glass beads, glass powder, milled fiber, silicates such as calcium silicate, aluminum silicate, clay, and diatomites, metal oxides such as iron oxide, titanium oxide, zinc oxide, and alumina, metal carbonates such as calcium carbonate and magnesium carbonate, metal sulfates such as calcium sulfate and barium sulfate, and metal powders. For purposes of delustering the fiber of the present invention, titanium dioxide is a preferred filler. In an embodiment of the process of the present invention, a filler may be incorporated in the flame retardant PTT containing co-polymer composition by heating the co-polymer composition to a temperature above the melting point of the co-polymer composition but below 280°C and mixing the filler in the molten co-polymer. Filler may be mixed in the flame retardant PTT containing composition such that the filler comprises from 0 wt.% to 5 wt. %, or from 0 wt.% to 2.5 wt.% or from 0.5 wt.% to 1.0 wt.% of the total weight of the flame retardant PTT containing co-polymer composition (including any other polymers, flame retardants, or modifying agents mixed with the flame retardant PTT co-polymer) and the filler.

In an embodiment of the process of the present invention, a modifying agent may be mixed into the flame retardant PTT containing co-polymer composition to be spun into fiber. "Modifying agent", as the term is used herein, is defined as a material useful to

modify the physical, chemical, color, or electrical characteristics of the flame retardant PTT co-polymer composition, excluding filler materials and reinforcing agents, as defined above. Modifying agents may include conventional antioxidants, lubricants, dyes and other colorants, UV absorbers, and antistatic agents. In an embodiment of the process of the present invention, a modifying agent may be incorporated in the flame retardant PTT containing co-polymer composition by heating the co-polymer composition to a temperature above the melting point of the co-polymer composition but below 280°C and mixing the modifying agent in the molten co-polymer. The modifying agent may be mixed in the flame retardant PTT containing co-polymer composition such that the modifying agent comprises from 0 wt.% to 25 wt. %, or from 0 wt.% to 10 wt.% or from 1 wt.% to 5 wt.% of the total weight of the flame retardant PTT containing co-polymer composition (including any other polymers, flame retardants, or filler mixed with the flame retardant PTT co-polymer) and the modifying agent.

Once formed, the flame retardant PTT co-polymer composition may be spun into a fiber. To spin the flame retardant PTT co-polymer into a fiber, the flame retardant PTT co-polymer may be heated (or maintained) at a temperature of from 240°C to 280°C and drawn or extruded through a spinneret die. The resulting fiber may then be solidified by cooling. A PTT co-polymer fiber of the present invention has a tenacity of at least 1.5 g/d, or at least 1.6 g/d, or at least 1.7 g/d.

In an embodiment of the process of the invention, the flame retardant PTT co-polymer, including any additional supplemental polymer, may be spun into a plurality of fibers that may be combined and formed into a fully oriented yarn, a partially oriented yarn, or an undrawn yarn useful in textile or carpet applications. Referring now to Fig. 1, the flame retardant PTT co-polymer may be melt blended in extruder at a temperature of from 180°C to 280°C, preferably from 240°C to 280°C, where the temperature is selected to be above the melting point of the flame retardant PTT co-polymer. The molten PTT co-polymer may then be passed through a spinneret **1** located at the extruder outlet into a plurality of melt spun continuous fibers/filaments **2** (as used herein a "filament" is a fiber of extreme length, and is intended to be encompassed within the definition of a fiber). The die holes in the spinneret **1** may have a size and shape selected to provide desired characteristics to a yarn **3** formed of a plurality of the filaments **2**. Multiple spinnerets (not shown) may be coupled to the extruder to enable multiple yarns to be spun simultaneously from the molten flame retardant PTT co-polymer.

The filaments **2** may be rapidly cooled and converged into a multifilament yarn **3**. The filaments **2** may be cooled by contacting the filaments **2** with cold air, preferably by blowing cold air over the filaments **2**. In one embodiment, the filaments **2** may pass through a quench air box or cylinder **4** surrounding the filaments which defines a cold air zone. The cold air may be directed inward from the interior surface of the quench air box or cylinder **4** to cool the filaments **2**.

The multi-filament yarn **3** may be passed through a spin finish applicator **5**, shown in Fig. 1 as an oiling roll, to apply a finishing agent on the yarn **3**. The finishing agent is preferably an oil agent containing a fatty acid ester and/or mineral oil, or a polyether.

10 The multi-filament flame retardant PTT yarn **3** may then be processed into a fully drawn yarn, a partially oriented yarn, or an undrawn yarn.

If the yarn **3** is to be a fully oriented yarn, the yarn **3** may be drawn in a one or two-stage drawing process over feed **6** and drawing rolls **7** and **8** prior to being taken up by a take-up mechanism **9**, where the feed **6** and drawing rolls **7** and **8** may include at least one heated roll and the relative speeds of the feed **6** and drawing rolls **7** and **8** and take-up mechanism **9** may be set to produce a fully oriented yarn. For example, a fully drawn yarn may be produced by drawing the yarn **3** at a first draw ratio of from 1.01 to 2, and the temperatures of the feed roller **6** and draw rollers **7** and **8** are controlled so the feed roller **6** is operated at a temperature of less than 100°C and the draw rollers **7** and **8** are operated at temperatures of greater than the temperature of the feed roller **6** and within the range of 50°C to 150°C. The first draw ratio may be controlled by controlling the speeds of the feed roller **6** relative to the draw roller **7**, for example, the feed roller **6** may rotate at a speed of 1000 m/min and the draw roller **7** may have a speed of 1050 m/min. The yarn is subsequently drawn at a second draw ratio of at least 2.2 times that of the first draw ratio where the draw roller **8** is heated to a temperature greater than the draw roller **7** and within the range of from 100°C to 200°C. The second draw ratio may be controlled by controlling the speeds of the draw roller **8** relative to the draw roller **7**, for example, the draw roller **8** may have a speed of 3000 m/min and the draw roller **7** may have a speed of 1050 m/min. The drawn yarn may subsequently be wound with the take-up mechanism **9**. Denier control rolls **10** and an optional relax roller **11** may be used to facilitate the yarn spinning process. The drawn yarn may be textured prior to or after winding in accordance with conventional yarn texturing processes.

If the yarn **3** is to be a partially oriented yarn, the yarn **3** may be either drawn in a one or two stage process over feed **6** and drawing rolls **7** and **8** prior to being taken up by a take-up mechanism **9**, or the yarn may be directly taken-up by the take-up mechanism **9**. If the partially oriented yarn is produced by drawing prior to being taken up by a take-up mechanism, the draw ratio is less than that used to produce a fully oriented yarn, as described above, resulting in only partial longitudinal orientation of the polymer molecules. For example, the yarn **3** may be heated above the glass transition temperature of the yarn, e.g. at least 45°C or at least 60°C, and drawn at a draw ratio of 0.7 to 1.3 in a single stage draw process where the feed roll **6** is operated at a speed of from 1800 to 3500 m/min and the draw rolls **7** and **8** are operated at the same speed of from 1250 m/min to 4550 m/min, where the relative speed of the draw rolls **7** and **8** to the feed roll **6** determines the draw ratio. If the partially oriented yarn is produced by being directly taken up by the take-up mechanism **9**, the take-up mechanism **9** is operated at a speed effective to induce partial orientation in the yarn. For example, the take-up mechanism **9** may operate at a speed of 3500 to 4500 m/min or at a speed of from 2000 to 2600 m/min to induce partial orientation in the yarn while winding the yarn. The partially oriented yarn may be wound onto a yarn package, and may be subsequently textured.

If the yarn **3** is to be an undrawn yarn, the yarn may be directly taken up by the take-up mechanism **9** at a speed that does not induce longitudinal orientation of the polymer molecules in the yarn fiber. For example, the take-up mechanism **9** may operate at a speed of from 500 m/min to 1500 m/min, or at a speed of from 800 m/min to 1200 m/min, to produce an undrawn yarn. The undrawn yarn may be subsequently stored in a tow can, textured, drawn, and cut into staple fibers.

The textured fully oriented yarn, textured partially oriented yarn, and textured undrawn yarn may be utilized to produce textiles or carpets in accordance with known conventional techniques for forming textiles or carpets from fully oriented, partially oriented, or undrawn yarns.

In another embodiment, as shown in Fig. 2, extruded filaments of the flame retardant PTT co-polymer may be formed into bulk continuous filaments particularly useful for forming carpets. Molten PTT polymer may be passed through a spinneret **13** into a plurality of continuous filaments **14**, at a temperature of from 180°C to 280°C, preferably from 240°C to 280°C, where the temperature is selected so the temperature is above the melting point of the flame retardant PTT co-polymer. The filaments **14** may be

rapidly cooled, preferably by contact with cold air, and converged into a multifilament yarn **15**. The multifilament yarn **15** may be contacted with a spin finish applicator **16** to apply a finishing agent on the yarn **15**. The finishing agent is preferably an oil agent containing a fatty acid ester and/or mineral oil, or a polyether.

5 The multifilament yarn **15** may be fed to a first drawing stage by control rolls **17** and **18**. The first drawing stage is defined by feed roll **19** and a draw roll **20**. Between rolls **19** and **20**, yarn **21** may drawn at a relatively low draw ratio, within the range of 1.01 to 2 and preferably within the range of 1.01 to 1.35, where the draw ratio is controlled by selecting the speed of the rolls **19** and **20**. The temperature of the feed roll **19** is kept low,
10 where preferably the feed roll **19** is unheated, but at most the temperature of the feed roll **19** is from 30°C to 80°C. The draw roll **20** may be heated to a temperature of from 50°C to 150°C, preferably about 90°C to 140°C, to facilitate drawing the yarn **21** without breaking the yarn.

 The drawn yarn **21** may be passed to a second drawing stage defined by draw rolls
15 **20** and **22**. The second stage draw may be carried out at a relatively high draw ratio with respect to the first stage draw ratio, generally at least 2.2 times that of the first stage draw ratio, preferably at a draw ratio within the range of 2.2 to 3.4 times of that of the first stage. Draw roll **22** may be maintained at a temperature in the range of 100 to 200°C. In general, the three rollers **18**, **19**, and **22** will be sequentially higher in temperature.

20 Drawn yarn **23** may be passed to heated rolls **24** and **25** to preheat the drawn yarn **23** prior to texturing. The heated drawn yarn **26** may then be texturized by passing the yarn **26** through a texturing air jet **27** for bulk enhancement of the yarn **26**, and then to a jet cooling drum **28**. The bulk textured yarn **29** may then be passed through tension controls **30**, **31**, and **32** and through idler **33** to an optional entangler **34** for yarn entanglement.
25 Entangled yarn **35** may be advanced by idler **36** to an optional spin finish applicator **37** and then is wound onto winder **38**. The bulk continuous filament yarn can then be processed by twisting, texturing, and heat-setting as desired and tufted into carpet according to conventional methods.

 In another aspect, the present invention is directed to a material comprising a
30 plurality of fibers wherein at least 5% of the fibers are comprised of a flame retardant PTT co-polymer comprising from 50 mol% to 99.9 mol% of a trimethylene terephthalate component of formula (I) and from 0.1 mol% to 50 mol% of a phosphorous containing component of formula (II), as described above. Such PTT containing co-polymer fibers

and processes for producing them are described above, and may include additives such as filler, particularly a delusterant, and supplementary polymers as described above.

In an embodiment, the material is a carpet. Preferably the carpet contains at least 50%, or at least 75%, or at least 90%, of the flame retardant PTT co-polymer fibers. The carpet may be prepared with the flame retardant PTT co-polymer fibers in accordance with conventional methods for producing carpets from synthetic polymer fibers. In an embodiment, the flame retardant PTT co-polymer fiber used to produce the carpet is a bulk continuous filament fiber. In another embodiment, the flame retardant PTT co-polymer fiber used to produce the carpet is a staple fiber having a length of from 0.5 cm to 15 cm (0.2 in. to 6 in.).

The carpet of the present invention is a PTT co-polymer fiber based carpet that is more surface flame resistant than conventional PTT homopolymer fiber based carpets. The carpet of the present invention may have sufficient flame resistance to pass a small-scale ignition test, in particular the "pill test" as described in 16 C.F.R. §1630 (§1630.1 – 1630.4) (1-1-06 Edition) or a comparable test with at least a 85% pass rate, or at least a 90 % pass rate. Specifically, the carpet of the present invention has a flame resistance such that the probability that a methanamine tablet ignited on the carpet in a pill test will char the carpet a distance of at most 7.62 cm (3 in.) from the tablet is at least 85% or at least 90%.

The "pill test" as provided in 16 C.F.R. §1630 (1-1-06 Edition) or a comparable test, for purposes of the present invention, includes the following steps and criteria. A sample of carpet that includes a circular area having a diameter greater than 20.32 cm (8 in.), more preferably having a diameter of 22.86 ± 0.64 cm ($9 \pm 1/4$ in.) is provided. For purposes of the present invention the sample may be any shape, e.g. square or circular, but the sample must include a circular area having a diameter of at least 20.32 cm—the C.F.R. test requires a square sample having 22.86 ± 0.64 cm sides. The sample may be washed and dried 10 times using a wash temperature of $60^\circ \pm 3^\circ \text{C}$ and a tumble dry exhaust temperature of $66^\circ \pm 5^\circ \text{C}$ (washing and drying is required in the CFR test, but is not necessary for a test in accordance with the present invention). The sample is cleaned until it is free of loose ends and any material that may have worked into the pile during handling, preferably with a vacuum cleaner. The sample is placed in a drying oven in a manner to permit free circulation of air at 105°C around the sample for 2 hours, and then is placed in a dessicator with the carpet traffic surface up until cooled to room temperature, but no less than 1 hour.

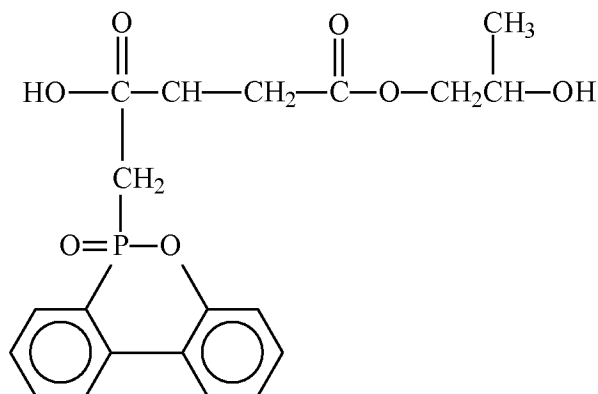
The sample is then removed from the dessicator and brushed with a gloved hand to raise the pile of the sample. The sample is placed horizontally flat in a test chamber and a metal plate flattening frame having 20.32 cm (8 in.) diameter hole in its center is centered and placed on top of the sample (preferably the metal plate is a 22.86 cm x 22.86 cm (9 in. x 9 in.) steel plate with an 20.32 cm diameter hole therein). A methenamine tablet weighing approximately 0.149 gram is then placed on the sample in the center of the 20.32 cm hole in the flattening frame. The tablet is ignited by touching a lighted match or an equivalent lighting source to the top of the tablet. The test is continued until either the last vestige of flame or glow disappears or the flaming or smoldering has approached to within 2.54 cm (1 in.) of the edge of the hole in the flattening frame at any point. When all combustion has ceased the shortest distance between the edge of the hole in the flattening frame and the charred area is measured and recorded. A sample that passes the test is a sample in which the charred area is more than 2.54 cm (1 in.) from the edge of the hole in the flattening frame at any point (is charred less than or equal to 7.62 cm (3 in.) from the location of the pill).

The carpet of the present invention may also possess sufficient flame resistance to meet Class I or Class II categories of the flooring radiant panel test of the American Association of Testing and Materials ASTM-E-648, incorporated herein by reference. A sample meeting the Class I category has an average minimum radiant flux of 0.45 watts per square centimeter, and a sample meeting the Class II category has an average minimum radiant flux of 0.22 watts per square centimeter. The flooring radiant panel test ASTM-E-648 includes the following steps. A 100x20 cm (39 in x 8 in.) carpet sample is horizontally mounted on the floor of a test chamber having an air/gas-fired radiant energy panel mounted above the specimen. The air/gas fired radiant energy panel is positioned to generate a maximum of approximately 1.1 watts per square centimeter of radiant energy immediately under the panel and a minimum of approximately 0.1 watts per square centimeter of radiant energy at the far end of the sample remote from the panel. A gas-fired pilot burner is used to initiate the flaming of the sample. The test is continued until the sample ceases to burn. The distance from the sample burns is measured and recorded. The radiant heat energy exposure at the point the sample "self-extinguished" is noted and is reported as the sample's critical radiant flux—which is the minimum energy needed to sustain flame propagation.

In another embodiment, the material is a textile. Preferably the textile contains at least 5%, or at least 10%, or at least 25%, or at least 50%, or at least 75%, or at least 90% of the flame retardant PTT co-polymer fibers. The textile may be prepared with the flame retardant PTT co-polymer fibers in accordance with conventional methods for producing textile from synthetic polymer fibers. In an embodiment, the flame retardant PTT co-polymer fiber used to produce the textile is a fully oriented yarn or a partially oriented yarn. In an embodiment, the flame retardant PTT co-polymer fiber used to produce the textile is a staple fiber.

EXAMPLE 1

A fiber composition of the present invention was made in accordance with the process of the present invention. Terephthalic acid and 1,3-propanediol were mixed to form a paste, where the molar ratio of terephthalic acid to 1,3-propanediol was 1: 1.25. 20 ppm cobalt acetate and 270 ppm Irganox 1076 were added to the terephthalic acid and 1,3-propanediol mixture. The paste was then gradually charged to an esterifier reactor over a period of 60 minutes, where the mass temperature in the esterifier reactor was maintained at a temperature of 250°C and the reaction was conducted under a nitrogen pressure of 0.2 MPa. The esterification reaction was conducted until 80% of the terephthalic acid was consumed, a period of 207 minutes, then the esterification product was transferred to a pre-polycondensation reactor. The esterification product was initially treated in the pre-polycondensation reactor at a temperature of 250°C and a pressure of 0.15 MPa for a period of 62 minutes. 60 ppm of a titanium catalyst and 3 wt.% of a mixture of the phosphorous compound shown below and ethylene glycol, where the ethylene glycol formed 33 wt.% of the mixture, was then added to the reaction mixture.



The pre-polycondensation reactor was then evacuated to a pressure of 2 kPa over a period of 25 minutes. After achieving vacuum pressure below 5 kPa the mass temperature in the reactor was increased to 265°C in two steps. After the 25 minute pressure drop in the pre-polycondensation reactor, the reaction mass was transferred to a polymerization reactor. In the polymerization reactor, the reaction pressure was decreased to below 1 kPa and the mass temperature of the reaction mass was initially increased to 268°C and then maintained at 264°C for the duration of the polymerization process. Polymerization was continued until the co-polymer had an intrinsic viscosity of 0.74 dl/g, a period of 84 minutes. The co-polymer was then cooled and casted for solid state polymerization. The solid co-polymer was then solid state polymerized in a tumbler drier at a temperature of 205°C for 7 hours to produce a final co-polymer product. Properties of the final co-polymer product are provided in Table 1.

15

TABLE 1

Glass Transition Temp. (T _g)	Cold Crystallization Temp (T _{cc})	Melting Temp (T _m)	Intrinsic Viscosity	Hunter Color L*	Hunter Color a	Hunter Color b	% dipropylene glycol ether
45.4°C	74°C	224.6°C	0.95 dl/g	80.5	-4.2	11.4	1.2

20

The final co-polymer product was heated to melt the co-polymer, and then was spun into fiber. The co-polymer was heated by feeding the co-polymer through an extruder having six heating zones, where the temperatures of the respective heating zones ranged from 235°C to 251°C, where the final heating zone had a temperature of 251°C. Upon passing through the extruder the molten co-polymer had a temperature of 260°C. The extruded molten co-polymer was then passed through a spinning pump operating at 16.8 rpm and extruded through a spinneret having a capillary size of 0.285 x 0.95 and 68 Y shaped die holes to form 68 filaments. The filaments were cooled and combined to form a PTT co-polymer yarn. A Lurol 8666 spin finish was applied to the PTT co-polymer yarn,

and the yarn was loaded onto a pretension godet roll operating at 1100 m/min. The PTT co-polymer yarn was then passed to a first draw roll operating at a speed of 1130 m/min and having temperature of 55°C, and was drawn between the first draw roll and a second draw roll operating at a speed of 3000 m/min at a temperature of 135°C. The draw ratio on the PTT co-polymer yarn was 2.7. The drawn PTT co-polymer yarn was then textured with hot air from an airheater having a temperature of 170°C. The textured PTT co-polymer yarn was then cooled on a cooling drum operating at 30 rpm and was drawn up by a third draw roll operating at a speed of 2488 m/min at ambient temperature. The PTT co-polymer yarn was then wound up on a winder operating at 2465 m/min to provide a bulk continuous filament PTT co-polymer yarn. Properties of the PTT co-polymer yarn are shown in Table 2.

TABLE 2

Denier	Tenacity (g/d)	Maximum elongation (%)	Elongation to Break (%)
1515	1.79	60	45

15

EXAMPLE 2

For comparative purposes, a fiber and yarn were prepared from a poly(trimethylene terephthalate) homopolymer. A poly(trimethylene terephthalate) polymer was prepared by esterifying 1,3-propanediol and terephthalic acid under the conditions set forth in Example 1, except no phosphorous containing compound was added during the pre-polycondensation step.

The final PTT polymer product was heated to melt the polymer, and then was spun into fiber. The PTT polymer was heated by feeding the polymer through an extruder having six heating zones, where the temperatures of the respective heating zones ranged from 235°C to 250°C, where the final heating zone had a temperature of 250°C. Upon passing through the extruder the molten PTT polymer had a temperature of 255°C. The extruded molten PTT polymer was then passed through a spinning pump operating at 16.8 rpm and extruded through a spinneret having a capillary size of 0.285 x 0.95 and 68 Y shaped die holes to form 68 filaments. The filaments were cooled and combined to form a PTT yarn. A Lurol 8666 spin finish was applied to the PTT yarn, and the PTT yarn was loaded onto a pretension godet roll operating at 1000 m/min. The PTT yarn was then passed to a first

draw roll operating at a speed of 1030 m/min and having temperature of 55°C, and was drawn between the first draw roll and a second draw roll operating at a speed of 3000 m/min at a temperature of 144°C. The draw ratio on the PTT yarn was 2.9. The drawn PTT yarn was then textured with hot air from an airheater having a temperature of 175°C.

- 5 The textured PTT yarn was then cooled on a cooling drum operating at 40 rpm and was drawn up by a third draw roll operating at a speed of 2519 m/min at ambient temperature. The PTT yarn was then wound up on a winder operating at 2505 m/min to provide a bulk continuous filament PTT yarn. Properties of the PTT yarn are shown in Table 3.

10

TABLE 3

Denier	Tenacity (g/d)	Maximum elongation (%)	Elongation to Break (%)
1515	1.85	62	45

It may be seen by comparing the tenacity of the PTT co-polymer yarn from Table 2 and the tenacity of the PTT yarn from Table 3 that the tenacity of the PTT co-polymer yarn is only slightly lower than the tenacity of the PTT yarn.

15

EXAMPLE 3

A carpet in accordance with the present invention was made from the PTT co-polymer yarn produced in Example 1, and a carpet for comparative purposes was made from the PTT polymer yarn produced in Example 2. The carpets formed from the yarn of

20 Example 1 and Example 2 contained no other fibers or yarns. The yarns were twisted at 4.75 twists-per-inch and Superba heat-set textured at 138°C (280°F). Each yarn was then back wound on 144 packages, and then was creeled and tufted as a 0.57 m (2 ft.) wide band in 28.8 cm (12 inch) wide broadloom carpet on a 5/32 gauge cutpile machine at 25 opsy. Filler yarn was used for the edge bands on either side. Each resulting carpet was then

25 beck-dyed in a dark red color in a pressure beck at atmospheric pressure and finished with a 600 filler load latex (no ATH). A pill test was conducted 16 times on samples from the carpets. The results are shown in Table 4 below.

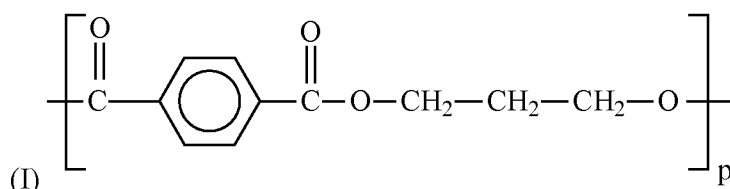
TABLE 4

Sample	Pill Test (Pass/Total)	Pill Test (% pass)
PTT co-polymer, 38 oz. latex weight (Example 1)	14/16	87.5
PTT polymer, 38 oz. latex weight (Example 2)	6/16	37.5

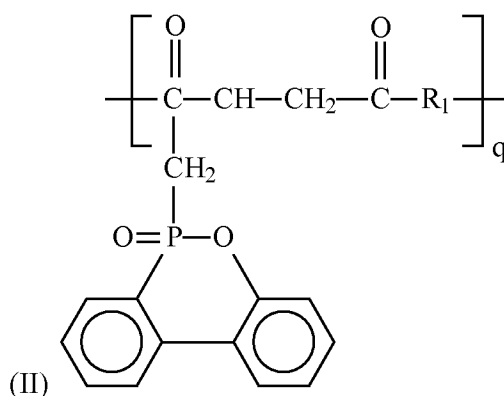
Table 4 shows that the carpets having the PTT co-polymer fibers exhibited reduced
5 flammability relative to carpets having PTT polymer fibers with no phosphorous
containing co-polymer, as shown by the pill test.

CLAIMS

1. A flame retardant polyester fiber comprised of a polymer formed of from 50 mol% to 99.9 mol% of a trimethylene terephthalate component of formula (I) and from 0.1 mol% to 50 mol% of a phosphorous containing component of formula (II)



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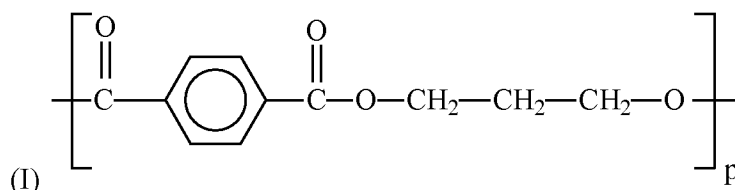


- where p is from 1 to 2500, q is from 1 to 1250, and R₁ is an alkyl alcohol residuum having from 1 to 5 carbon atoms, an alkyl acid residuum having from 1 to 5 carbon atoms, an alkyl ester residuum having from 1 to 5 carbon atoms, or an oxygen atom;
- 15 where the fiber has a tenacity of at least 1.5 g/d.

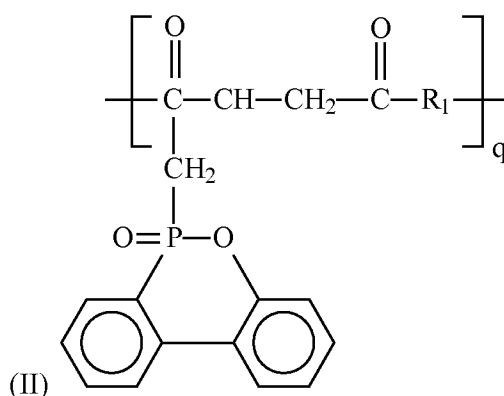
2. The flame retardant polyester fiber of claim 1 further comprising from 0.5 wt.% to 25 wt.% of a polyamide or a polyester other than the polymer formed of the trimethylene terephthalate component of formula (I) and the phosphorous containing component of formula (II).
- 20

3. A material, comprising a plurality of fibers wherein at least 5% of the fibers are comprised of a polymer comprised of from 50 mol% to 99.9 mol% of a trimethylene

terephthalate component of formula (I) and from 0.1 mol% to 50 mol% of a phosphorous containing component of formula (II)



5



where p is from 1 to 2500, q is from 1 to 1250, and R₁ is an alkyl alcohol residuum having from 1 to 5 carbon atoms, an alkyl acid residuum having from 1 to 5 carbon atoms, an alkyl ester residuum having from 1 to 5 carbon atoms, or an oxygen atom.

4. The material of claim 3 wherein the fibers comprised of the trimethylene terephthalate component of formula (I) and the phosphorous containing component of formula (II) have a tenacity of at least 1.5 g/d.

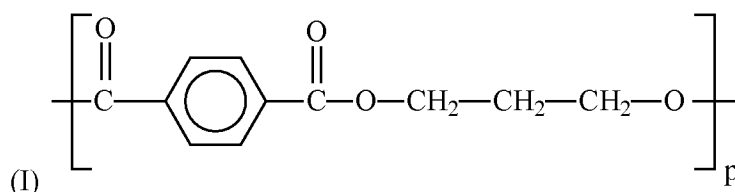
5. The material of claim 3 or claim 4 wherein the material is a carpet.

6. The carpet material of claim 5 having a flame resistance such that the probability that a methanamine tablet ignited on the carpet material in a pill test will char the carpet material a distance of at most 7.62 cm from the tablet is at least 85% or at least 90%.

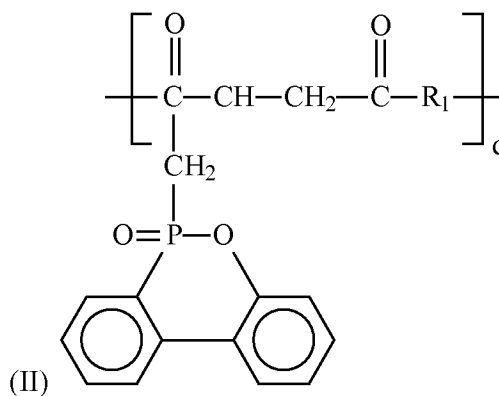
7. The carpet material of claim 5 or claim 6 wherein the carpet material has an average minimum radiant flux of at least 0.22 watts per square centimeter or at least 0.45 watts per square centimeter.

5 8. The material of claim 3 or claim 4 wherein the material is a textile.

9. A process for producing a flame retardant polyester fiber, comprising:
 providing a flame retardant poly(trimethylene terephthalate) co-polymer
 comprising from 50 mol% to 99.9 mol% of a trimethylene terephthalate component of
 10 formula (I) and from 0.1 mol% to 50 mol% of a phosphorous containing component of
 formula (II)



15



where p is from 1 to 2500, q is from 1 to 1250, and R₁ is an alkyl alcohol residuum having
 20 from 1 to 5 carbon atoms, an alkyl acid residuum having from 1 to 5 carbon atoms, an alkyl
 ester residuum having from 1 to 5 carbon atoms, or an oxygen atom;

heating the poly(trimethylene terephthalate) co-polymer to a temperature of from
 240°C to 280°C to melt the co-polymer; and

passing the molten poly(trimethylene terephthalate) co-polymer through a spinneret to form a fiber.

10. The process of claim 9 further comprising providing a supplementary polymer
5 selected from the group consisting of a polyamide, a polyester different from the poly(trimethylene terephthalate) co-polymer, and mixtures thereof, mixing the supplementary polymer and the poly(trimethylene terephthalate) co-polymer at a temperature of from 240°C to 280°C to form a molten mixture of the supplementary polymer and the co-polymer, and passing the molten mixture through a spinneret to form a
10 fiber.

11. The process of claim 9 or claim 10 wherein the fiber is a filament and further comprising combining the filament with a plurality of filaments comprised of the trimethylene terephthalate component of formula (I) and the phosphorous containing
15 component of formula (II) and forming the combined filaments into a fully oriented yarn.

12. The process of claim 9 or claim 10 wherein the fiber is a filament and further comprising combining the filament with a plurality of filaments comprised of the trimethylene terephthalate component of formula (I) and the phosphorous containing
20 component of formula (II) and forming the combined filaments into a partially oriented yarn.

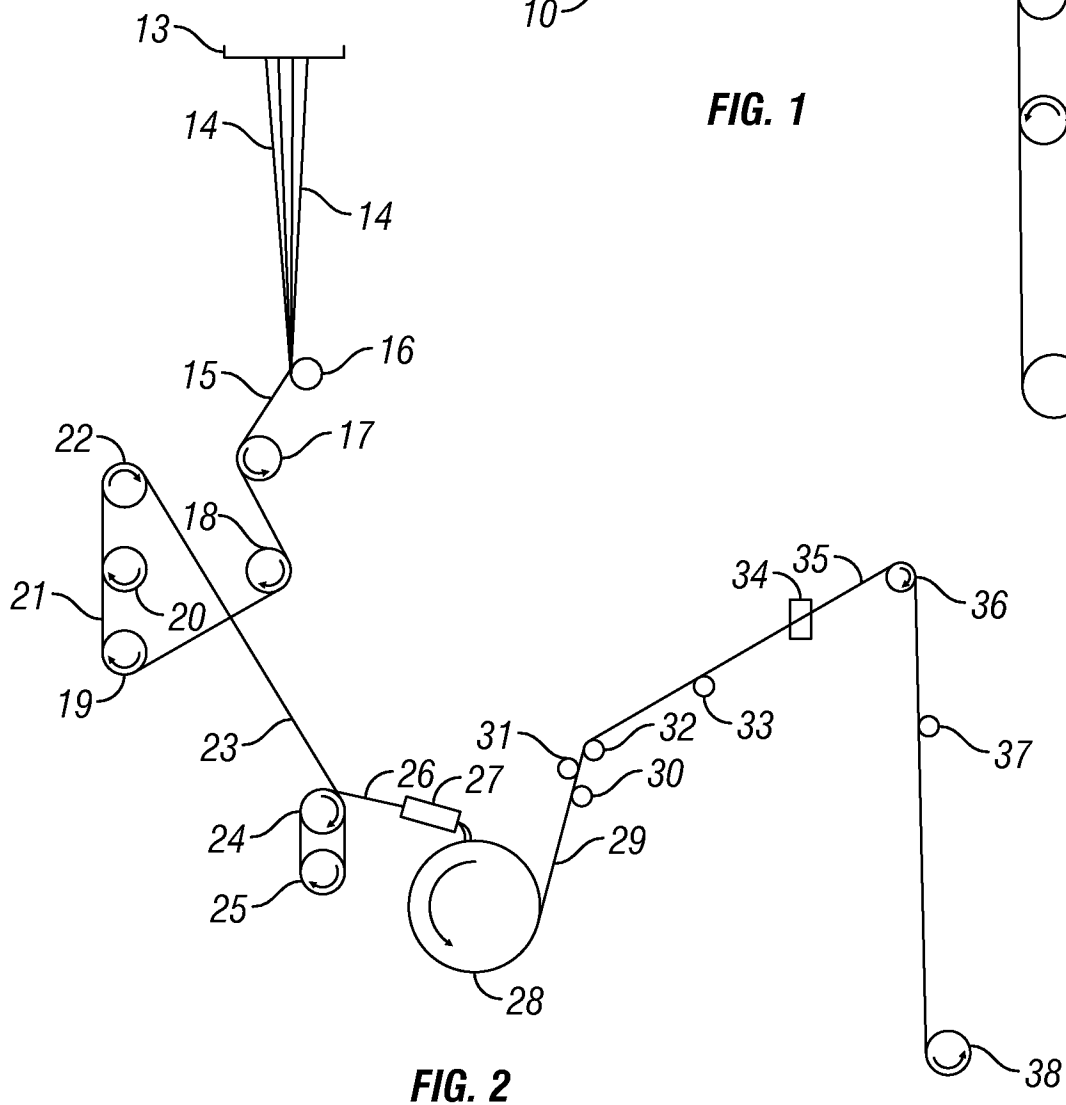
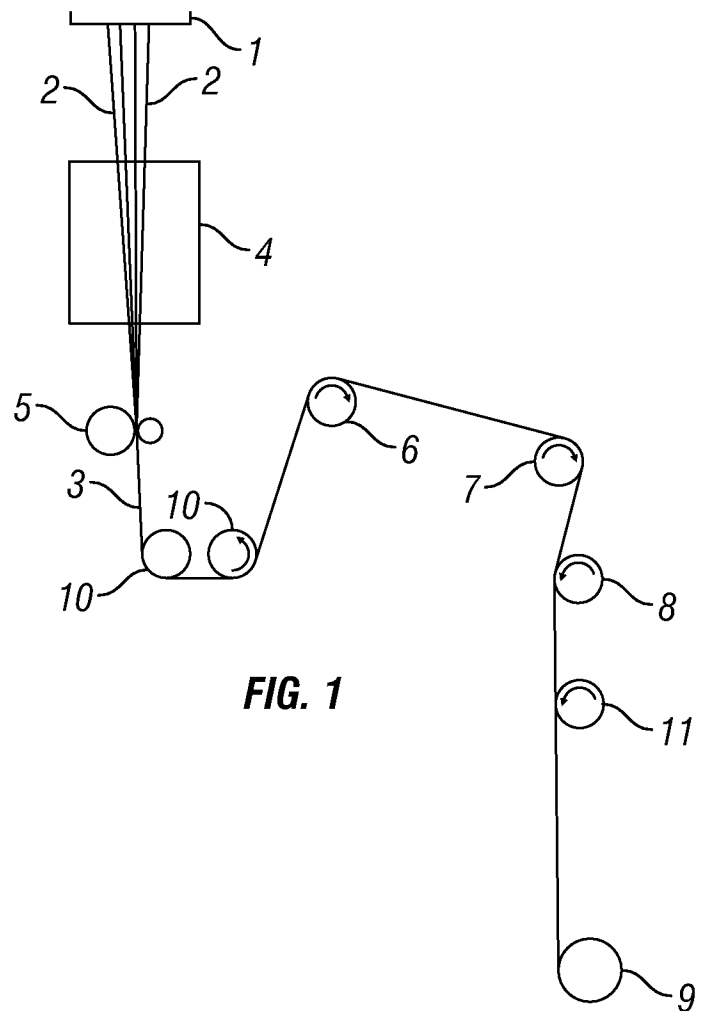
13. The process of claim 9 or claim 10 wherein the fiber is a filament further comprising combining the filament with a plurality of filaments comprised of the trimethylene terephthalate component of formula (I) and the phosphorous containing
25 component of formula (II) and forming the combined filaments into an undrawn yarn.

14. The process of claim 13 further comprising drawing and texturing the undrawn yarn, and cutting the drawn, textured yarn into staple fibers having a length of from 0.5 cm
30 to 15 cm.

15. The process of claim 9 or claim 10 wherein the fiber is a filament further comprising combining the filament with a plurality of filaments comprised of the

trimethylene terephthalate component of formula (I) and the phosphorous containing component of formula (II) and forming the filaments into a bulk continuous filament yarn.

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INTERNATIONAL SEARCH REPORT

International application No
PCT/US2008/086968

A. CLASSIFICATION OF SUBJECT MATTER
INV. D01F6/84 D01F1/07

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)
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 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.
P,A	WO 2008/061087 A (SHELL OIL CO [US]; SHELL INT RESEARCH [NL]; CHUAH HOE HIN [US]; DANGAY) 22 May 2008 (2008-05-22) the whole document	1-15
A	EP 1 489 206 A (ASAHI CHEMICAL IND [JP]) 22 December 2004 (2004-12-22) the whole document	1-15

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

☒ 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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- *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.
- *G* document member of the same patent family

Date of the actual completion of the international search

13 February 2009

Date of mailing of the international search report

19/02/2009

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2008/086968

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 2008061087	A	22-05-2008	NONE	
EP 1489206	A	22-12-2004	NONE	