



(43) International Publication Date  
15 June 2017 (15.06.2017)

(10) International Publication Number  
**WO 2017/100397 A1**

- (51) International Patent Classification:  
*B29C 67/00* (2017.01) *C08K 5/523* (2006.01)
- (21) International Application Number:  
PCT/US2016/065516
- (22) International Filing Date:  
8 December 2016 (08.12.2016)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:  
62/266,021 11 December 2015 (11.12.2015) US
- (71) Applicant: **SABIC GLOBAL TECHNOLOGIES B.V.**  
[NL/NL]; Plasticslaan 1, 4612 PX Bergen op Zoom (NL).
- (72) Inventor; and  
(71) Applicant (for BZ only): **SYBERT, Paul Dean** [US/US];  
1 Lexan Lane, Mt. Vernon, Indiana 47620-9367 (US).
- (72) Inventors: **HE, Yuanqing**; 1 Lexan Lane, Mount Vernon,  
Indiana 47620-9367 (US). **GALLUCCI, Robert Russell**;  
1 Lexan Lane, Mt. Vernon, Indiana 47620-9367 (US). **BI-  
HARI, Malvika**; 1 Lexan Lane, Mt. Vernon, Indiana  
47620-9367 (US).
- (74) Agent: **SIMONS, William A.**; Cantor Colburn LLP, 20  
Church Street, 22nd Floor, Hartford, Connecticut 06103  
(US).
- (81) Designated States (unless otherwise indicated, for every  
kind of national protection available): AE, AG, AL, AM,

AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY,  
BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM,  
DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT,  
HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KH, KN,  
KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA,  
MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG,  
NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS,  
RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY,  
TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN,  
ZA, ZM, ZW.

- (84) Designated States (unless otherwise indicated, for every  
kind of regional protection available): ARIPO (BW, GH,  
GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ,  
TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU,  
TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE,  
DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU,  
LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK,  
SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ,  
GW, KM, ML, MR, NE, SN, TD, TG).

**Declarations under Rule 4.17:**

- as to applicant's entitlement to apply for and be granted a  
patent (Rule 4.17(ii))
- as to the applicant's entitlement to claim the priority of the  
earlier application (Rule 4.17(iii))

**Published:**

- with international search report (Art. 21(3))

(54) Title: ADDITIVE MANUFACTURING ARTICLES USEFUL IN AIRCRAFT

(57) Abstract: Disclosed are methods of making articles useful in aircraft or other passenger conveyance (and specific articles made), these methods including melt extruding a plurality of layers comprising a thermoplastic polymer composition in a preset pattern; and fusing the plurality of layers to provide the article; wherein the thermoplastic polymer composition is a combination of polycarbonate polymer or copolymer, a polyetherimide polymer or copolymer, a polyarylethersulfone polymer or copolymer, and a non-brominated and non-chlorinated organic phosphorus-containing additive that will lower the Tg of the thermoplastic polymer from 5 to 100 degrees C, wherein the article meets Federal Aviation Regulation FAR 25.853 (d).



WO 2017/100397 A1

## ADDITIVE MANUFACTURING ARTICLES USEFUL IN AIRCRAFT

## BACKGROUND

[0001] Additive manufacturing (also known in the art as “three-dimensional or “3D” printing) is a process for the manufacture of three-dimensional objects by formation of multiple fused layers. Because multiple layers, for example greater than fifty (or more), are formed in AM processes, interlayer adhesion is an important consideration for both process parameter and final product specifications. Accordingly, there remains a need for AM methods that allow for better interlayer adhesion, especially when used in aircraft useful in aircraft or other passenger conveyances.

## BRIEF DESCRIPTION

[0002] One embodiment is a method of making an article useful in aircraft or other passenger conveyances, the method comprising: melt extruding a plurality of layers comprising a thermoplastic polymer composition in a preset pattern; and fusing the plurality of layers to provide the article; wherein the thermoplastic polymer composition comprises a combination of a polycarbonate polymer or copolymer, a polyetherimide polymer or copolymer, a polyarylethersulfone polymer or copolymer, or a combination comprising at least one of the foregoing thermoplastic polymers, and a non-brominated and non-chlorinated organic phosphorus-containing additive that will lower the Tg of the thermoplastic polymer from 5 to 100 degrees C and wherein the article has a 2 minute integrated heat release rate of less than or equal to 65 kilowatt-minutes per square meter (kW-min/m<sup>2</sup>) and a peak heat release rate of less than 65 kilowatts per square meter (kW/m<sup>2</sup>) as measured using the method of FAR F25.4, in accordance with Federal Aviation Regulation FAR 25.853 (d).

[0003] Another embodiment is an article useful in aircraft or other passenger conveyances comprising a plurality of layers of a material in a preset pattern of at least twenty fused, melt-extruded layers comprising a thermoplastic polymer composition, wherein the thermoplastic polymer composition comprises a combination of a polycarbonate polymer or copolymer, a polyetherimide polymer or copolymer, a polyarylethersulfone polymer or copolymer, or a combination comprising at least one of the foregoing thermoplastic polymers, and a non-brominated and non-chlorinated organic phosphorus-containing that will lower the Tg of the thermoplastic polymer and wherein the article has a 2 minute integrated heat release rate of less than or equal to 65 kilowatt-minutes per square meter (kW-min/m<sup>2</sup>) and a peak heat

release rate of less than 65 kilowatts per square meter (kW/m<sup>2</sup>) as measured using the method of FAR F25.4, in accordance with Federal Aviation Regulation FAR 25.853 (d).

[0004] The above described and other features are exemplified by the following detailed description.

#### DETAILED DESCRIPTION

[0005] Described herein are methods for manufacturing thermoplastic engineering blended articles by additive manufacturing processes such as by fused deposition modeling (FDM) for use in aircraft. By using formulations containing polycarbonate or polyetherimide or polyphenylethersulfone polymers with selective phosphate additives, the resulting polymeric compositions have a lower glass transition temperature (T<sub>g</sub>) are achieved which would lead to AM parts with better physical properties because the fused AM layers can have better interfacial adhesion as a result of the better flow and a longer time in the molten state. In addition, these phosphate blends comply with Federal Aviation Regulation (FAR) rating for aircraft interiors and EN-45545 ratings railway and railway applications and have excellent PC-PE-SI and vertical burn properties.

[0006] In some embodiments of the methods, a plurality of layers is formed in a preset pattern by an additive manufacturing process. “Plurality” as used in the context of additive manufacturing includes 20 or more layers. The maximum number of layers can vary greatly, determined, for example, by considerations such as the size of the article being manufactured, the technique used, the capabilities of the equipment used, and the level of detail desired in the final article. For example, 20 to 100,000 layers can be formed, or 50 to 50,000 layers can be formed.

[0007] As used herein, “layer” is a term of convenience that includes any shape, regular or irregular, having at least a predetermined thickness. In some embodiments, the size and configuration two dimensions are predetermined, and on some embodiments, the size and shape of all three dimensions of the layer is predetermined. The thickness of each layer can vary widely depending on the additive manufacturing method. In some embodiments the thickness of each layer as formed differs from a previous or subsequent layer. In some embodiments, the thickness of each layer is the same. In some embodiments the thickness of each layer as formed is 0.5 millimeters (mm) to 5 mm. In other embodiments, the article is made from a monofilament additive manufacturing process. For example, the monofilament can comprise an aromatic phosphate modified thermoplastic polymer with a diameter of from 0.1 to 5.0 mm.

[0008] The preset pattern can be determined from a three-dimensional digital representation of the desired article as is known in the art and described in further detail below.

[0009] Any additive manufacturing process can be used, provided that the process allows formation of at least one layer of a thermoplastic material that is fusible to the next adjacent layer.

[0010] The plurality of layers in the predetermined pattern are fused to provide the article. Any method effective to fuse the plurality of layers during additive manufacturing can be used. In some embodiments, the fusing occurs during formation of each of the layers. In some embodiments the fusing occurs while subsequent layers are formed, or after all layers are formed.

[0011] In some embodiments, an additive manufacturing technique known generally as material extrusion can be used. In material extrusion, an article can be formed by dispensing a flowable material (“the build material”) in a layer-by-layer manner and fusing the layers. “Fusing” as used herein includes the chemical or physical interlocking of the individual layers, and provides a “build structure”. The flowable build material can be rendered flowable by dissolving or suspending the material in a solvent. In other embodiments, the flowable material can be rendered flowable by melting. In other embodiments, a flowable prepolymer composition that can be crosslinked or otherwise reacted to form a solid can be used. Fusing can be by removal of the solvent, cooling of the melted material, or reaction of the prepolymer composition.

[0012] In particular, an article can be formed from a three-dimensional digital representation of the article by depositing the flowable material as one or more roads on a substrate in an x-y plane to form the layer. The position of the dispenser (e.g., a nozzle) relative to the substrate is then incremented along a z-axis (perpendicular to the x-y plane), and the process is then repeated to form an article from the digital representation. The dispensed material is thus also referred to as a “modeling material” as well as a “build material.” In some embodiments a support material as is known in the art can optionally be used to form a support structure. In these embodiments, the build material and the support material can be selectively dispensed during manufacture of the article to provide the article and a support structure. The support material can be present in the form of a support structure, for example, a scaffolding that can be mechanically removed or washed away when the layering process is completed to the desired degree.

[0013] Systems for material extrusion are known. An exemplary material extrusion additive manufacturing system includes a build chamber and a supply source for the

thermoplastic material. The build chamber includes a build platform, a gantry, and a dispenser for dispensing the thermoplastic material, for example an extrusion head. The build platform is a platform on which the article is built, and desirably moves along a vertical z-axis based on signals provided from a computer-operated controller. The gantry is a guide rail system that can be configured to move the dispenser in a horizontal x-y plane within the build chamber, for example based on signals provided from a controller. The horizontal x-y plane is a plane defined by an x-axis and a y-axis where the x-axis, the y-axis, and the z-axis are orthogonal to each other. Alternatively the platform can be configured to move in the horizontal x-y plane and the extrusion head can be configured to move along the z-axis. Other similar arrangements can also be used such that one or both of the platform and extrusion head are moveable relative to each other. The build platform can be isolated or exposed to atmospheric conditions.

[0014] For some embodiments, both the build structure and the support structure of the article formed can include a fused expandable layer. In other embodiments, the build structured includes a fused expandable layer and the support material does not include an expandable layer. In still other embodiments, the build structure does not include an expandable layer and the support structure does include a fused expandable layer. In those embodiments where the support structure includes an expandable layer, the lower density of the expanded layer can allow for the support material to be easily or more easily broken off than the non-expanded layer, and re-used or discarded.

[0015] In some embodiments, the support structure can be made purposely breakable, to facilitate breakage where desired. For example, the support material can have an inherently lower tensile or impact strength than the build material. In other embodiments, the shape of the support structure can be designed to increase the breakability of the support structure relative to the build structure.

[0016] For example, in some embodiments, the build material can be made from a round print nozzle or round extrusion head. A round shape as used herein means any cross-sectional shape that is enclosed by one or more curved lines. A round shape includes circles, ovals, ellipses, and the like, as well as shapes having an irregular cross-sectional shape. Three dimensional articles formed from round shaped layers of build material can possess strong structural strength. In other embodiments, the support material for the articles can be made from a non-round print nozzle or non-round extrusion head. A non-round shape means any cross-sectional shape enclosed by at least one straight line, optionally together with one or more curved lines. A non-round shape can include squares, rectangles, ribbons, horseshoes, stars, T

head shapes, X shapes, chevrons, and the like. These non-round shapes can render the support material weaker, brittle and with lower strength than round shaped build material.

[0017] The above material extrusion techniques include techniques such as fused deposition modeling and fused filament fabrication as well as others as described in ASTM F2792-12a. In fused material extrusion techniques, an article can be produced by heating a thermoplastic material to a flowable state that can be deposited to form a layer. The layer can have a predetermined shape in the x-y axis and a predetermined thickness in the z-axis. The flowable material can be deposited as roads as described above, or through a die to provide a specific profile. The layer cools and solidifies as it is deposited. A subsequent layer of melted thermoplastic material fuses to the previously deposited layer, and solidifies upon a drop in temperature. Extrusion of multiple subsequent layers builds the desired shape. In some embodiments at least one layer of an article is formed by melt deposition, and in other embodiments, more than 10, or more than 20, or more than 50 of the layers of an article are formed by melt deposition, up to and including all of the layers of an article being formed by melt deposition.

[0018] In some embodiments the thermoplastic polymer is supplied in a melted form to the dispenser. The dispenser can be configured as an extrusion head. The extrusion head can deposit the thermoplastic composition as an extruded material strand to build the article. Examples of average diameters for the extruded material strands can be from 1.27 millimeters (0.050 inches) to 3.0 millimeters (0.120 inches). Depending on the type of thermoplastic material, the thermoplastic material can be extruded at a temperature of 200 to 450°C. In some embodiments the thermoplastic material can be extruded at a temperature of 300 to 415°C. The layers can be deposited at a build temperature (the temperature of deposition of the thermoplastic extruded material) that is 50 to 200°C lower than the extrusion temperature. For example, the build temperature can be 15 to 250°C. In some embodiments the thermoplastic material is extruded at a temperature of 200 to 450°C, or 300 to 415°C, and the build temperature is maintained at ambient temperature.

[0019] Methods are known for pre-incorporating a Tg-lowering additive into a thermoplastic material, then forming the thermoplastic material into a desired shape. For example, a Tg-lowering additive can be incorporated into a melt of the thermoplastic material, then the melt formed into the desired shape and cooled. Alternatively, can be added directly to the melt used in the additive manufacturing process, or pre-incorporated or blended into the thermoplastic polymer material and the mixture can be melted together during the additive manufacturing process. In this instance, for passenger safety considerations, the Tg lowering

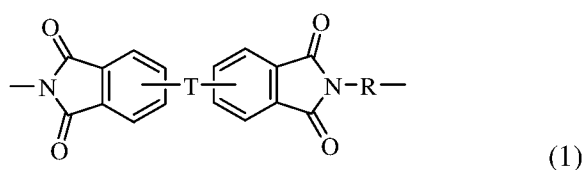
additive must not compromise the rigorous FAR flame resistance of the monofilament manufactured article.

[0020] Examples of thermoplastic polymers that can be used herein include polyarylsulfones, polycarbonates (including polycarbonate homopolymers and polycarbonate copolymers such as polycarbonate-siloxanes, polycarbonate-esters, and polycarbonate-ester-siloxanes), polyetherimides (including homopolymers and copolymers such as polyetherimide-siloxane copolymers), or a combination comprising at least one of the foregoing thermoplastic polymers. In some embodiments, polyarylsulfone, polycarbonate, polyetherimide, homopolymers and copolymers, are especially useful in a wide variety of articles, have good processability, and are recyclable.

[0021] Exemplary polycarbonates are described, for example, in US 7,790,292 B2, US 2007/0066737 A1, WO 2013/175448 A1, US 2014/0295363, and WO 2014/072923.

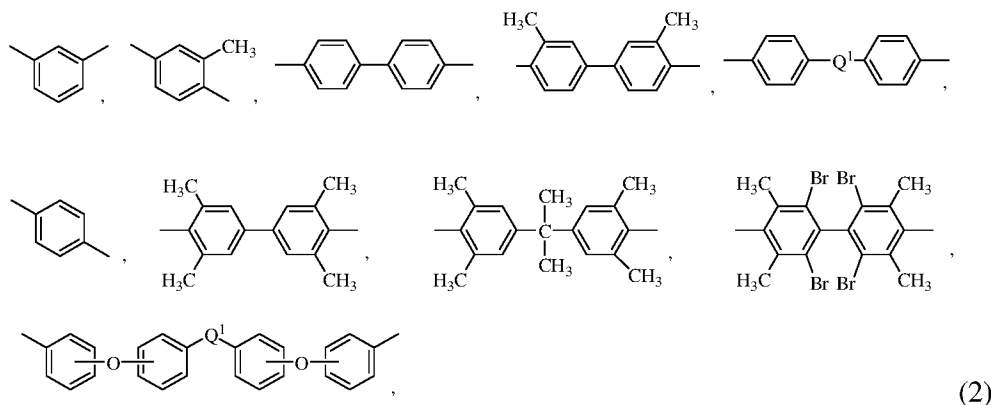
Polycarbonates are generally manufactured from bisphenol compounds such as 2,2-bis(4-hydroxyphenyl) propane (“bisphenol-A” or “BPA”), 3,3-bis(4-hydroxyphenyl) phthalimidine, 1,1-bis(4-hydroxy-3-methylphenyl)cyclohexane, or 1,1-bis(4-hydroxy-3-methylphenyl)-3,3,5-trimethylcyclohexane, or a combination comprising at least one of the foregoing bisphenol compounds can also be used. In a specific embodiment, the polycarbonate is a homopolymer derived from BPA or a copolymer derived from BPA and another bisphenol or dihydroxy aromatic compound such as resorcinol. Other polycarbonate copolymers include poly(aliphatic ester-carbonate) poly(siloxane-carbonate), and polycarbonate-ester-siloxanes). Other specific polycarbonates that can be used include poly(ester-carbonate-siloxane)s comprising bisphenol A carbonate units, isophthalate-terephthalate-bisphenol A ester units, and siloxane units, for example blocks containing 5 to 50 dimethylsiloxane units, such as those commercially available under the trade name PC-PE-SI from the Innovative Plastics division of SABIC or those described in claim 1 of US Patent No. 7,790,292, which is incorporated herein in its entirety.

[0022] Polyetherimides comprise more than 1, for example 10 to 1000, or 10 to 500, structural units of formula (1):



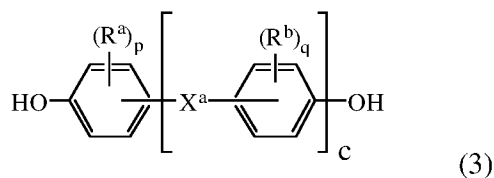
wherein each R is the same or different, and is a substituted or unsubstituted divalent organic group, such as a C6-20 aromatic hydrocarbon group or a halogenated derivative thereof, a straight or branched chain C2-20 alkylene group or a halogenated derivative thereof, a C3-8

cycloalkylene group or halogenated derivative thereof, in particular a divalent group of formula (2):



wherein Q1 is -O-, -S-, -C(O)-, -SO<sub>2</sub>-, -SO-, -CyH<sub>2</sub>y- wherein y is an integer from 1 to 5 or a halogenated derivative thereof (which includes perfluoroalkylene groups), or -(C<sub>6</sub>H<sub>10</sub>)z- wherein z is an integer from 1 to 4. In an embodiment R is m-phenylene, p-phenylene, or a diaryl sulfone.

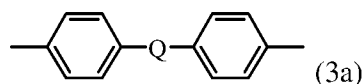
[0023] Further in formula (1), T is -O- or a group of the formula -O-Z-O- wherein the divalent bonds of the -O- or the -O-Z-O- group are in the 3,3', 3,4', 4,3', or the 4,4' positions. The group Z in -O-Z-O- of formula (1) is also a substituted or unsubstituted divalent organic group, and can be an aromatic C<sub>6</sub>-24 monocyclic or polycyclic moiety optionally substituted with 1 to 6 C<sub>1</sub>-8 alkyl groups, 1 to 8 halogen atoms, or a combination thereof, provided that the valence of Z is not exceeded. Exemplary groups Z include groups derived from a dihydroxy compound of formula (3):



wherein Ra and Rb can be the same or different and are a halogen atom or a monovalent C1-6 alkyl group, for example; p and q are each independently integers of 0 to 4; c is 0 to 4; and Xa is a bridging group connecting the hydroxy-substituted aromatic groups, where the bridging group and the hydroxy substituent of each C6 arylene group are disposed ortho, meta, or para (specifically para) to each other on the C6 arylene group. The bridging group Xa can be a single bond, -O-, -S-, -S(O)-, -S(O)2-, -C(O)-, or a C1-18 organic bridging group. The C1-18 organic bridging group can be cyclic or acyclic, aromatic or non-aromatic, and can further comprise heteroatoms such as halogens, oxygen, nitrogen, sulfur, silicon, or phosphorous. The C1-18 organic group can be disposed such that the C6 arylene groups connected thereto are each



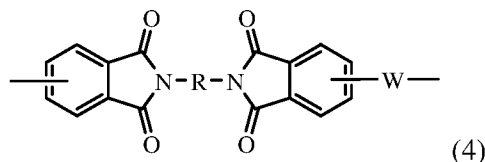
connected to a common alkylidene carbon or to different carbons of the C1-18 organic bridging group. A specific example of a group Z is a divalent group of formula (3a):



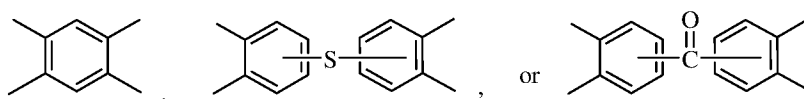
wherein Q is -O-, -S-, -C(O)-, -SO<sub>2</sub>-, -SO-, or -CyH<sub>2</sub>y- wherein y is an integer from 1 to 5 or a halogenated derivative thereof (including a perfluoroalkylene group). In a specific embodiment Z is derived from bisphenol A, such that Q in formula (3a) is 2,2-isopropylidene.

[0024] In an embodiment in formula (1), R is m-phenylene or p-phenylene and T is -O-Z-O wherein Z is a divalent group of formula (3a). Alternatively, R is m-phenylene or p-phenylene and T is -O-Z-O wherein Z is a divalent group of formula (3a) and Q is 2,2-isopropylidene.

[0025] In some embodiments, the polyetherimide can be a copolymer, for example, a polyetherimide sulfone copolymer comprising structural units of formula (1) wherein at least 50 mole% of the R groups are of formula (2) wherein Q<sub>1</sub> is -SO<sub>2</sub>- and the remaining R groups are independently p-phenylene or m-phenylene or a combination comprising at least one of the foregoing; and Z is 2,2'-(4-phenylene)isopropylidene. Alternatively, the polyetherimide optionally comprises additional structural imide units, for example imide units of formula (4):

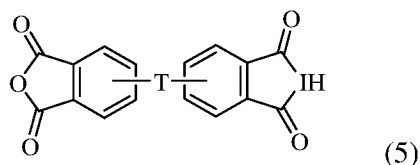


wherein R is as described in formula (1) and W is a linker of the formulas:

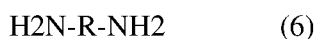


[0026] These additional structural imide units can be present in amounts from 0 to 10 mole % of the total number of units, specifically 0 to 5 mole %, more specifically 0 to 2 mole %. In an embodiment no additional imide units are present in the polyetherimide.

[0027] The polyetherimide can be prepared by any of the methods well known to those skilled in the art, including the reaction of an aromatic bis(ether anhydride) of formula (5):



with an organic diamine of formula (6)



wherein T and R are defined as described above. Copolymers of the polyetherimides can be manufactured using a combination of an aromatic bis(ether anhydride) of formula (4) and a different bis(anhydride), for example a bis(anhydride) wherein T does not contain an ether functionality, for example T is a sulfone.

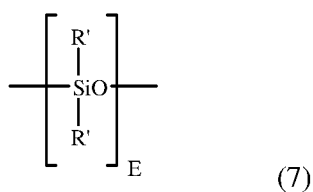
[0028] Illustrative examples of bis(anhydride)s include 3,3-bis[4-(3,4-dicarboxyphenoxy)phenyl]propane dianhydride; 4,4'-bis(3,4-dicarboxyphenoxy)diphenyl ether dianhydride; 4,4'-bis(3,4-dicarboxyphenoxy)diphenyl sulfide dianhydride; 4,4'-bis(3,4-dicarboxyphenoxy)benzophenone dianhydride; 4,4'-bis(3,4-dicarboxyphenoxy)diphenyl sulfone dianhydride; 2,2-bis[4-(2,3-dicarboxyphenoxy)phenyl]propane dianhydride; 4,4'-bis(2,3-dicarboxyphenoxy)diphenyl ether dianhydride; 4,4'-bis(2,3-dicarboxyphenoxy)diphenyl sulfide dianhydride; 4,4'-bis(2,3-dicarboxyphenoxy)benzophenone dianhydride; 4,4'-bis(2,3-dicarboxyphenoxy)diphenyl sulfone dianhydride; 4-(2,3-dicarboxyphenoxy)-4'-(3,4-dicarboxyphenoxy)diphenyl-2,2-propane dianhydride; 4-(2,3-dicarboxyphenoxy)-4'-(3,4-dicarboxyphenoxy)diphenyl ether dianhydride; 4-(2,3-dicarboxyphenoxy)-4'-(3,4-dicarboxyphenoxy)diphenyl sulfide dianhydride; 4-(2,3-dicarboxyphenoxy)-4'-(3,4-dicarboxyphenoxy)benzophenone dianhydride; and, 4-(2,3-dicarboxyphenoxy)-4'-(3,4-dicarboxyphenoxy)diphenyl sulfone dianhydride, as well as various combinations thereof.

[0029] Examples of organic diamines include ethylenediamine, propylenediamine, trimethylenediamine, diethylenetriamine, triethylene tetramine, hexamethylenediamine, heptamethylenediamine, octamethylenediamine, nonamethylenediamine, decamethylenediamine, 1,12-dodecanediamine, 1,18-octadecanediamine, 3-methylheptamethylenediamine, 4,4-dimethylheptamethylenediamine, 4-methylnonamethylenediamine, 5-methylnonamethylenediamine, 2,5-dimethylhexamethylenediamine, 2,5-dimethylheptamethylenediamine, 2,2-dimethylpropylenediamine, N-methyl-bis (3-aminopropyl) amine, 3-methoxyhexamethylenediamine, 1,2-bis(3-aminopropoxy) ethane, bis(3-aminopropyl) sulfide, 1,4-cyclohexanediamine, bis-(4-aminocyclohexyl) methane, m-phenylenediamine, p-phenylenediamine, 2,4-diaminotoluene, 2,6-diaminotoluene, m-xylylenediamine, p-xylylenediamine, 2-methyl-4,6-diethyl-1,3-phenylene-diamine, 5-methyl-4,6-diethyl-1,3-phenylene-diamine, benzidine, 3,3'-dimethylbenzidine, 3,3'-dimethoxybenzidine, 1,5-diaminonaphthalene, bis(4-aminophenyl) methane, bis(2-chloro-4-amino-3,5-diethylphenyl) methane, bis(4-aminophenyl) propane, 2,4-bis(p-amino-t-butyl) toluene, bis(p-amino-t-butylphenyl) ether, bis(p-methyl-o-aminophenyl) benzene, bis(p-methyl-o-aminopentyl) benzene, 1,3-diamino-4-isopropylbenzene, bis(4-aminophenyl) sulfide, bis-(4-aminophenyl)

sulfone, and bis(4-aminophenyl) ether. Combinations of these compounds can also be used. In some embodiments the organic diamine is m-phenylenediamine, p-phenylenediamine, sulfonyl dianiline, or a combination comprising one or more of the foregoing.

[0030] The polyetherimides can have a melt index of 0.1 to 10 grams per minute (g/min), as measured by American Society for Testing Materials (ASTM) D1238 at 340 to 370°C, using a 6.7 kilogram (kg) weight. In some embodiments, the polyetherimide polymer has a weight average molecular weight (Mw) of 1,000 to 150,000 grams/mole (Dalton), as measured by gel permeation chromatography, using polystyrene standards. In some embodiments the polyetherimide has an Mw of 10,000 to 80,000 Daltons. Such polyetherimide polymers typically have an intrinsic viscosity greater than 0.2 deciliters per gram (dl/g), or, more specifically, 0.35 to 0.7 dl/g as measured in m-cresol at 25°C.

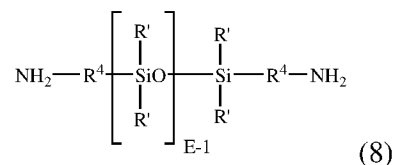
[0031] The thermoplastic composition can also comprise a poly(siloxane-etherimide) copolymer comprising polyetherimide units of formula (1) and siloxane blocks of formula (7):



wherein each R' is independently a C1-13 monovalent hydrocarbyl group. For example, each R' can independently be a C1-13 alkyl group, C1-13 alkoxy group, C2-13 alkenyl group, C2-13 alkenyloxy group, C3-6 cycloalkyl group, C3-6 cycloalkoxy group, C6-14 aryl group, C6-10 aryloxy group, C7-13 arylalkyl group, C7-13 arylalkoxy group, C7-13 alkylaryl group, or C7-13 alkylaryloxy group. The foregoing groups can be fully or partially halogenated with fluorine, chlorine, bromine, or iodine, or a combination comprising at least one of the foregoing. In an embodiment no halogens are present. Combinations of the foregoing R groups can be used in the same copolymer. In an embodiment, the polysiloxane blocks comprises R' groups that have minimal hydrocarbon content. In a specific embodiment, an R' group with a minimal hydrocarbon content is a methyl group.

[0032] The poly(siloxane-etherimide) can be a block or graft copolymer. Block poly(siloxane-etherimide) copolymers comprise etherimide units and siloxane blocks in the polymer backbone. The etherimide units and the siloxane blocks and the can be present in random order, as blocks (i.e., AABB), alternating (i.e., ABAB), or a combination thereof. Graft poly(siloxane-etherimide) copolymers are non-linear copolymers comprising the siloxane blocks connected to linear or branched polymer backbone comprising etherimide blocks.

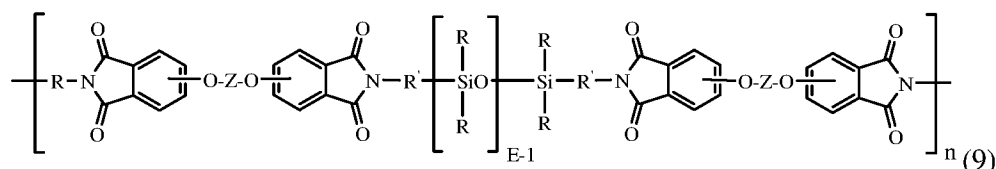
[0033] The poly (siloxane-etherimide)s can be formed by polymerization of an aromatic bisanhydride (4) and a diamine component comprising an organic diamine (6) as described above or mixture of diamines, and a polysiloxane diamine of formula (8):



wherein R' and E are as described in formula (7), and R<sup>4</sup> is each independently a C<sub>2</sub>-C<sub>20</sub> hydrocarbon, in particular a C<sub>2</sub>-C<sub>20</sub> arylene, alkylene, or arylenealkylene group. In an embodiment R<sup>4</sup> is a C<sub>2</sub>-C<sub>20</sub> alkyl group, specifically a C<sub>2</sub>-C<sub>20</sub> alkyl group such as propylene, and E has an average value of 5 to 100, 5 to 75, 5 to 60, 5 to 15, or 15 to 40. Procedures for making the polysiloxane diamines of formula (22) are well known in the art.

[0034] In some poly(siloxane-etherimide)s the diamine component can contain 10 to 90 mole percent (mol %), or 20 to 50 mol%, or 25 to 40 mol% of polysiloxane diamine (7) and 10 to 90 mol%, or 50 to 80 mol%, or 60 to 75 mol% of diamine (5), for example as described in US Patent 4,404,350. The diamine components can be physically mixed prior to reaction with the bisanhydride(s), thus forming a substantially random copolymer. Alternatively, block or alternating copolymers can be formed by selective reaction of (5) and (7) with aromatic dianhydrides (20), to make polyimide blocks that are subsequently reacted together. Thus, the poly(siloxane-imide) copolymer can be a block, random, or graft copolymer.

[0035] Examples of specific poly(siloxane-etherimide) are described in US Pat. Nos. 4,404,350, 4,808,686 and 4,690,997. In an embodiment, the poly(siloxane-etherimide) has units of formula (9):



wherein R' and E of the siloxane are as in formula (6), the R and Z of the imide are as in formula (1), R<sup>4</sup> is the same as R<sup>4</sup> as in formula (8), and n is an integer from 5 to 100. In a specific embodiment, the R of the etherimide is a phenylene, Z is a residue of bisphenol A, R<sup>4</sup> is n-propylene, E is 2 to 50, 5, to 30, or 10 to 40, n is 5 to 100, and each R' of the siloxane is methyl.

[0036] The relative amount of polysiloxane units and etherimide units in the poly(siloxane-etherimide) depends on the desired properties, and are selected using the guidelines provided herein. In particular, as mentioned above, the block or graft poly(siloxane-etherimide) copolymer is selected to have a certain average value of E, and is selected and used

in amount effective to provide the desired wt% of polysiloxane units in the composition. In an embodiment the poly(siloxane-etherimide) comprises 10 to 50 wt%, 10 to 40 wt%, or 20 to 35 wt% polysiloxane units, based on the total weight of the poly(siloxane-etherimide).

[0037] The term “alkyl” includes branched or straight chain, unsaturated aliphatic C1-30 hydrocarbon groups e.g., methyl, ethyl, n-propyl, i-propyl, n-butyl, s-butyl, t-butyl, n-pentyl, s-pentyl, n- and s-hexyl, n- and s-heptyl, and, n- and s-octyl. “Alkenyl” means a straight or branched chain, monovalent hydrocarbon group having at least one carbon-carbon double bond (e.g., ethenyl (-HC=CH<sub>2</sub>)). “Alkoxy” means an alkyl group that is linked via an oxygen (i.e., alkyl-O-), for example methoxy, ethoxy, and sec-butyloxy groups.

[0038] “Alkylene” means a straight or branched chain, saturated, divalent aliphatic hydrocarbon group (e.g., methylene (-CH<sub>2</sub>-) or, propylene (-CH<sub>2</sub>)<sub>3</sub>-).

[0039] “Cycloalkylene” means a divalent cyclic alkylene group, -C<sub>n</sub>H<sub>2n-x</sub>, wherein x represents the number of hydrogens replaced by cyclization(s). “Cycloalkenyl” means a monovalent group having one or more rings and one or more carbon-carbon double bond in the ring, wherein all ring members are carbon (e.g., cyclopentyl and cyclohexyl).

[0040] The term “aryl” means an aromatic hydrocarbon group containing the specified number of carbon atoms, such as to phenyl, tropone, indanyl, or naphthyl.

[0041] The prefix “halo” means a group or compound including one more of a fluoro, chloro, bromo, iodo, and astatino substituent. A combination of different halo groups (e.g., bromo and fluoro) can be present. In an embodiment only chloro groups are present.

[0042] The prefix “hetero” means that the compound or group includes at least one ring member that is a heteroatom (e.g., 1, 2, or 3 heteroatom(s)), wherein the heteroatom(s) is each independently N, O, S, or P.

[0043] “Substituted” means that the compound or group is substituted with at least one (e.g., 1, 2, 3, or 4) substituents independently selected from, a C1-9 alkoxy, a C1-9 haloalkoxy, a nitro (-NO<sub>2</sub>), a cyano (-CN), a C1-6 alkyl sulfonyl (-S(=O)<sub>2</sub>-alkyl), a C6-12 aryl sulfonyl (-S(=O)<sub>2</sub>-aryl), a thiol (-SH), a thiocyno (-SCN), a tosyl (CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>-), a C3-12 cycloalkyl, a C2-12 alkenyl, a C5-12 cycloalkenyl, a C6-12 aryl, a C7-13 arylalkylene, a C4-12 heterocycloalkyl, and a C3-12 heteroaryl instead of hydrogen, provided that the substituted atom's normal valence is not exceeded.

[0044] Polyarylethersulfones include polyphenylethersulfone which is an amorphous plastic. This material combines a high melting temperature with quite a low moisture absorption. Furthermore, it has good impact strength and chemical resistance.

[0045] The thermoplastic polysulfones, polyethersulfones and polyphenylene ether sulfones polyethersulfones can be prepared as described in U.S. Patent Nos. 3,634,355, 4,008,203, 4,108,837 and 4,175,175, all of which are incorporated by reference herein in their entireties.

[0046] Polyaryl ether sulfones, also referred to as polysulfones, polyether sulfones and polyphenylene ether sulfones are linear thermoplastic polymers that possess a number of attractive features such as high temperature resistance, good electrical properties, and good hydrolytic stability. A variety of polyaryl ether sulfones are commercially available, including the polycondensation product of dihydroxy diphenyl sulfone with dichloro diphenyl sulfone and known as polyether sulfone (PES), and the polymer of bisphenol-A and dichloro diphenyl sulfone known in the art as polysulfone (PSu or PSF). Other polyaryl ether sulfones are the polybiphenyl ether sulfones, available from Solvay Inc. under the trade mark of RADEL R. This polymer can be described as the product of the polycondensation of biphenol with 4,4'-dichlorodiphenyl sulfone and also is known and described in the art, for example, in Canadian Patent No. 847,963, which is incorporated by reference herein in its entirety.

[0047] Polysulfones are sold by Solvay Co. under the UDEL trade name. Polyethersulfones are sold by Solvay under the RADEL A trade names and by BASF Co, as ULTRASON E.

[0048] Methods for the preparation of polyaryl ether sulfones are widely known and several suitable processes have been well described in the art. Two methods, the carbonate method and the alkali metal hydroxide method, are known and used for this purpose. In the alkali metal hydroxide method, a double alkali metal salt of a dihydric phenol is contacted with a dihalobenzenoid compound in the presence of a dipolar, aprotic solvent under substantially anhydrous conditions. The carbonate method, in which at least one dihydric phenol and at least one dihalobenzenoid compound are heated, for example, with sodium carbonate or bicarbonate and a second alkali metal carbonate or bicarbonate is also disclosed in the art, for example in U.S. Patent No. 4,176,222, which is incorporated by reference herein in its entirety. Alternatively, the polybiphenyl ether sulfone, PSu and PBS polymer components can be prepared by any of the variety of methods known in the art for the preparation of polyaryl ether polymers.

[0049] The molecular weight of the polysulfone, as indicated by reduced viscosity data in an appropriate solvent such as methylene chloride, chloroform, N-methylpyrrolidone or the like, will be at least 0.3 dl/ g, preferably at least 0.4 dl/ g and, typically, will not exceed about 1.5 dl/ g. In some instances the polysulfone weight average molecular weight can vary from 10,000

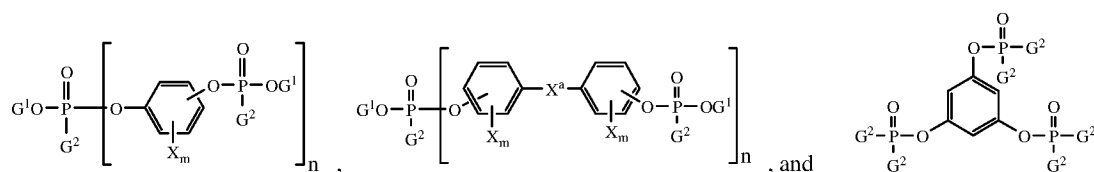
to 100,000. Polysulfones can have glass transition temperatures from 180 to 250°C in some instances.

[0050] Polysulfones are further described in ASTM method D6394 Standard Specification for Sulfone Plastics.

[0051] A variety of PBS copolymers, for example comprising bisphenol A (BPA) moieties, other bisphenols and diphenyl ether sulfone moieties in molar ratios other than 1:1, can be used.

[0052] Additives that reduce the Tg of the thermoplastic polymer can include one or more non-brominated and non-chlorinated organic phosphorus-containing plasticizers such as an aromatic phosphate of the formula (GO)3P=O, wherein each G is independently an alkyl, cycloalkyl, aryl, alkylaryl, or aralkyl group, provided that at least one G is an aromatic group. Two of the G groups can be joined together to provide a cyclic group, for example, diphenyl pentaerythritol diphosphate. aromatic phosphates include, phenyl bis(dodecyl) phosphate, phenyl bis(neopentyl) phosphate, phenyl bis(3,5,5'-trimethylhexyl) phosphate, ethyl diphenyl phosphate, 2-ethylhexyl di(p-tolyl) phosphate, bis(2-ethylhexyl) p-tolyl phosphate, tritolyl phosphate, bis(2-ethylhexyl) phenyl phosphate, tri(nonylphenyl) phosphate, bis(dodecyl) p-tolyl phosphate, dibutyl phenyl phosphate, 2-chloroethyl diphenyl phosphate, p-tolyl bis(2,5,5'-trimethylhexyl) phosphate, 2-ethylhexyl diphenyl phosphate, or the like. A specific aromatic phosphate is one in which each G is aromatic, for example, triphenyl phosphate, tricresyl phosphate, isopropylated triphenyl phosphate, and the like.

[0053] Di- or polyfunctional aromatic phosphorus-containing compounds are also useful, for example, compounds of the formulas below:



wherein each G<sup>1</sup> is independently a hydrocarbon having 1 to 30 carbon atoms; each G<sup>2</sup> is independently a hydrocarbon or hydrocarbonoxy having 1 to 30 carbon atoms; each X is independently a bromine or chlorine; m is 0 to 4, and n is 1 to 30. Di- or polyfunctional aromatic phosphorus-containing compounds of this type include resorcinol tetraphenyl diphosphate (RDP), the bis(diphenyl) phosphate of hydroquinone and the bis(diphenyl) phosphate of bisphenol A, respectively, their oligomeric and polymeric counterparts, and the like.

[0054] The amount of Tg-lowering additive can vary from wherein the amount of Tg-lowering additive is from 0.5% to 15 %, from 1% to 12%, or from 2% to 10% or any range within 1% to 30%, by weight, based on the weight of the thermoplastic polymer.

[0055] The thermoplastic polymer composition can include various other additives ordinarily incorporated into polymer compositions of this type, with the proviso that any additives is selected so as to not significantly adversely affect the desired properties of the thermoplastic composition, in particular the adhesion properties. Such additives can be mixed at a suitable time during the mixing of the components for forming the composition. Additives include nucleating agents, fillers, reinforcing agents, antioxidants, heat stabilizers, light stabilizers, ultraviolet (UV) light stabilizers, , lubricants, mold release agents, surfactants, antistatic agents, colorants such as titanium dioxide, carbon black, and organic dyes, surface effect additives, radiation stabilizers, flame retardants, and anti-drip agents. A combination of additives can be used, for example a combination of a heat stabilizer and ultraviolet light stabilizer. In general, the additives are used in the amounts generally known to be effective. For example, the total amount of the additives (other than any impact modifier, filler, or reinforcing agents) can be 0.01 to 5 wt.%, based on the total weight of the thermoplastic material.

[0056] In an embodiment, the thermoplastic composition and articles comprising the thermoplastic composition, including a sheet, window article, window, trays, seating, storage compartments, ventilation systems, duct work, blower, fans, sanitary fixtures, mirrors, cabin walls and partitions, lighting systems, safety equipment, doors, shutters, electrical components, wiring, computers and communication equipment and other aircraft interior articles disclosed herein can exhibit at least one of the following desirable properties: a 2 minute integrated heat release rate of less than or equal to 65 kilowatt-minutes per square meter (kW-min/m<sup>2</sup>), specifically less than or equal to 55 kW-min/m<sup>2</sup>, and a peak heat release rate of less than 65 kilowatts per square meter (kW/m<sup>2</sup>), specifically less than or equal to 55 kW/m<sup>2</sup> as measured using the method of FAR F25.4, in accordance with Federal Aviation Regulation FAR 25.853 (d).

[0057] In some instances the article will be used in the interior of an aircraft or in construction of other passenger conveyances. Such conveyances can be private or commercial conveyances and can be regulated by various governmental regulations concerning passenger safety in the event of a fire. Examples of passenger conveyances include airplanes, helicopters, trains, commuter trains, busses, ships, excursion tour vehicles, tram cars, trolley cars, mobile homes, sleep-in recreation vehicles and the like.



## EXAMPLES

[0058] Sample preparation: Seven formulations were prepared using the raw material shown in Table 1 in the weight percentages shown in Table 2. The useful range of each ingredient is shown in Table 1.

Table 1: Raw Materials

| Materials        | Chemical Description                                                                                                                                                                                               | Source, Vendor       | Weight % |
|------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------|----------|
| PC-PE            | Poly(carbonate-ester) derived from resorcinol and bisphenol A with p-cumylphenol endcaps, having a weight average molecular weight of 18,000-24,000 g/mol powder [CAS: 235420-85-6]                                | SABIC                | 0-80     |
| PC-PE-SiPC-PE-Si | Poly(carbonate-ester-siloxane) derived from resorcinol, siloxane, and bisphenol A, with 1% D10 siloxane, having a weight average molecular weight of 21,000-27,000 g/mole [CAS: 915977-87-6]                       | SABIC                | 0-99.9   |
| PC-Si            | Poly(carbonate-siloxane) derived from bisphenol A, with dimethyl siloxane and p-cumylphenol end-capped, with 20% wt % of a D45 siloxane and having a weight average molecular weight of 27,000-32,000 g/mol 30,000 | SABIC                | 0-15     |
| PEI 1            | Polyetherimide (PEI), having a weight average molecular weight of 53,000-60,000 g/mol                                                                                                                              | SABIC                | 0-80     |
| PEI-Si           | Poly(etherimide-siloxane), random copolymer with 34% dimethyl siloxane units                                                                                                                                       | SABIC                | 0-6      |
| PPSU             | Polyphenylsulfone, RADEL R-5100 NT, fine grinds                                                                                                                                                                    | SOLVAY               | 0-99     |
| BPA-DP           | Bisphenol A diphosphate, tradename CR-741 [CAS: 5945-33-5]                                                                                                                                                         | Nagase (Europa) GmbH | 0-12     |
| Sol-DP           | Aryl phosphate flame retardant, FYROFLEX SOL-DP, powder                                                                                                                                                            | ICL-IP               | 0-12     |
| HS1              | Tri-aryl phosphite stabilizer, ALKANOX 240, powder                                                                                                                                                                 | Chemtura             | 0-0.2    |
| HS2              | Tris(2,4-di-t-butylphenyl)phosphite, IRGAFOS 168                                                                                                                                                                   | Ciba                 | 0-0.2    |
| TiO <sub>2</sub> | Titanium dioxide, TIONA 188                                                                                                                                                                                        | Millennium           | 0-8      |

Table 2: Sample formulations and flame performance

| Component                                       | Unit | PC-PE-SiPC-PE-SI* | PC-PE-SiPC-PE-SI with BPA-DP | PC-PE-SiPC-PE-SI with Sol-DP | PEI Blend* | PEI Blend with Sol-DP | PPSU* | PPSU with Sol-DP |
|-------------------------------------------------|------|-------------------|------------------------------|------------------------------|------------|-----------------------|-------|------------------|
| Sol-DP                                          | %    |                   |                              | 6.5                          |            | 6.5                   |       | 6.5              |
| PC-PE-SiPC-PE-SI                                | %    | 99.94             | 92.44                        | 93.44                        |            |                       |       |                  |
| HS1                                             | %    | 0.06              | 0.06                         | 0.06                         |            |                       |       |                  |
| BPA-DP                                          | %    |                   | 7.5                          |                              |            |                       |       |                  |
| PEI 1                                           | %    |                   |                              |                              | 49.9       | 46.6                  |       |                  |
| PC-Si                                           | %    |                   |                              |                              | 8          | 7.5                   |       |                  |
| PC-PE                                           | %    |                   |                              |                              | 39         | 36.5                  |       |                  |
| PEI-Si                                          | %    |                   |                              |                              | 3          | 2.8                   |       |                  |
| HS2                                             | %    |                   |                              |                              | 0.1        | 0.1                   | 0.1   | 0.1              |
| PPSU                                            | %    |                   |                              |                              |            |                       | 96.1  | 89.8             |
| TiO <sub>2</sub>                                | %    |                   |                              |                              |            |                       | 3.8   | 3.6              |
| ASTM Smoke Density (Ds-4)                       |      | <100              |                              |                              |            |                       |       |                  |
| Vertical burn, 60 sec (15 s / 6 inches / 3 sec) |      | Fail              | Pass                         | Pass                         | Pass       | Pass                  | Pass  | Pass             |

\*Comparative

[0059] It was found that 5.5 to 10 wt.% of an aromatic organophosphorus compound comprising non-alkylated phenoxy units attached to the phosphorus (an organophosphorus compound in an amount effective to provide 0.1-1 wt% phosphorus, based on the total weight in the composition), such as in BPADP or Sol-DP, FP-800 and the like, can be used to prepare a compound for aircraft and railway applications that comply with Federal Aviation Regulation (FAR) and EN-45545 railway rating.

[0060] The polymers used in this study are described in Table 1. Examples of formulation that are useful for this invention are shown in Table 2 (Examples PC-PE-SiPC-PE-SI with Sol DP, PC-PE-SiPC-PE-SI with BPADP, PEI Blend with Sol-DP, and PPSU w Sol DP). Table 2 also shows comparative examples (PC-PE-SiPC-PE-SI, PEI blend, and PPSU).

[0061] Extrusions of the blends listed in Table 2 were carried out on a WERNER & PFLEIDERER 30 mm co-rotating twin screw extruder. The powder blends were feed in the feed throat into the line before the Zone 1. At Zone 4, a vacuum vent is attached to the line and at Zone 5 a liquid injection system is attached via which the liquid flame retardants (BPADP) were injected.

[0062] Typical temperature profile and processing conditions employed are shown in Table 3 below. All solid raw materials were pre-blended in a super blender and then fed into the extruder. All the solid components were fed from the main feed throat from upper stream.

Table 3: Typical extrusion conditions (set value)

| Parameters                    | Unit | PC-PE-SI formulations | PEI blend formulations | PPSU formulations |
|-------------------------------|------|-----------------------|------------------------|-------------------|
| Zone 1 temperature            | °F   | 350-400               | 400-500                | 500-550           |
| Zone 2 temperature            | °F   | 400-500               | 500-540                | 560-620           |
| Zone 3 temperature            | °F   | 450-500               | 540-560                | 620-640           |
| Zone 4 temperature            | °F   | 520-550               | 580-620                | 640-680           |
| Zone 5 temperature            | °F   | 520-550               | 580-620                | 640-680           |
| Zone 6 temperature            | °F   | 520-550               | 580-620                | 640-680           |
| Zone 7 (Die Head) temperature | °F   | 520-550               | 580-620                | 640-680           |
| Screw speed                   | RPM  | 300 to 500            |                        |                   |
| Torque                        | %    | 40 to 90              |                        |                   |
| Throughput                    | kg/h | 25 to 60              |                        |                   |

[0063] Table 4 depicts the molding conditions to mold strips of 5 x 0.5 x 0.04 inches (127 x 12.7 x 1 mm). All the samples could be molded successfully except the PPSU sample. PPSU sample could not fill in the 1mm strip tool due to very high melt viscosity. However with addition of Sol-DP, the sample (PPSU with Sol-DP) showed better flowability to the 1mm strip tool.

Table 4: Typical molding conditions (set value)

|                             | Unit  | PC-PE-SI formulations | PEI blend formulations | PPSU formulations |
|-----------------------------|-------|-----------------------|------------------------|-------------------|
| Drying temperature          | °F    | 220-250               | 270-290                | 270-290           |
| Drying time                 | hours | 4-6                   | 4-6                    | 4-6               |
| Melt temperature            | °F    | 550-580               | 620-680                | 650-720           |
| Nozzle temperature          | °F    | 550-580               | 620-680                | 650-720           |
| Front - Zone 3 temperature  | °F    | 550-580               | 620-680                | 650-720           |
| Middle - Zone 2 temperature | °F    | 520-580               | 600-680                | 650-720           |
| Rear - Zone 1 temperature   | °F    | 520-550               | 600-650                | 650-700           |
| Mold Temperature            | °F    | 150-170               | 150-170                | 160-180           |
| Back pressure               | MPa   | 0.3 to 0.7            | 0.3 to 0.7             | 0.3 to 0.7        |
| Screw speed                 | RPM   | 40 to 100             | 40 to 100              | 40 to 100         |

#### Description of Lap Shear Adhesion test:

[0064] Sample strips of 5 x 0.5 x 0.04 inches (127 x 12.7 x 1 mm) were molded. Two such strips were stacked one on top of the other with 0.5 inch overlap. The samples were then sandwiched between quarter inch thick metal bars and placed in the oven at optimum temperature for appropriate time. A clip was used to clamp the 2 metal bars to ensure good contact between sample strips. The samples were then taken out and the strips were subjected to lap shear test using an Instron mechanical tester at a temperature of 23°C and testing speed of 50 mm/min. Comparisons were made among various samples and depending on the decreasing order of force required to peel them apart and observing the sample failure mode, the type of break was classified as cohesive failure, adhesive failure and no breaks or yield and draw. A

cohesive failure is defined as any failure or break away from the bonded surface. An adhesive failure is defined as failure at the bonded interface.

[0065] Type I: Adhesive failure; Type II: Cohesive failure; Type III: No failure

Table 5: Adhesion test on two layer structure

| Condition    | Material           | Force-Break (N) | Lap Shear Test  |
|--------------|--------------------|-----------------|-----------------|
| 20 min@130°C | PC-PE-SI           | 96              | Type I          |
|              | PC-PE-SI w BPADP   | 811             | Type II and III |
|              | PC-PE-SI w Sol-DP  | 869             | Type II and III |
| 10 min@170°C | PEI Blend          | 79              | Type I          |
|              | PEI Blend w Sol-DP | 781             | Type I and III  |

Table 6: Adhesion test on sandwich structure

| Condition    | Material           | Force-Break (N) | Lap Shear Test  |
|--------------|--------------------|-----------------|-----------------|
| 10 min@150°C | PC-PE-SI           | 266             | Type I          |
|              | PC-PE-SI w BPA-DP  | 835             | Type II and III |
|              | PC-PE-SI w Sol-DP  | 739             | Type II and III |
| 10 min@190°C | PEI blend          | 401             | Type I and II   |
|              | PEI Blend w Sol-DP | 830             | Type II and III |

[0066] Table 5 and 6 shows the results of the lap shear test for samples prepared under 2 types of structures: two layers and sandwich structure.

[0067] The aromatic organophosphorus such as BPADP and Sol-DP here can provide a plasticized effect in the blends. It can be seen from the data that the materials containing BPADP or Sol-DP shows cohesive failure for both the conditions tested thus exhibiting better interlayer adhesion. The control sample either does not stick or undergoes adhesive failure under the two conditions.

[0068] Table 7 shows the decreasing Tg and increasing MVR of the materials with addition of BPADP or Sol-DP.

| Table 7 Samples    | Tg (°C) | MVR cm <sup>3</sup> /10 min (300°C; 5 Kg) | MVR cm <sup>3</sup> /10 min (330°C; 5 Kg) |
|--------------------|---------|-------------------------------------------|-------------------------------------------|
| PC-PE-SI           | 140     | 17                                        | 47                                        |
| PC-PE-SI w BPADP   | 118     | 39                                        | 106                                       |
| PC-PE-SI w Sol-DP  | 115     | 41                                        | 105                                       |
| PEI 1 Blend        | 182     | 6                                         | 21                                        |
| PEI Blend w Sol-DP | 155     | 16                                        | 47                                        |
| PPSU               | 224     | n/a                                       | 4                                         |
| PPSU w Sol-DP      | 183     | 4                                         | 13                                        |

[0069] The present invention is further illustrated by the following embodiments.

[0070] Embodiment 1. A method of making an article useful in aircraft or other passenger conveyance interiors, the method comprising: melt extruding a plurality of layers comprising a thermoplastic polymer composition in a preset pattern; and fusing the plurality of layers to provide the article; wherein the thermoplastic polymer composition comprises a

polycarbonate polymer or copolymer, a polyetherimide polymer or copolymer, a polyarylethersulfone polymer or copolymer, or a combination comprising at least one of the foregoing thermoplastic polymers and a non-brominated and non-chlorinated organic phosphorus-containing additive that will lower the Tg of the thermoplastic polymer from 5 to 100 degrees C and wherein the article has a 2 minute integrated heat release rate of less than or equal to 65 kilowatt-minutes per square meter (kW-min/m<sup>2</sup>) and a peak heat release rate of less than 65 kilowatts per square meter (kW/m<sup>2</sup>) as measured using the method of FAR F25.4, in accordance with Federal Aviation Regulation FAR 25.853 (d).

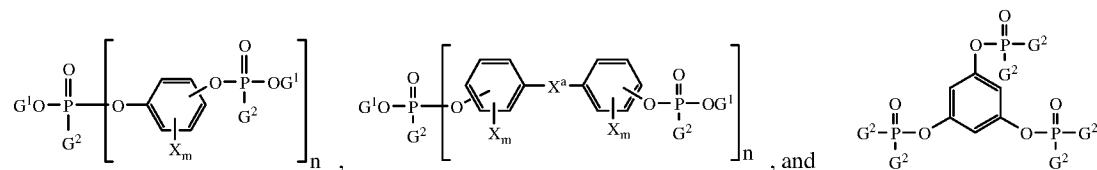
[0071] Embodiment 2. The method of Embodiment 1, wherein the thermoplastic polymer is a polycarbonate polymer or copolymer or a combination comprising at least one of the foregoing thermoplastic polymers and, optionally, wherein the article is made from layers built from a monofilament having a diameter from 0.1 to 5.0 mm.

[0072] Embodiment 3. The method of Embodiment 1, wherein the thermoplastic polymer comprise poly(ester-carbonate-siloxane)s comprising bisphenol A carbonate units, isophthalate-terephthalate-bisphenol A ester units, and siloxane units.

[0073] Embodiment 4. The method of Embodiment 1, wherein the thermoplastic polymer is a polyetherimide polymer or copolymer or a combination comprising at least one of the foregoing thermoplastic polymers.

[0074] Embodiment 5. The method of Embodiment 1, wherein the thermoplastic polymer is a polyphenylethersulfone polymer or copolymer or a combination comprising at least one of the foregoing thermoplastic polymers.

[0075] Embodiment 6. The method of any of the preceding Embodiments, wherein the non-brominated and non-chlorinated organic phosphorus-containing additive is an aromatic phosphate of the formula (GO)3P=O, wherein each G is independently an alkyl, cycloalkyl, aryl, alkylaryl, or aralkyl group, provided that at least one G is an aromatic group or a di- or polyfunctional aromatic phosphorus-containing compounds of the formulas below:



herein each G<sup>1</sup> is independently a hydrocarbon having 1 to 30 carbon atoms; each G<sup>2</sup> is independently a hydrocarbon or hydrocarbonoxy having 1 to 30 carbon atoms; each X is independently a bromine or chlorine; m is 0 to 4, and n is 1 to 30, or a combination comprising

at least one of the foregoing non-brominated and non-chlorinated organic phosphorus-containing additives.

[0076] Embodiment 7. The method of any of the preceding Embodiments, wherein the non-brominated and non-chlorinated organic phosphorus-containing additive is selected from the group consisting of triphenyl phosphate, tri cresyl phosphates, tri xylyl phosphates, tri mesityl phosphates, bisphenol A diphosphates, resorcinol diphosphates, biphenol diphosphates, hydroquinone diphosphates, acetophenone bisphenol diphosphates, dihydroxy diphenyl ether diphosphates their oligomeric and polymeric counterparts, or a combination comprising at least one of the foregoing non-brominated and non-chlorinated organic phosphorus-containing additives.

[0077] Embodiment 8. The method of any of the preceding Embodiments, wherein the non-brominated and non-chlorinated organic phosphorus-containing additive is selected from the group consisting of resorcinol tetraphenyl diphosphate (RDP), the bis(diphenyl) phosphate of hydroquinone and the bis(diphenyl) phosphate of bisphenol A, their oligomeric and polymeric counterparts, or a combination comprising at least one of the foregoing non-brominated and non-chlorinated organic phosphorus-containing additives.

[0078] Embodiment 9. The method of any of the preceding Embodiments, wherein the non-brominated and non-chlorinated organic phosphorus-containing additive has a weight average molecular weight 300 to 2000 Daltons and a boiling point of at least 300 degrees C.

[0079] Embodiment 10. The method of any of the preceding Embodiments, wherein the amount of the non-brominated and non-chlorinated organic phosphorus-containing additive is from 0.5% to 15 %, from 1% to 12%, or from 2% to 10% or any range within 1% to 30%, by weight, based on the weight of the thermoplastic polymer.

[0080] Embodiment 11. The method of any of the preceding Embodiments, wherein the forming a plurality of layers comprises melt-extruding layers a thermoplastic material.

[0081] Embodiment 12. The method of any of the preceding Embodiments, wherein the thermoplastic polymer composition has a glass transition temperature (T<sub>g</sub>) as measured as per ASTM method D3418 from 100 to 250°C.

[0082] Embodiment 13. The method of any of the preceding Embodiments, wherein the plurality of layers comprises at least twenty layers.

[0083] Embodiment 14. The method of any of the preceding Embodiments, wherein the thermoplastic polymer composition has less than 500 ppm of bromine or chlorine and has a change in melt viscosity as measured by ASTM method D4440-15 at 300°C for 30 minutes of less than 30% of the initial viscosity value.

[0084] Embodiment 15. An article made by any of the preceding method Embodiments.

[0085] Embodiment 16. An article useful in aircraft or other passenger conveyances comprising a plurality of layers of a material in a preset pattern of at least twenty fused, melt-extruded layers comprising a thermoplastic polymer composition, wherein the thermoplastic polymer composition comprises a polycarbonate polymer or copolymer, a polyetherimide polymer or copolymer, a polyarylethersulfone polymer or copolymer, or a combination comprising at least one of the foregoing thermoplastic polymers and a non-brominated and non-chlorinated organic phosphorus-containing that will lower the Tg of the thermoplastic polymer and wherein the article has a 2 minute integrated heat release rate of less than or equal to 65 kilowatt-minutes per square meter (kW-min/m<sup>2</sup>) and a peak heat release rate of less than 65 kilowatts per square meter (kW/m<sup>2</sup>) as measured using the method of FAR F25.4, in accordance with Federal Aviation Regulation FAR 25.853 (d).

[0086] Embodiment 17. The article made by any of Embodiments 15-16, wherein the article has having a thickness of from 1 to 10 mm.

[0087] Embodiment 18. The article made by any of Embodiments 15-17, wherein the article contains at least 0.5 volume % of non-spherical voids.

[0088] Embodiment 19. The article made by any of Embodiments 15-18, wherein the article is made by monofilament deposition using monofilament strands having a diameter from 0.1 to 5.0 mm.

[0089] Embodiment 20. The article made by any of Embodiments 15-19, wherein the layers alternate in an overlapping pattern wherein at least half of the layers intersect at an angle of from 60 to 120 degrees.

[0090] The compositions, methods, and articles can alternatively comprise, consist of, or consist essentially of, any appropriate components or steps herein disclosed. The compositions, methods, and articles can additionally, or alternatively, be formulated so as to be devoid, or substantially free, of any steps, components, materials, ingredients, adjuvants, or species that are otherwise not necessary to the achievement of the function and/or objectives of the compositions, methods, and articles.

[0091] All ranges disclosed herein are inclusive of the endpoints, and the endpoints are independently combinable with each other (e.g., ranges of “up to 25 wt.%, or, more specifically, 5 wt.% to 20 wt.%”, is inclusive of the endpoints and all intermediate values of the ranges of “5 wt.% to 25 wt.%,” etc.). “Combination” is inclusive of blends, mixtures, alloys, reaction products, and the like. Furthermore, the terms “first,” “second,” and the like, herein do not denote any order, quantity, or importance, but rather are used to denote one element from

another. The terms “a” and “an” and “the” herein do not denote a limitation of quantity, and are to be construed to cover both the singular and the plural, unless otherwise indicated herein or clearly contradicted by context. Reference throughout the specification to “an embodiment”, “another embodiment”, “some embodiments”, and so forth, means that a particular element (e.g., feature, structure, and/or characteristic) described in connection with the embodiment is included in at least one embodiment described herein, and may or may not be present in other embodiments. In addition, it is to be understood that the described elements can be combined in any suitable manner in the various embodiments.

[0092] Unless defined otherwise, technical and scientific terms used herein have the same meaning as is commonly understood by one of skill in the art to which this invention belongs. All cited patents, patent applications, and other references are incorporated herein by reference in their entirety. However, if a term in the present application contradicts or conflicts with a term in the incorporated reference, the term from the present application takes precedence over the conflicting term from the incorporated reference.

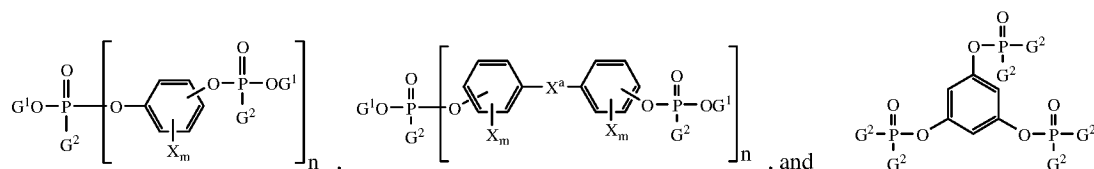
[0093] While particular embodiments have been described, alternatives, modifications, variations, improvements, and substantial equivalents that are or may be presently unforeseen may arise to applicants or others skilled in the art. Accordingly, the appended claims as filed and as they may be amended are intended to embrace all such alternatives, modifications variations, improvements, and substantial equivalents.



## CLAIMS:

1. A method of making an article useful in aircraft or other passenger conveyances, the method comprising:
  - melt extruding a plurality of layers comprising a thermoplastic polymer composition in a preset pattern; and
  - fusing the plurality of layers to provide the article;
  - wherein the thermoplastic polymer composition comprises
    - a combination of a polycarbonate homopolymer or copolymer, a polyetherimide homopolymer or copolymer, a polyarylethersulfone, or a combination comprising at least one of the foregoing thermoplastic polymers, and
    - a non-brominated and non-chlorinated organic phosphorus-containing additive that will lower the Tg of the thermoplastic polymer from 5 to 100 degrees C andwherein the article has a 2 minute integrated heat release rate of less than or equal to 65 kilowatt-minutes per square meter (kW-min/m<sup>2</sup>) and a peak heat release rate of less than 65 kilowatts per square meter (kW/m<sup>2</sup>) as measured using the method of FAR F25.4, in accordance with Federal Aviation Regulation FAR 25.853 (d).
2. The method of claim 1, wherein the thermoplastic polymer is a polycarbonate polymer or copolymer or a combination comprising at least one of the foregoing thermoplastic polymers and, optionally, wherein the article is made from layers built from a monofilament having a diameter from 0.1 to 5.0 mm.
3. The method of claim 1, wherein the thermoplastic polymer comprises a poly(ester-carbonate-siloxane) comprising bisphenol A carbonate units, isophthalate-terephthalate-bisphenol A ester units, and siloxane units.
4. The method of claim 1, wherein the thermoplastic polymer is a polyetherimide homopolymer or copolymer or a combination comprising at least one of the foregoing thermoplastic polymers.
5. The method of claim 1, wherein the thermoplastic polymer is a polyphenylethersulfone homopolymer or copolymer or a combination comprising at least one of the foregoing thermoplastic polymers.

6. The method of any of the preceding claims, wherein the non-brominated and non-chlorinated organic phosphorus-containing additive is an aromatic phosphate of the formula  $(GO)_3P=O$ , wherein each G is independently an alkyl, cycloalkyl, aryl, alkylaryl, or aralkyl group, provided that at least one G is an aromatic group or a di- or polyfunctional aromatic group, preferably a compound of the formulas below:



wherein each  $G^1$  is independently a hydrocarbon having 1 to 30 carbon atoms; each  $G^2$  is independently a hydrocarbon or hydrocarbonoxy having 1 to 30 carbon atoms; each X is independently a bromine or chlorine; m is 0 to 4, and n is 1 to 30, or a combination comprising at least one of the foregoing non-brominated and non-chlorinated organic phosphorus-containing additives.

7. The method of any of the preceding claims, wherein the non-brominated and non-chlorinated organic phosphorus-containing additive is triphenyl phosphate, a tricresyl phosphate, a trixylyl phosphate, a trimesityl phosphate, bisphenol A diphosphate, resorcinol diphosphate, biphenol diphosphate, hydroquinone diphosphate, acetophenone bisphenol diphosphate, dihydroxy diphenyl ether diphosphate an oligomeric counterpart of any of the foregoing, a polymeric counterpart of any of the foregoing, or a combination comprising at least one of the foregoing non-brominated and non-chlorinated organic phosphorus-containing additives.

8. The method of any of the preceding claims, wherein the non-brominated and non-chlorinated organic phosphorus-containing additive is resorcinol tetraphenyl diphosphate (RDP), the bis(diphenyl) phosphate of hydroquinone, the bis(diphenyl) phosphate of bisphenol A, an oligomeric counterpart of any of the foregoing, a polymeric counterpart of any of the foregoing, or a combination comprising at least one of the foregoing non-brominated and non-chlorinated organic phosphorus-containing additives.

9. The method of any of the preceding claims, wherein the non-brominated and non-chlorinated organic phosphorus-containing additive has a weight average molecular weight of 300 to 2000 Daltons and a boiling point of at least 300 degrees C.

10. The method of any of the preceding claims, wherein the amount of the non-brominated and non-chlorinated organic phosphorus-containing additive is from 0.5% to 15 %, from 1% to 12%, or from 2% to 10% or any range within 1% to 30%, by weight, based on the weight of the thermoplastic polymer.
11. The method of any of the preceding claims, wherein the forming a plurality of layers comprises melt-extruding at least a portion of the layers comprising the thermoplastic polymer composition.
12. The method of any of the preceding claims, wherein the thermoplastic polymer composition has a glass transition temperature (T<sub>g</sub>) as measured as per ASTM method D3418 from 100 to 250°C.
13. The method of any of the preceding claims, wherein the plurality of layers comprises at least twenty layers.
14. The method of any of the preceding claims, wherein the thermoplastic polymer composition has less than 500 ppm of bromine or chlorine and has a change in melt viscosity as measured by ASTM method D4440-15 at 300C for 30 minutes of less than 30% of the initial viscosity value.
15. An article made by any of the preceding method claims.
16. An article useful in aircraft or other passenger conveyances comprising a plurality of layers of a material in a preset pattern of at least twenty fused, melt-extruded layers comprising a thermoplastic polymer composition, wherein the thermoplastic polymer composition comprises a combination of a polycarbonate homopolymer or copolymer, a polyetherimide homopolymer or copolymer, a polyarylethersulfone , or a combination comprising at least one of the foregoing thermoplastic polymers, and a non-brominated and non-chlorinated organic phosphorus-containing that will lower the T<sub>g</sub> of the thermoplastic polymer and wherein the article has a 2 minute integrated heat release rate of less than or equal to 65 kilowatt-minutes per square meter (kW-min/m<sup>2</sup>) and a peak heat release rate of less than 65

kilowatts per square meter ( $\text{kW/m}^2$ ) as measured using the method of FAR F25.4, in accordance with Federal Aviation Regulation FAR 25.853 (d).

17. The article made by any of claims 15-16, wherein the article has a thickness of from 1 to 10 mm.

18. The article made by any of claims 15-17, wherein the article contains at least 0.5 volume % of non-spherical voids.

19. The article made by any of claims 15-18, wherein the article is made by monofilament deposition using monofilament strands having a diameter from 0.1 to 5.0 mm.

20. The article made by any of claims 15-19, wherein the layers alternate in an overlapping pattern wherein at least half of the layers intersect at an angle of from 60 to 120 degrees.

## INTERNATIONAL SEARCH REPORT

International application No

PCT/US2016/065516

A. CLASSIFICATION OF SUBJECT MATTER  
 INV. B29C67/00 C08K5/523  
 ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
 B29C C08K

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

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

EPO-Internal, WPI Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages                                                                                                                        | Relevant to claim No. |
|-----------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------|
| X         | WO 2015/134316 A1 (SABIC GLOBAL TECHNOLOGIES BV [NL]; GALLUCCI ROBERT RUSSELL [US])<br>11 September 2015 (2015-09-11)<br>claims 1,7-9,13,14,19<br>examples<br>paragraphs [0032], [0035] - [0037]<br>----- | 1-20                  |
| X         | WO 2015/077053 A1 (SABIC GLOBAL TECHNOLOGIES BV [NL]; GALLUCCI ROBERT R [US]) 28 May 2015 (2015-05-28)<br>claims 1,2,6-8,14,17,20<br>paragraphs [0028], [0030], [0031], [0040], [0041]<br>-----           | 1-20                  |



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

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"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

"&" document member of the same patent family

Date of the actual completion of the international search

9 March 2017

Date of mailing of the international search report

16/03/2017

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2  
 NL - 2280 HV Rijswijk  
 Tel. (+31-70) 340-2040,  
 Fax: (+31-70) 340-3016

Authorized officer

Schlicke, Benedikt

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2016/065516

| Patent document<br>cited in search report | Publication<br>date | Patent family<br>member(s) | Publication<br>date |
|-------------------------------------------|---------------------|----------------------------|---------------------|
| WO 2015134316      A1                     | 11-09-2015          | CN      106068177 A        | 02-11-2016          |
|                                           |                     | EP      3113934 A1         | 11-01-2017          |
|                                           |                     | WO      2015134316 A1      | 11-09-2015          |
| -----                                     |                     |                            |                     |
| WO 2015077053      A1                     | 28-05-2015          | CN      105873742 A        | 17-08-2016          |
|                                           |                     | EP      3071393 A1         | 28-09-2016          |
|                                           |                     | KR      20160086826 A      | 20-07-2016          |
|                                           |                     | US      2016298268 A1      | 13-10-2016          |
|                                           |                     | WO      2015077053 A1      | 28-05-2015          |
| -----                                     |                     |                            |                     |