Abstract Title: A composition and methods including the composition

A method for making a polytetrafluoroethylene (PTFE) membrane comprising metal oxide(s), the method comprising the steps of: a) mixing a PTFE resin, a lubricating agent and a metal oxide wherein a weight of the lubricating agent comprises between 15 and 25 percent of a weight of the PTFE resin, wherein a weight of the metal oxide comprises up to 10 percent of the weight of the PTFE resin, and wherein the metal oxide has at least one dimension less than 100 nm: b) forming a pre-form comprising a mixture of the PTFE resin, the lubricating agent and the metal oxide: c) extruding the pre-form to form a tape: d) calendaring the tape to facilitate evaporation of the lubricating agent: e) tentering the tape through bi-axially stretching to form a membrane and f) sintering the membrane. Also claimed is a method of incorporating a metal oxide into a mixture comprising a PTFE resin and a lubricating agent, the method characterised by mixing in a V blender and wicking. Also claimed is a composition characterised by an isoparaffinic solvent and a metal oxide having a specific surface area.
METHODS OF MAKING A MIXTURE FOR A PTFE MEMBRANE WITH METAL OXIDES, AND COMPOSITIONS RELATED THERETO

BACKGROUND OF THE INVENTION

Embodiments of the present invention generally relate to making an expanded polytetrafluoroethylene (ePTFE) membrane containing metal oxide(s).

Materials including polytetrafluoroethylene (PTFE) are known in the art. PTFE has various well-established uses, including, for example, applications requiring lubricity (e.g., bearings, bushings, etc.) and applications requiring a porous membrane. These membrane-related applications may include, for example, filtration, venting, and/or diffusion/barrier applications. Filtration may use discs or sheets.

Additive-containing PTFE products are known. See, e.g., U.S. Pat. No. 5,697,390 to Garrison et al.; 5,827,327 to McHaney et al.; 6,120,532 to Goldfarb; and 6,270,707 to Hori et al.

BRIEF DESCRIPTION OF THE INVENTION

In an embodiment of the present invention, there is a method for making a polytetrafluoroethylene membrane comprising metal oxide(s). The method may comprise the steps of: (a) mixing a polytetrafluoroethylene resin having a weight, a lubricating agent having a weight, and a metal oxide having a weight, wherein the weight of the lubricating agent comprises between 15 and 25 percent of the weight of the polytetrafluoroethylene resin, wherein the weight of the metal oxide comprises up to 10 percent of the weight of the polytetrafluoroethylene resin, and
wherein the metal oxide has at least one dimension less than 100 nm; (b) forming a preform comprising a mixture of the polytetrafluoroethylene resin, the lubricating agent, and the metal oxide; (c) extruding the preform to form a tape having a thickness between 1 and 100 mil; (d) calendaring the tape to facilitate evaporation of the lubricating agent; (e) tentering the tape through biaxially stretching in a first direction and a second direction perpendicular to the first direction to form a membrane; and (f) sintering the membrane at a temperature between 400°F and 750°F for a period of time between 1 and 120 seconds, wherein the membrane after sintering has a thickness between 0.05 and 20 mil.

In an embodiment of the present invention, there is a method of incorporating a metal oxide into a mixture comprising a polytetrafluoroethylene resin and a lubricating agent. The method may comprise the steps of: a) mixing the polytetrafluoroethylene resin with the lubricating agent in a V blender for a period of time between 1 and 60 minutes to form a resin/lubricant mixture; (b) wicking the resin/lubricant mixture for a period of time between 1 and 120 hours; and (c) mixing the resin/lubricant mixture with the metal oxide in a V blender for a period of time between 1 and 60 minutes; wherein a weight of the lubricating agent comprises between 15 and 25 percent of a weight of the polytetrafluoroethylene resin, wherein a weight of the metal oxide comprises up to 10 percent of the weight of the polytetrafluoroethylene resin, and wherein the metal oxide has at least one dimension less than 100 nm.
In an embodiment of the present invention, there is a composition comprising: a polytetrafluoroethylene resin; a lubricating agent comprising an isoparaffinic solvent; and a metal oxide; wherein a weight of the lubricating agent comprises between 15 and 25 percent of a weight of the polytetrafluoroethylene resin; wherein a weight of the metal oxide comprises up to 10 percent of the weight of the polytetrafluoroethylene resin; and wherein the metal oxide has at least one dimension less than 100 nm and has a specific surface area greater than 50 m²/g.

DETAILED DESCRIPTION OF THE INVENTION

Certain aspects of the present invention may related to extruding into tape polytetrafluoroethylene (PTFE) that includes metal oxide nanocomposites, then converting the extruded PTFE tape into a membrane through biaxial stretching.

In certain embodiments, a combination of PTFE and metal oxide(s) (e.g., nanocomposites) may be prepared by dispersing metal oxide(s), such as titanium dioxide (TiO₂), zinc oxide (ZnO), aluminum oxides (Al₂O₃), magnesium oxide (MgO), silver oxide (AgO), and other nanomaterials, into a mixture containing PTFE resin. The PTFE composite may be then extruded into tape and converted into a membrane by biaxial stretching.

Suitable metal oxides may include, for example, copper(I) oxide (Cu₂O); silver(I) oxide (Ag₂O); thallium oxide (Tl₂O); sodium oxide (Na₂O); aluminum monoxide (AlO); barium oxide (BaO); beryllium oxide (BeO); cadmium oxide (CdO); calcium oxide (CaO); cobalt(II) oxide (CoO); copper(II) oxide (CuO); iron(II) oxide (FeO); magnesium
oxide (MgO); mercury(II) oxide (HgO); nickel(II) oxide (NiO); palladium(II) oxide (PdO); silver(II) oxide (AgO); strontium oxide (SrO); tin(II) oxide (SnO); titanium(II) oxide (TiO); vanadium(II) oxide (VO); zinc oxide (ZnO); aluminium oxide (Al₂O₃); antimony trioxide (Sb₂O₃); bismuth trioxide (Bi₂O₃); chromium(III) oxide (Cr₂O₃); erbium(III) oxide (Er₂O₃); gadolinium(III) oxide (Gd₂O₃); gallium(III) oxide (Ga₂O₃); holmium(III) oxide (Ho₂O₃); indium(III) oxide (In₂O₃); iron(III) oxide (Fe₂O₃); lanthanum(III) oxide (La₂O₃); lutetium(III) oxide (Lu₂O₃); nickel(III) oxide (Ni₂O₃); promethium(III) oxide (Pm₂O₃); rhodium(III) oxide (Rh₂O₃); samarium(III) oxide (Sm₂O₃); scandium(III) oxide (Sc₂O₃); terbium(III) oxide (Tb₂O₃); thallium(III) oxide (Tl₂O₃); thulium(III) oxide (Tm₂O₃); titanium(III) oxide (Ti₂O₃); tungsten(III) oxide (W₂O₃); vanadium(III) oxide (V₂O₃); ytterbium(III) oxide (Yb₂O₃); yttrium(III) oxide (Y₂O₃); cerium(IV) oxide (CeO₂); chromium(IV) oxide (CrO₂); germanium dioxide (GeO₂); hafnium(IV) oxide (HfO₂); manganese(IV) oxide (MnO₂); plutonium dioxide (PuO₂); ruthenium(IV) oxide (RuO₂); thorium dioxide (ThO₂); tin dioxide (SnO₂); titanium dioxide (TiO₂); tungsten(IV) oxide (WO₂); vanadium(IV) oxide (VO₂); zirconium dioxide (ZrO₂); antimony pentoxide (Sb₂O₅); tantalum pentoxide (Ta₂O₅); vanadium(V) oxide (V₂O₅); chromium trioxide (CrO₃); molybdenum(VI) oxide (MoO₃); rhenium trioxide (ReO₃); tungsten trioxide (WO₃); manganese(VII) oxide (Mn₂O₇); rhenium(VII) oxide (Re₂O₇); osmium tetroxide (OsO₄); ruthenium tetroxide (RuO₄); and permutations and combinations of those (and other) metal oxides.

A membrane containing metal oxide(s) may have a high porosity/surface area and may be used, at least in some
instances, in the decontamination of chemical and/or biological agents. For example, silver oxide and magnesium oxide may impart antimicrobial properties. For another example, silver oxide (when converted to Ag⁺ when contacted with water, including, for example, bodily fluids like sweat) may kill microorganisms.

In some instances, the metal oxide nanoparticles may impart properties, such as increased abrasion resistance, increased tensile strength, increased tensile modulus, etc., that may enhance the mechanical stability and/or durability of the membrane.

In certain embodiments, the metal oxide(s) may be, for example, small particles with at least one dimension less than 100 nm. Preferably, the metal oxide(s) have at least one dimension less than 50 nm, and even more preferably the particles have at least one dimension less than 30 nm. Suitable nanoparticles may have a high surface area to volume (or mass) ratio. For example, suitable nanoparticles may have a specific surface area of greater than 10m²/g, greater than 50m²/g, or greater than 90m²/g. In some embodiments, the specific surface area may be about 100m²/g. A suitable inorganic porous material may comprise zinc oxide nanopowder available from Aldrich Chemical Co.

In preferred embodiments, certain aspects of the present invention relate to a method of making a PTFE membrane containing a metal oxide. In general, the steps may include one or more of the following steps: (1) mixing PTFE resin with a lubricating agent, then wicking the resin/lubricant mixture; (2) mixing the resin/lubricant mixture with a metal oxide (such as zinc oxide
nanopowder); (3) preforming the wet-mixture into a billet; (4) extruding the mixture into tape; (5) calendaring the tape; (6) biaxially stretching the tape to form a membrane; and (7) sintering the membrane to stabilize its microstructure.

Due to the use of a lubricating agent that is removed from the extrudate following the application of heat, this process may be generally known as a "wet-process" and not a "dry-process" (which generally relies on friction-free air blending in an environment without shear).

In an exemplary embodiment, a suitable PTFE resin comprises DuPont Teflon® PTFE 601A, available from E. I. du Pont de Nemours and Co. Other PTFE resins may comprise Daikin F107, Dupont 603A, and/or Dupont 60A. And in an exemplary embodiment, a suitable lubricating agent includes a hydrocarbon-based liquid, such as the isoparaaffinic solvents sold under the Isopar tradename by the ExxonMobil Chemical Co. A preferred lubricating agent may comprise Isopar K, Isopar M, and/or Isopar G. The PTFE resin powder may be mixed with the lubricating agent in a V blender for between 1 and 60 minutes (preferably about 30 minutes), for example, until the mixture is approximately homogenous. In certain embodiments, the weight percentage of the lubricating agent may range between 15 and 25% (and all subranges therebetween) of weight of the resin. This weight percentage, which is commonly known as the "lube rate," may vary, for example, depending on the specific processing parameters of the equipment being used in the extrusion process.
Wicking occurs after mixing, and the resin/lubricant mixture may be held at a temperature of 90°F for 18 hours. In certain embodiments, the temperature may be higher (e.g., 200°F) or lower (e.g., 40°F), and the time may be shorter (e.g., 1 hour) or longer (e.g., 120 hours). In other embodiments, the wicking may be optional.

The wicked resin/lubricant mix may then be mixed with metal oxide using a V blender, e.g., at ambient temperature for between 1 and 60 minutes, preferably between 15 and 30 minutes. In some embodiments, the metal oxide comprises up to 10 wt% of the PTFE resin. In other embodiments, the metal oxide comprises up to 5 wt% of the PTFE resin. In yet further embodiments, the metal oxide comprises up to 3 wt% of the PTFE resin.

In certain embodiments, the lubricating agent may assist in dispersing the metal oxide(s). In certain embodiments, the metal oxide may be mixed with the resin and/or lubricant in various permutations. For example, they may be all mixed together at the same time, or the lubricant and metal oxide may be mixed prior to mixing with the PTFE resin.

The resin/lubricant/additive mixture may then be preformed, e.g., through charging into a cylinder, then pressed under pressure to form a preform. In some embodiments, the cylinder may be 50 inches, and the 150 psi of pressure is used to force the mixture into the preform at ambient temperature. Of course, other process parameters may also be used.

The preform may then be extruded into tape, e.g., Ram extruder. In some embodiments, the extrusion occurs at a
temperature between 80°F and 100°F and at a rate between 80 and 200 in/min. The final thickness of the tape may vary between 1 and 100 mil, preferably between 5 and 75 mil, and even more preferably between 10 and 40 mil. Of course, other process parameters may also be used.

After extrusion, the tape may then be calendered, by passing the mixture through hot calendar rolls to facilitate the obtainment of tape uniformity as well as the evaporation of the lubricating agent. The calendering may occur at a temperature between 300°F and 400°F and at a rate between 10 and 20 ft/min. The calendar rolls may be 20 inches wide, and calendar rolls may be spaced between 10 and 17 mil apart. Of course, other process parameters may also be used.

After calendering, the tape may then be formed into a membrane via tentering. During this process, the tape is stretched biaxially to form a thin membrane. Preferably, the stretching occurs at a line speed between 30 ft/min and 80 ft/min. Preferably, the stretching occurs multiple times, even in the same direction. For example, the tape may be stretched between 1 and 20 times (preferably between 10 and 12 times) in the transverse direction and between 1 and 5 times (preferably 3 times) in the machine direction. Various temperatures may be used, e.g., between 150°F and 800°F, such as, for example, at 200°F, at 500°F, at 650°F, or at 700°F. These temperatures may increase or otherwise vary with the stretch cycles.

After tentering, the membrane may be heat treated to stabilize the microstructure of a membrane. This sintering may occur in an oven at a temperature between
400°F and 750°F, preferably between 650°F and 750°F, for a period of time between 1 and 120 seconds, and preferably between 10 and 30 seconds. The final thickness of the membrane may range between 0.05 and 20 mil (preferably 2 mil).

Examples were prepared in accordance with an exemplary embodiment of the present invention.

Example no. 1 was prepared with 3 wt% zinc oxide Nanopowder (using the weight of the PTFE resin as the basis). The PTFE resin used was DuPont Teflon® PTFE 601A, and the lubricating agent was Isopar K. The resulting membranes were compared to the specifications for two commercially available PTFE membranes from GE Energy: QMO8 and QMO11.

Example 1

DuPont 601 A resin fine powder was mixed with 20 wt% of Isopar K using a V blender at ambient condition for about 30 min. The resin/isopar mix was wicked at 90°F for 24 hours. The wicked PTFE/Isopar mix was blended with 3 wt% of Zinc Oxide nanopowder using a V blender for about 15 min. The resin/isopar/zinc oxide was shaped into cylindrical form (preform) by pressure of 150 psi using a billet press. The preform was extruded into a tape at a temperature 80°F using a Ram extruder. The isopar was removed from the tape by passing it through series of hot Calendar rolls at a temperature of 200°F. The tape was stretched biaxially to form a porous PTFE membrane (stretched 2 times in the machine direction and 8 times in the transverse direction). The microstructure of PTFE
membrane was stabilized by applying heat at temperature of 680°F.

The membrane was tested as per product test specifications and compared with GE standard commercialized membrane. It was found that the Zinc Oxide nanopowder additive dispersed uniformly within PTFE matrix and locked in the microstructure.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Standard GE Membrane Eg: QMO11</th>
<th>Example No. 1: ePTFE/Metal Oxide Composite Membrane</th>
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<tr>
<td>Unit weight (oz/yard²)</td>
<td>0.54</td>
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<td>Thickness (mil)</td>
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<td>XD 114</td>
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Table 1: Comparison of Example No. 1 with specifications for a standard GE membrane (e.g., QMO11).
Tensile strength and elongation were measured using ASTM D5035, and Mullen was measured using ASTM D751-00 Method A, procedure 1.

Example 2

DuPont 603 A resin fine powder was mixed with 22 wt% of Isopar M using a V blender at ambient condition for about 20 min. The resin/isopar mix was wicked at 110°F for 48 hours. The wicked PTFE/Isopar mix was blended with 7 wt% of Zinc Oxide nanopowder using a V blender for about 30 min. The resin/isopar/zinc oxide was shaped into cylindrical form (preform) by applying pressure of 100 psi using a billet press. The preform was extruded into a tape at a temperature 110°F using a Ram extruder. The isopar was removed from the tape by passing it through series of hot Calendar rolls at a temperature of 250°F. The tape was stretched biaxially to form a porous PTFE membrane (stretched 5 times in the machine direction and 12 times in the transverse direction). The microstructure of PTFE membrane was stabilized by applying heat at temperature of 720°F.

The membrane was tested as per product test specifications and compared with GE standard commercialized membrane. It was found that the Zinc Oxide nanopowder additive dispersed uniformly within PTFE matrix and locked in the microstructure.

All disclosed and claimed numbers and numerical ranges are approximate and include at least some variation and deviation.
While the invention has been described in connection with what is presently considered to be the most practical and preferred embodiment, it is to be understood that the invention is not to be limited to the disclosed embodiment, but on the contrary, is intended to cover various modifications and equivalent arrangements included within the scope of the appended claims.
CLAIMS:

1. A method for making a polytetrafluoroethylene membrane comprising metal oxide(s), the method comprising the steps of:

   a) mixing a polytetrafluoroethylene resin having a weight, a lubricating agent having a weight, and a metal oxide having a weight,

   wherein the weight of the lubricating agent comprises between 15 and 25 percent of the weight of the polytetrafluoroethylene resin,

   wherein the weight of the metal oxide comprises up to 10 percent of the weight of the polytetrafluoroethylene resin, and

   wherein the metal oxide has at least one dimension less than 100 nm;

   (b) forming a preform comprising a mixture of the polytetrafluoroethylene resin, the lubricating agent, and the metal oxide;

   (c) extruding the preform to form a tape having a thickness between 1 and 100 mil;

   (d) calendaring the tape to facilitate evaporation of the lubricating agent;

   (e) tentering the tape through biaxially stretching in a first direction and a second direction perpendicular to the first direction to form a membrane; and

   (f) sintering the membrane at a temperature between 400°F and 750°F for a period of time between 1 and 120 seconds, wherein the membrane after sintering has a thickness between 0.05 and 20 mil.
2. The method of claim 1, wherein step (a) comprises the steps of:

mixing the polytetrafluoroethylene resin with the lubricating agent in a V blender for a period of time between 1 and 60 minutes to form a resin/lubricant mixture;

wicking the resin/lubricant mixture for a period of time between 1 and 120 hours; and

mixing the resin/lubricant mixture with the metal oxide in a V blender for a period of time between 1 and 60 minutes.

3. The method of claim 1 or claim 2, wherein the lubricating agent comprises an isoparaffinic solvent.

4. The method of any preceding claim, wherein the metal oxide comprises titanium dioxide, zinc oxide, aluminum oxide, magnesium oxide, silver oxide, or a mixture thereof.

5. The method of any preceding claim, wherein the metal oxide has at least one dimension less than 50 nm.

6. The method of any preceding claim, wherein the metal oxide has at least one dimension less than 30 nm.

7. The method of any preceding claim, wherein the metal oxide has a specific surface area greater than 10 m²/g.

8. The method of any preceding claim, wherein the metal oxide has a specific surface area greater than 50 m²/g.

9. The method of any preceding claim, wherein the metal oxide has a specific surface area greater than 90 m²/g.
10. A method of incorporating a metal oxide into a mixture comprising a polytetrafluoroethylene resin and a lubricating agent, the method comprising the steps of:

(a) mixing the polytetrafluoroethylene resin with the lubricating agent in a V blender for a period of time between 1 and 60 minutes to form a resin/lubricant mixture;

(b) wicking the resin/lubricant mixture for a period of time between 1 and 120 hours; and

(c) mixing the resin/lubricant mixture with the metal oxide in a V blender for a period of time between 1 and 60 minutes;

wherein a weight of the lubricating agent comprises between 15 and 25 percent of a weight of the polytetrafluoroethylene resin,

wherein a weight of the metal oxide comprises up to 10 percent of the weight of the polytetrafluoroethylene resin, and

wherein the metal oxide has at least one dimension less than 100 nm.

11. The method of claim 10, wherein step (b) occurs at a temperature between 40°F and 200°F.

12. The method of claim 10 or claim 11, wherein the lubricating agent comprises an isoparaffinic solvent.

13. The method of any one of claims 10 to 12, wherein the metal oxide comprises zinc oxide, aluminum oxide, or silver oxide and has a specific surface area greater than 90 m²/g and having at least one dimension less than 50 nm.
14. A composition comprising:

a polytetrafluoroethylene resin;

a lubricating agent comprising an isoparaffinic solvent; and

a metal oxide;

wherein a weight of the lubricating agent comprises between 15 and 25 percent of a weight of the polytetrafluoroethylene resin;

wherein a weight of the metal oxide comprises up to 10 percent of the weight of the polytetrafluoroethylene resin; and

wherein the metal oxide has at least one dimension less than 100 nm and has a specific surface area greater than 50 m$^2$/g.

15. The composition of claim 14, wherein the metal oxide comprises zinc oxide, aluminum oxide, or silver oxide.

16. The composition of claim 14, wherein the metal oxide comprises zinc oxide.

17. The composition of any one of claims 14 to 16, wherein the lubricating agent comprises an isoparaffinic solvent.

18. The composition of any one of claims 14 to 17, wherein the metal oxide has at least one dimension less than 50 nm and has a specific surface area greater than 90 m$^2$/g.
Application No: GB0902515.6
Claims searched: 1 - 9
Examiner: Beverley Lloyd
Date of search: 6 July 2009

Patents Act 1977: Search Report under Section 17

Documents considered to be relevant:

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<td>US6218000 B1 (RUDOLF et al) See description</td>
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Categories:

- X Document indicating lack of novelty or inventive step
- Y Document indicating lack of inventive step if combined with one or more other documents of same category.
- Member of the same patent family
- A Document indicating technological background and/or state of the art.
- P Document published on or after the declared priority date but before the filing date of this invention.
- E Patent document published on or after, but with priority date earlier than, the filing date of this application.

Field of Search:
Search of GB, EP, WO & US patent documents classified in the following areas of the UKC:
Worldwide search of patent documents classified in the following areas of the IPC:
B01D, B29C, C08J, C08L
The following online and other databases have been used in the preparation of this search report:
WPI, EPDOC, TXTE

International Classification:

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