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# (54) Title: MICROPOROUS MEMBRANES AND METHODS FOR MAKING AND USING SUCH MEMBRANES

**(57) Abstract:** The invention relates to a particular multi-layer microporous membrane having a good balance of important properties, including excellent electrochemical stability and low heat shrinkage, while maintaining high permeability and heat resistance, with good mechanical strength, compression resistance and electrolytic solution absorption. The invention further relates to battery separators comprising the multi-layer microporous membrane and batteries utilizing the battery separators.

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Description

# MICROPOROUS MEMBRANES AND METHODS FOR MAKING AND USING SUCH MEMBRANES

## FIELD OF THE INVENTION

**[0001]** The present invention relates to a multi-layer microporous membrane having a good balance of important properties, including excellent electrochemical stability and low heat shrinkage, as well as high permeability and heat resistance, when used as a battery separator. This multi-layer microporous membrane also has good mechanical strength, electrolytic solution absorption and compression resistance properties. The invention also relates to a method for producing such a multi-layer microporous membrane, to battery separators comprising such a multi-layer microporous membrane, and to batteries utilizing such battery separators.

## BACKGROUND OF THE INVENTION

**[0002]** Microporous polyolefin membranes can be used as battery separators in, for example, primary and secondary lithium batteries, lithium polymer batteries, nickel-hydrogen batteries, nickel-cadmium batteries, nickel-zinc batteries, silver-zinc secondary batteries, etc. When microporous polyolefin membranes are used for battery separators, particularly lithium ion battery separators, the membranes' performance significantly affects the properties, productivity and safety of the batteries. Accordingly, the microporous polyolefin membrane should have suitable mechanical properties, heat resistance, permeability, dimensional stability, shut down properties, melt down properties, etc. As is known, it is desirable for the batteries to have a relatively low shut down temperature and a relatively high melt down temperature for improved battery safety properties, particularly for batteries that are exposed to high temperatures during manufacturing, charging, re-charging, use, and/or storage. Improving separator permeability generally leads to an improvement in the battery's storage capacity. High shut down speed is desired for improved battery safety, particularly when the battery is operated under overcharge conditions. Improving pin puncture strength is desired because roughness of the battery's electrode can puncture the separator during manufacturing leading to a short circuit. Improved thickness uniformity is desired because thickness variations lead to manufacturing difficulties when winding the film on a core. Thickness variations can also lead to non-isotropic temperature variations in the battery, which can lead to battery hot-spots (regions of higher temperature) where the separator is relatively thin.

**[0003]** In general, microporous membranes containing only polyethylene (i.e., the membrane consists of, or consists essentially of, polyethylene) have low melt down temperatures, while microporous membranes containing only polypropylene have high shut down temperatures. Accordingly, microporous membranes comprising polyethylene and polypropylene as main components have been proposed as improved battery separators. It is therefore desired to provide microporous membranes formed from polyethylene resins and polypropylene resins, and multi-layer microporous membranes comprising polyethylene and polypropylene.

**[0004]** JP7-216118A, for example, discloses a battery separator having a suitable shut down temperature and mechanical strength. The patent publication discloses a battery separator comprising a multi-layer porous film having two microporous layers. Both layers can contain polyethylene and polypropylene, but in different relative amounts. For example, the percentage of the polyethylene is 0 to 20 wt. % in the first microporous layer, and 21 to 60 wt. % in the second microporous layer, based on the combined weight of the polyethylene and polypropylene. The total amount of polyethylene in both microporous layers is 2 to 40 wt. %, based on the weight of the multi-layer microporous membrane.

**[0005]** JP10-195215A discloses a relatively thin battery separator having acceptable shut down and pin-pulling characteristics. The term "pin pulling" refers to the relative ease of pulling a metal pin from a laminate of a separator, a cathode sheet and an anode sheet, which is wound around the pin, to form a toroidal laminate. The multi-layer porous film contains polyethylene and polypropylene, but in different relative amounts. The percentage of polyethylene is 0 to 20 wt. % in the inner layer and 61 to 100 wt. % in the outer layer, based on the total weight of the polyethylene and polypropylene.

**[0006]** JP10-279718A discloses a separator designed to prevent unacceptably large temperature increases in a lithium battery when the battery is overcharged. The separator is formed from a multi-layer porous film made of polyethylene and polypropylene, with different relative amounts of polyethylene and polypropylene in each layer. The film has a polyethylene-poor layer whose polyethylene content is 0 to 20 wt. %, based on the weight of the polyethylene-poor layer. The second layer is a polyethylene-rich layer which contains 0.5 wt. % or more of polyethylene having a melt index of 3 or more and a total polyethylene content of 61 to 100 wt. %, based on the weight of the polyethylene-rich layer.

**[0007]** It is desirable to further improve the permeability, pin puncture strength, and shutdown speed of microporous polyolefin membranes. Moreover, it is desirable to further improve the thickness uniformity of microporous polyolefin membranes in order to reduce the likelihood of short-circuiting when used as battery separators. Particularly, it is desirable to provide a microporous membrane having excellent electrochemical stability and low heat shrinkage, as well as high permeability and heat resistance, when used as a battery separator.

## SUMMARY OF THE INVENTION

**[0008]** In an embodiment, the invention relates to a multi-layer microporous membrane comprising polyethylene and polypropylene and having a pin puncture strength $\geq$ 3500 mN, an electrolytic solution absorption speed $\geq$ 3.5, and an air permeability after heat compression $\leq$ 1000 seconds/cm$^3$.

**[0009]** In another embodiment, the invention relates to a battery separator formed by such a multi-layer microporous membrane. In another embodiment, the invention relates to a battery comprising such a separator formed by such a multi-layer microporous membrane.

**[0010]** In one embodiment, the invention relates to a polyolefin membrane comprising a first layer and a second layer. The first layer comprises a first layer material which can be produced from a first polyolefin solution. The second layer comprises a second layer material which can be produced from a second polyolefin solution. The multi-layer microporous membrane comprises at least these two layers and can optionally comprise additional layers. For example, the multilayer microporous membrane can comprise a third layer in planar contact with the second layer which in turn is in planar contact with the first layer. In other words, the second layer can be a middle layer between the first and third layers. In this embodiment, the first and third layers generally comprise the first layer material and the second layer generally comprises the second layer material. In yet another embodiment, the multi-layer microporous membrane is a three-layer membrane where the first layer (comprising the first layer material) is the middle layer with the second and third layers comprising outer (or skin) layers of the membrane. In this embodiment, the second and third layers can both comprise the second layer material. In other embodiments, the membrane contains one or more layers comprising the first layer material and one or more layers comprising the second layer material, such as for example a layer comprising the first layer material layers on one or both sides of a layer comprising the second layer material, wherein the first layer material comprises polyethylene and polypropylene and the second material layer comprises polyethylene. In an embodiment, the membrane contains at least one layer comprising a first layer material and a second layer comprising a second layer material wherein

(i) the first layer material comprises from about 30 to about 70%, for example from about 40 to about 60%, of a first polyethylene; from about 20 to about 40%, for example from about 25 to about 40% of a first polypropylene; and from about 10 to about 30%, for example from about 10 to about 25% of a second polypropylene, the percentages being based on the weight of the first material layer;

(ii) the second layer material comprises from about 60 to about 90%, for example from about 70 to about 85%, of the first polyethylene; and from about 10 to about 40%, for example from about 15 to about 30%, of a second polyethylene, the percentages being based on the weight of the second material layer.

**[0011]** In an embodiment, the first layer material comprises (a) from about 30 to about 70%, for example from about 40 to about 60%, of a first polyethylene having a weight average molecular weight ("Mw") $< 1.0 \times 10^6$, e.g., in the range of from about $4.5 \times 10^5$ to about $6.5 \times 10^5$ and a molecular weight distribution ("MWD") $\leq 100$, e.g., in the range of about 2 to about 10, or about 3 to about 5, (b) from about 20 to about 40 %, for example from about 25 to about 40%, of a first polypropylene having an Mw $\geq 0.8 \times 10^6$, e.g., in the range of from about $0.9 \times 10^6$ to about $2 \times 10^6$, an MWD $\leq 100$, e.g., in the range of about 1.5 to about 10, or about 2 to about 6, and a heat of fusion ("ΔHm") $\geq 80$ J/g, e.g., in the range of $105 \leq \Delta Hm \leq 125$, or in the range of 110 J/g to 120 J/g, and (c) from about 10 to about 30%, for example from about 10 to about 25%, of a second polypropylene having an Mw $< 0.8 \times 10^6$, e.g., in the range of from about $4 \times 10^5$ to about $7.5 \times 10^5$, an MWD $\leq 100$, e.g., in the range of from about 2 to about 20, and $\Delta Hm \geq 80$ J/g, e. g., in the range of about $90 \leq \Delta Hm < 105$, the percentages being based on the weight of the first layer material; and the second layer material comprises (a) from about 60 to about 90%, for example from about 70 to about 85%, of a first polyethylene having an Mw $<1.0 \times 10^6$, e.g., in the range of from about $4.5 \times 10^5$ to about $6.5 \times 10^5$ and an MWD $\leq 100$, e.g., in the range of from about 2 to about 10, and (a') from about 10 to about 40%, for example from about 15% to 30% of a second polyethylene having an Mw $\geq 1.0 \times 10^6$, e.g., in the range of about $1.1 \times 10^6$ to about $5 \times 10^6$, and an MWD $\leq 100$, e.g., in the range of about 2 to about 10, the percentages being based on the weight of the second layer material.

**[0012]** In a further embodiment of the present invention, the multi-layer microporous membrane of the present invention can be produced by steps comprising layering, such as for example by coextrusion, one or more layers comprising a first layer material with one or more layers comprising a second layer material, the layers containing the first layer material can be on one or both sides of the layers containing the second layer material. The first layer material can be produced by (1) combining a first polyolefin composition and at least one diluent or solvent, for example a membrane-forming solvent, to form a first mixture, e.g., a polyolefin solution, the first polyolefin composition comprising (a) from about 30 to about 70%, for example from about 40 to about 60%, of a first polyethylene resin having an Mw $< 1.0 \times 10^6$, e.g., in the range of from about $4.5 \times 10^5$ to about $6.5 \times 10^5$ and an MWD $\leq 100$, e.g., in the range of about 2 to about 10, or about 3 to about 5, (b) from about 20 to about 40 %, for example from about 25 to about 40 %, of a first polypropylene resin having an Mw $\geq 0.8 \times 10^6$, e.g., in the range of from about $0.9 \times 10^6$ to about $2 \times 10^6$, an MWD $\leq 100$, e.g., in the range of about 1.5 to about 10, or about 2 to about 6, and a $\Delta Hm \geq 80$ J/g, e.g., in the range of $105 \leq \Delta Hm \leq 125$, or in the range of 110 J/g to 120 J/g, and (c) from about 10 to about 30 %, for example from about 10 to about 25%, of a second polypropylene resin having an Mw $< 0.8 \times 10^6$, e.g., in the range of from about $4 \times 10^5$ to about $7.5 \times 10^5$, an MWD $\leq 100$, e.g., in the range of from about 2 to about 20, and $\Delta Hm \geq 80$ J/g, e. g., in the range of about $90 \leq \Delta Hm < 105$, the percentages being based on the weight of the first polyolefin composition, (2) extruding the first mixture through a die to form an extrudate, (3) cooling the extrudate to form a cooled extrudate, e.g., one having a high polyolefin content, (4) stretching the cooled extrudate in at least one direction to form a stretched sheet, (5) removing at least a portion of the diluent from the stretched sheet to form a membrane, (6) stretching the membrane in at least one direction to form a stretched membrane, and (7) heat-setting the membrane product of step (6) to form a microporous layer comprising the first layer material. The second layer material can be produced by steps comprising (1) combining a second polyolefin composition and at least one diluent (e.g., a solvent, for example a membrane-forming solvent) to form a second mixture, e.g., a second polyolefin solution, the second polyolefin composition comprising (a) from about 60 to about 90%, for example from about 70 to about 85%, of a first polyethylene resin having an $Mw < 1.0 \times 10^6$, e.g., in the range of from about $4.5 \times 10^5$ to about $6.5 \times 10^5$ and an $MWD \leq 100$, e.g., in the range of about 2 to about 10, or about 3 to about 5, and (a') from about 10 to about 40%, for example from about 15 to about 30%, of a second polyethylene resin having an $Mw > 1.0 \times 10^6$, e.g., in the range of from about $1.1 \times 10^6$ to about $5 \times 10^6$ and an $MWD \leq 100$, e.g., in the range of about 2 to about 10, or about 4 to about 6, the percentages being based on the weight of the second polyolefin composition, (2) extruding the second mixture through a die to form an extrudate, (3) cooling the extrudate to form a cooled extrudate, e.g., one having a high polyolefin content, (4) stretching the cooled extrudate in at least one direction to form a stretched sheet, (5) removing at least a portion of the diluent from the stretched sheet to form a membrane, (6) stretching the membrane in at least one direction to form a stretched membrane, and (7) heat-setting the membrane product of step (6) to form a second microporous layer comprising the second layer material. The first and second layers may be layered with each other downstream of the above step (7), or may be layered with each other at any of steps (3) through (7), or may be coextruded, i.e. extruded simultaneously through separate dies, at step (2). Identifying layers comprising the first microporous layer material as "a" and layers comprising the second microporous layer material as "b", the multilayer membrane can have the form of, e.g., a/b, a/b/a, b/a/b, a/b/a/b, b/a/b/a/b, a/b/a/b/a, etc. The ratio of the sum of the thickness of the layers comprising the first layer material to the sum of the thickness of the layers comprising the second layer material can be, e.g., from about 10/90 to about 75/25, for example from about 20/80 to about 50/50.

**[0013]** When the layers comprising the first layer material are layered with layers comprising the second layer material, e.g., by coextrusion, the multi-layer microporous membrane of the present invention is produced by steps of (1a) combining a first polyolefin composition and at least one diluent or solvent, for example a membrane-forming solvent, to form a first mixture (e.g., a polyolefin solution), the first polyolefin composition comprising (a) from about 30 to about 70%, for example from about 40 to about 60%, of a first polyethylene resin having an Mw in the range of about $4.5 \times 10^5$ to about $6.5 \times 10^5$ and an MWD in the range of from about 3 to about 5, (b) from about 20 to about 40 %, for example from about 25 to about 40 %, of a first polypropylene resin having an Mw in the range of from about $0.9 \times 10^6$ to about $2 \times 10^6$, an MWD in the range of from about 2 to about 6, and $\Delta Hm \geq 80$ J/g, e.g., in the range of $105 \leq \Delta Hm \leq 125$, and (c) from about 10 to about 30%, for example from about 10 to about 25 %, of a second polypropylene resin having an Mw in the range of from about $4 \times 10^5$ to about $7.5 \times 10^5$, an MWD in the range of from about 2 to about 20, and ΔHm in the range of about $90 \leq \Delta Hm < 105$, the percentages being based on the weight of the first polyolefin composition, (1b) combining a second polyolefin composition and at least one diluent, for example a membrane-forming solvent, to form a second mixture (e.g., a polyolefin solution), the second polyolefin composition comprising (a) from about 60 to about 90%, for example from about 70 to about 85 %, of a first polyethylene resin having an Mw in the range of from about $4.5 \times 10^5$ to about $6.5 \times 10^5$ and an MWD in the range of about 2 to about 10, or about 3 to about 5, and (a') from about 10 to about 40%, for example from about 15 to about 30%, of a second polyethylene resin having an Mw in the range of from $1.0 \times 10^6$ to about $5 \times 10^6$ and an MWD in the range of about 2 to about 10, or about 4 to about 6, the percentages being based on the weight of the second polyolefin composition, (2) simultaneously extruding the first and second mixtures through dies to form first and second extrudates such that they are in planar contact one with the other, (3) simultaneously cooling the first and second extrudates to form cooled extrudates having high polyolefin contents, (4) simultaneously stretching the cooled extrudates in at least one direction at a high stretching temperature to form a stretched sheet comprising a first layer material and a second layer material, (5) removing at least a portion of the diluents from the stretched sheet to form a membrane comprising a first layer comprising the first layer material and a second layer comprising the second layer material, (6) stretching the membrane in at least one direction to form a stretched membrane comprising a first layer material and a second layer material, and (7) heat-setting the stretched membrane product of step (6) to form the microporous membrane comprising a first microporous layer and a second microporous layer.

**[0014]** The membrane can comprise more than one layer comprising the first layer material and more that one layer comprising the second layer material by way of extruding any number of polyolefin solutions comprising respective polyolefin compositions such that step (2) of the method of the invention results in simultaneously extruding the various polyolefin solutions through dies to form respective extrudates such that they are in planar contact one with the other. For example, the extrudates in planar contact one with the other may comprise a first layer and a second layer; a first layer, a second layer, and a first layer; a first layer, a second layer, a first layer, and a second layer; etc.

**[0015]** The present invention also relates to a battery separator formed by the multi-layer microporous membrane recited in any one of the preceding embodiments.

**[0016]** The invention also relates to a battery comprising a separator formed by the multi-layer microporous membrane recited in any of the preceding embodiments, and the use of such a battery as a power source, e.g., in electric or hybrid electric vehicles.

**[0017]** In related embodiments, the multi-layer microporous membrane of the present invention can be characterized by the following independently-selected features, either alone or in combination:

(1) The first polyethylene has an Mw $< 1.0 \times 10^6$, e.g., in the range of from about $4.5 \times 10^5$ to about $6.5 \times 10^5$ and an MWD $\leq 100$, e.g., in the range of about 2 to about 10, or about 3 to about 5.

(2) The second polyethylene has an Mw $\geq 1.0 \times 10^6$, e.g., in the range of from $1.1 \times 10^6$ to about $5 \times 10^6$ and an MWD $\leq 100$, e.g., in the range of about 2 to about 10, or about 4 to about 6.

(3) The first polyethylene is selected from one or more of a high density polyethylene, a medium density polyethylene, a branched low density polyethylene, or a linear low density polyethylene.

(4) The first polyethylene is at least one of (i) an ethylene homopolymer or (ii) a copolymer of ethylene and a third α-olefin selected from the group consisting of propylene, butene-1, pentene-1, hexene-1, 4-methylpentene-1, octene-1, vinyl acetate, methyl methacrylate, styrene, butadiene, 1,5-hexadiene, 1,7-octadiene and 1,9-decadiene.

(5) The second polyethylene is an ultra-high molecular weight polyethylene.

(6) The second polyethylene is at least one of (i) an ethylene homopolymer or (ii) a copolymer of ethylene and a third α-olefin selected from the group consisting of propylene, butene-1, pentene-1, hexene-1, 4-methylpentene-1, octene-1, vinyl acetate,

methyl methacrylate, styrene, butadiene, 1,5-hexadiene, 1,7-octadiene and 1,9-decadiene.

(7) The first and second polypropylene are at least one or more of (i) a propylene homopolymer or (ii) a copolymer of propylene and a fourth olefin selected from one or more of α-olefins such as ethylene, butene-1, pentene-1, hexene-1, 4-methylpentene-1, octene-1, vinyl acetate, methyl methacrylate, styrene, butadiene, 1,5-hexadiene, 1,7-octadiene and 1,9-decadiene.

(8) The first polypropylene has an $Mw \geq 0.8 \times 10^6$, e.g., in the range of from about $0.9 \times 10^6$ to about $2 \times 10^6$, an $MWD \leq 100$, e.g., in the range of about 1.5 to about 10, or about 2 to about 6, and a $\Delta Hm \geq 80$ J/g, e.g., in the range of $105 \leq \Delta Hm \leq 125$, or in the range of 110 J/g to 120 J/g.

(9) The second polypropylene has having an $Mw < 0.8 \times 10^6$, e.g., in the range of from about $4 \times 10^5$ to about $7.5 \times 10^5$, an $MWD \leq 100$, e.g., in the range of from about 2 to about 20, and $\Delta Hm \geq 80$ J/g, e. g., in the range of about $90 \leq \Delta Hm < 105$.

(10) The multi-layer microporous membrane of the present invention constitutes two layers, a skin layer composed of the first layer material and a core layer composed of the second layer material, such that the layer thickness ratio of the first layer to the second layer is from about 10/90 to about 75/25.

(11) The multi-layer microporous membrane constitutes three layers, e.g., one having a first layer of thickness T1 comprising the first layer material, a third layer of Thickness T3 and comprising the first layer material, the first and third layers being opposite planar surface sides of a second (or core) layer having a thickness T2 and comprising the second layer material, such that the ratio (T1 + T3)/T2 is in the range of from about 10/90 to about 75/25, for example from about 20/80 to about 50/50.

(12) The multi-layer microporous membrane exhibits a porosity of from about 25% to about 80%.

(13) The multi-layer microporous membrane exhibits an air permeability of from about 20 seconds/100 $cm^3$ to about 400 seconds/100 $cm^3$ (referenced to an air permeability value for a microporous polyolefin membrane having a 20 μm thickness).

(14) The multi-layer microporous membrane exhibits a pin puncture strength of at least about 2,000 mN/20μm.

(15) The multi-layer microporous membrane exhibits a tensile strength of at least about 49,000 kPa.

(16) The multi-layer microporous membrane exhibits a tensile elongation of at least about 100 %.

(17) The multi-layer microporous membrane exhibits a heat shrinkage ratio of about 12 % or less in the machine and transverse directions as measured after the microporous membrane has been held at a temperature of about 105°C for 8 hours.

(18) The multi-layer microporous membrane exhibits a thickness variation ratio that does not exceed about 15 %.

(19) The multi-layer microporous membrane exhibits a shut down temperature of about 140°C or lower.

(20) The multi-layer microporous membrane exhibits a melt down temperature of at least about 150°C.

(21) The multi-layer microporous membrane exhibits a shut down speed that does not exceed about 10 seconds.

(22) The multi-layer microporous membrane exhibits a maximum shrinkage in the molten state (about 140°C) of less than about 20%.

## DETAILED DESCRIPTION OF THE INVENTION

**[0018]** The present invention relates to the discovery of a particular multi-layer microporous membrane having a good balance of important properties, including excellent electrochemical stability and low heat shrinkage, while maintaining high permeability and heat resistance, with good mechanical strength, compression resistance and electrolytic solution absorption. Of particular importance when used as a battery separator, the present multi-layer microporous membrane exhibits excellent heat shrinkage, melt down temperature and thermal mechanical properties, i.e. low maximum shrinkage in the molten state. The multi-layer microporous membrane of the present invention is manufactured by layering, such as for example by coextrusion, one or more microporous membrane first layers and one or more microporous membrane second layers, such as on one or both sides of a first layer. The first layer generally comprises or consists of or consists essentially of a first layer material. The second layer generally comprises or consists of or consists essentially of a second layer material. Accordingly, in an embodiment, the invention relates to a multi-layer microporous membrane having suitably well-balanced permeability, pin puncture strength, shut down temperature, shut down speed, melt down temperature, and thickness uniformity, along with enhanced electrochemical stability and low heat shrinkage. In another embodiment, the invention relates to a method for making the multi-layer microporous membrane. "Well-balanced" in this context means that a particular property of the membrane (e.g., permeability) is not degraded to an undesirable value in order to improve another membrane property (e.g., electrochemical stability and low heat shrinkage).

## [1] Composition and Structure of the multi-layer microporous membrane

**[0019]** In an embodiment, the multi-layer microporous membrane comprises two layers. The first layer comprises a first microporous layer material, and the second layer comprises a second microporous layer material. For example, the membrane has a planar top layer when viewed from above on an axis approximately perpendicular to the transverse and machine directions of the membrane, with the bottom planar layer hidden from view by the top layer. In another embodiment, the multi-layer microporous membrane comprises three or more layers, wherein the outer layers (also called the "surface" or "skin" layers) are microporous layers comprising the first microporous layer material and at least one intermediate layer comprising the second microporous layer material. Alternatively, the multi-layer microporous membrane comprises three or more layers, wherein the outer layers (also called the "surface" or "skin" layers) are microporous layers comprising the second microporous layer material and at least one intermediate layer comprising the first microporous layer material. In a related embodiment, where the multi-layer microporous membrane comprises two layers, the first layer consists essentially of the first microporous layer material and the second layer consists essentially of the second microporous layer material. In a related embodiment where the multi-layer microporous membrane comprises three or more layers, the outer layers consist essentially of the first microporous layer material and at least one intermediate layer consists essentially of the second microporous layer material.

**[0020]** When the multi-layer microporous membrane has three or more layers, it has at least one layer comprising the first microporous layer material and at least one layer comprising the second microporous layer material.

**[0021]** The first and second microporous layer materials each contain a first polyethylene. The first polyethylene of the first layer material can be independently selected from the first polyethylene of the second layer material. The second layer material contains a greater amount of the first polyethylene than the first layer material, and the total amount of first polyethylene in the multi-layer microporous membrane is at least 37.5 wt. % based on the weight of the multi-layer microporous membrane. The second microporous layer material also contains a second polyethylene.

**[0022]** In an embodiment, the first microporous layer material comprises from about 30 to about 70%, for example from about 40 to about 60 wt. %, of the first polyethylene; from about 20 to about 40%, for example from about 25 to about 40 wt. %, of the first polypropylene; and from about 10 to about 30%, for example from about 10 to about 25 wt. %, of the second polypropylene, the percentages being based on the weight of the first microporous layer material. The first polyethylene can be, for example, a high density polyethylene ("HDPE"), and the second polyethylene can be, for example, ultra-high molecular weight polyethylene ("UHMWPE").

**[0023]** In an embodiment, the second microporous layer material comprises the first polyethylene and a second polyethylene. The second microporous layer material comprises from about 60 to about 90%, for example from about 70 to about 85 wt. %, of the first polyethylene, and from about 10 to about 40%, for example from about 15 to about 30%, of a second polyethylene, the percentages being based on the weight of the second microporous layer material. Again, the first polyethylene can be, for example, HDPE, and the second polyethylene can be, for example UHMWPE.

### A. The first polyethylene

**[0024]** In an embodiment, the first polyethylene has an Mw $< 1.0 \times 10^6$, e.g., in the range of from about $4.5 \times 10^5$ to about $6.5 \times 10^5$ and an MWD $\leq 100$, e.g., in the range of about 2 to about 10, or about 3 to about 5. For example, the first polyethylene can be one or more of an HPDE, a medium density polyethylene, a branched low density polyethylene, or a linear low density polyethylene. In an embodiment, the first polyethylene is at least one of (i) an ethylene homopolymer or (ii) a copolymer of ethylene and a third $\alpha$-olefin such as propylene, butene-1, hexene-1, etc, typically in a relatively small amount compared to the amount of ethylene. The amount of the third olefin can be less than 10% by mole based on 100% by mole of the entire copolymer. Such a copolymer can be produced using a single-site catalyst. Although it is not critical, the first polyethylene can have terminal unsaturation of, for example, two or more per 10,000 carbon atoms in the polyethylene. Terminal unsaturation can be measured by, for example, conventional infrared spectroscopic or nuclear magnetic resonance methods.

### B. The second polyethylene

**[0025]** In an embodiment, the second polyethylene has an Mw $\geq 1.0 \times 10^6$, e.g., in the range of from $1.1 \times 10^6$ to about $5 \times 10^6$ and an MWD $\leq 100$, e.g., in the range of about 2 to about 10, or about 4 to about 6. For example, the second polyethylene can be an UHMWPE. In an embodiment, the second polyethylene is at least one of (i) an ethylene homopolymer or (ii) a copolymer of ethylene and a third α-olefin which is typically present in a relatively small amount compared to the amount of ethylene. The third α-olefin can be, for example, one or more of propylene, butene-1, pentene-1, hexene-1, 4-methylpentene-1, octene-1, vinyl acetate, methyl methacrylate, or styrene. The amount of the third olefin can be less than 10 % by mole based on 100% by mole of the entire copolymer.

### C. The first polypropylene

**[0026]** In an embodiment, the first polypropylene has an Mw $\geq 0.8 \times 10^6$, e.g., in the range of from about $0.9 \times 10^6$ to about $2 \times 10^6$, an MWD $\leq 100$, e.g., in the range of about 1.5 to about 10, or about 2 to about 6, and a $\Delta Hm \geq 80$ J/g, e.g., in the range of $105 \leq \Delta Hm \leq 125$, or in the range of 110 J/g to 120 J/g. The first polypropylene can be, for example, one or more of (i) a propylene homopolymer or (ii) a copolymer of propylene and a fourth olefin. The copolymer can be a random or block copolymer. The fourth olefin can be, for example, one or more of α-olefins such as ethylene, butene-1, pentene-1, hexene-1, 4-methylpentene-1, octene-1, vinyl acetate, methyl methacrylate, and styrene, etc.; and diolefins such as butadiene, 1,5-hexadiene, 1,7-octadiene, 1,9-decadiene, etc. The amount of the fourth olefin in the copolymer is preferably in a range that does not adversely affect properties of the multi-layer microporous membrane such as heat resistance, compression resistance, heat shrinkage resistance, etc. For example, the amount of the fourth olefin can be less than 10 % by mole based on 100 % by mole of the entire copolymer. Optionally, the first polypropylene has one or more of the following properties: (i) the polypropylene is isotactic; (ii) the polypropylene has a heat of fusion of at least about 90 J/g, for example from about 90 to about 120 J/g; (iii) the polypropylene has a melting peak (second melt) of at least about 160°C; (iv) the polypropylene has a Trouton's ratio of at least about 15 when measured at a temperature of about 230°C and a strain rate of 25 $sec^{-1}$; and/or (v) the polypropylene has an elongational viscosity of at least about 50,000 Pa sec at a temperature of 230°C and a strain rate of 25 $sec^{-1}$.

## D. The second polypropylene

**[0027]** In an embodiment, the second polypropylene has an $Mw < 0.8 \times 10^6$, e.g., in the range of from about $4 \times 10^5$ to about $7.5 \times 10^5$, an $MWD \leq 100$, e.g., in the range of from about 2 to about 20, or about 3 to about 15, and $\Delta Hm \geq 80$ J/g, e. g., in the range of about $90 \leq \Delta Hm < 105$. The second polypropylene can be, for example, one or more of (i) a propylene homopolymer or (ii) a copolymer of propylene and a fourth olefin. The copolymer can be a random or block copolymer. The fourth olefin can be, for example, one or more of α-olefins such as ethylene, butene-1, pentene-1, hexene-1, 4-methylpentene-1, octene-1, vinyl acetate, methyl methacrylate, and styrene, etc.; and diolefins such as butadiene, 1,5-hexadiene, 1,7-octadiene, 1,9-decadiene, etc. The amount of the fifth olefin in the copolymer is preferably in a range that does not adversely affect properties of the multi-layer microporous membrane such as heat resistance, compression resistance, heat shrinkage resistance, etc. For example, the amount of the fourth olefin can be less than 10% by mole based on 100 % by mole of the entire copolymer. Optionally, the second polypropylene has one or more of the following properties: (i) the polypropylene is isotactic; (ii) the polypropylene has a heat of fusion of at least about 90 J/g, for example from about 90 to about 120 J/g; (iii) the polypropylene has a melting peak (second melt) of at least about 160°C; (iv) the polypropylene has a Trouton's ratio of at least about 15 when measured at a temperature of about 230°C and a strain rate of 25 $sec^{-1}$; and/or (v) the polypropylene has an elongational viscosity of at least about 50,000 Pa sec at a temperature of 230°C and a strain rate of 25 $sec^{-1}$. In one embodiment, the second polypropylene has a ΔHm that is less than the ΔHm of the first polypropylene.

**[0028]** MWD is equal to the ratio of Mw to the number-average molecular weight (“Mn"). The MWD of the polymers used to produce the microporous membrane can be controlled e.g., by a multi-stage polymerization. The MWD of the polyethylene composition can be controlled by controlling the molecular weights and mixing ratios of the polyethylene components.

**[0029]** Mw and Mn of the polyethylenes are determined using a High Temperature Size Exclusion Chromatograph, or "SEC", (GPC PL 220, Polymer Laboratories), equipped with a differential refractive index detector (DRI). Three PLgel Mixed-B columns (available from Polymer Laboratories) are used. The nominal flow rate is 0.5 $cm^3$/min, and the nominal injection volume was 300 mL. Transfer lines, columns, and the DRI detector were contained in an oven maintained at 145°C. The measurement is made in accordance with the procedure disclosed in "*Macromolecules*, Vol. 34, No. 19, pp. 6812-6820 (2001)".

**[0030]** The GPC solvent used is filtered Aldrich reagent grade 1,2,4-Trichlorobenzene (TCB) containing approximately 1000 ppm of butylated hydroxy toluene (BHT). The TCB was degassed with an online degasser prior to introduction into the SEC. Polymer solutions were prepared by placing dry polymer in a glass container, adding the desired amount of above TCB solvent, then heating the mixture at 160°C with continuous agitation for about 2 hours. The concentration of UHMWPE solution was 0.25 to 0.75mg/ml. Sample solution will be filtered off-line before injecting to GPC with 2μm filter using a model SP260 Sample Prep Station (available from Polymer Laboratories).

**[0031]** The separation efficiency of the column set is calibrated with a calibration curve generated using a seventeen individual polystyrene standards ranging in Mp from about 580 to about 10,000,000, which is used to generate the calibration curve. The polystyrene standards are obtained from Polymer Laboratories (Amherst, MA). A calibration curve (logMp vs. retention volume) is generated by recording the retention volume at the peak in the DRI signal for each PS standard, and fitting this data set to a 2nd-order polynomial. Samples are analyzed using IGOR Pro, available from Wave Metrics, Inc.

**[0032]** The Mw, MWD and the ΔHm of the polypropylene are measured in accordance with the procedures described in patent publication US 2008/0057389, which is incorporated by reference herein in its entirety.

## [2] Materials

### A. Polymer resins used for the first polyolefin composition

**[0033]** The first microporous layer material can be produced from a first mixture, e.g., a first polyolefin solution. The first mixture comprises a first polyolefin composition and a diluent. Since the process produces a microporous membrane, the diluent may be referred to as a membrane-forming solvent. The first polyolefin composition comprises a first polyethylene resin, a first polypropylene resin, and a second polypropylene resin. The amount of the first polyethylene resin in the first polyolefin composition is from about 30 to about 70 %, for example from about 40 to about 60%, based on the weight of the first polyolefin composition. The amount of the first polypropylene resin in the first polyolefin composition is from about 20 to about 40%, for example from about 25 to about 40%, based on the weight of the first polyolefin composition. The amount of the second polypropylene resin in the first polyolefin composition is from about 10 to about 30%, for example from about 10 to about 25%, based on the weight of the first polyolefin composition.

**[0034]** The first polyethylene resin has an Mw $< 1.0 \times 10^6$, e.g., in the range of from about $4.5 \times 10^5$ to about $6.5 \times 10^5$ and an MWD $\leq 100$, e.g., in the range of about 2 to about 10, or about 3 to about 5. A non-limiting example of the first polyethylene resin for use herein is one that has an Mw of from about $4.5 \times 10^5$ to about $6 \times 10^5$ and an MWD in the range of from 3 to 5. The first polyethylene resin can be an ethylene homopolymer, or an ethylene/α-olefin copolymer, such as, for example, one containing a small amount, e.g. about 5 mole %, of a third α-olefin. The third α-olefin, which is not ethylene, is preferably propylene, butene-1, pentene-1, hexene-1, 4-methylpentene-1, octene-1, vinyl acetate, methyl methacrylate, or styrene or combinations thereof. Such copolymer is preferably produced using a single-site catalyst.

**[0035]** The first polypropylene resin has an Mw $\geq 0.8 \times 10^6$, e.g., in the range of from about $0.9 \times 10^6$ to about $2 \times 10^6$, an MWD $\leq 100$, e.g., in the range of about 1.5 to about 10, or about 2 to about 6, and a $\Delta Hm \geq 80$ J/g, e.g., in the range of $105 \leq \Delta Hm \leq 125$, or in the range of 110 J/g to 120 J/g. The first polypropylene resin can be, for example, one or more of (i) a propylene homopolymer or (ii) a copolymer of propylene and a fourth olefin. The copolymer can be a random or block copolymer. The fourth olefin can be, for example, one or more of α-olefins such as ethylene, butene-1, pentene-1, hexene-1, 4-methylpentene-1, octene-1, vinyl acetate, methyl methacrylate, and styrene, etc.; and diolefins such as butadiene, 1,5-hexadiene, 1,7-octadiene, 1,9-decadiene, etc. The amount of the fourth olefin in the copolymer is preferably in a range that does not adversely affect properties of the multi-layer microporous membrane such as heat resistance, compression resistance, heat shrinkage resistance, etc. For example, the amount of the fourth olefin can be less than 10 % by mole based on 100% by mole of the entire copolymer.

**[0036]** The second polypropylene resin has an Mw $< 0.8 \times 10^6$, e.g., in the range of from about $4 \times 10^5$ to about $7.5 \times 10^5$, an MWD $\leq 100$, e.g., in the range of from about 2 to about 20, or from about 3 to about 15, and $\Delta Hm \geq 80$ J/g, e. g., in the range of about $90 \leq \Delta Hm < 105$. The second polypropylene resin can be, for example, one or more of (i) a propylene homopolymer or (ii) a copolymer of propylene and a fourth olefin. The copolymer can be a random or block copolymer. The fourth olefin can be, for example, one or more of α-olefins such as ethylene, butene-1, pentene-1, hexene-1, 4-methylpentene-1, octene-1, vinyl acetate, methyl methacrylate, and styrene, etc.; and diolefins such as butadiene, 1,5-hexadiene, 1,7-octadiene, 1,9-decadiene, etc. The amount of the fifth olefin in the copolymer is preferably in a range that does not adversely affect properties of the multi-layer microporous membrane such as heat resistance, compression resistance, heat shrinkage resistance, etc. For example, the amount of the fourth olefin can be less than 10 % by mole based on 100 % by mole of the entire copolymer.

## B. Polymer resins used for the second polyolefin composition

**[0037]** The second microporous layer material can be produced from a second mixture, e.g., a second polyolefin solution that is selected independently of the first mixture. The second mixture comprises a second polyolefin composition and a diluent or solvent which can be the same as the diluent or solvent used in the first mixture. As is the case in the first mixture, this diluent can be referred to as a membrane-forming solvent. The second polyolefin composition comprises the first polyethylene resin and a second polyethylene resin. The amount of the first polyethylene resin in the second polyolefin composition is from about 60 to about 90%, for example from about 70 to about 85%, based on the weight of the second polyolefin composition. The amount of the second polyethylene resin in the second polyolefin composition is from about 10 to about 40 wt. %, for example from about 15 to about 30%, based on the weight of the second polyolefin composition.

**[0038]** The first polyethylene resin for use in the second polyolefin composition is as described above for the first polyolefin composition.

**[0039]** The second polyethylene resin, for example an ultra-high molecular weight polyethylene (UHMWPE) resin, has an Mw $\geq 1.0 \times 10^6$, e.g., in the range of from about $1.1 \times 10^6$ to about $5 \times 10^6$ and an MWD $\leq 100$, e.g., in the range of about 2 to about 10, or about 4 to about 6. A non-limiting example of the second polyethylene resin for use herein is one that has a weight average molecular weight of from about $1.5 \times 10^6$ to about $3 \times 10^6$, for example about $1.9 \times 10^6$. The second polyethylene resin can be an ethylene homopolymer, or an ethylene/α-olefin copolymer, such as, for example, one containing a small amount, e.g. about 5 mole %, of a third α-olefin. The third α-olefin, which is not ethylene, can be, for example, propylene, butene-1, pentene-1, hexene-1, 4-methylpentene-1, octene-1, vinyl acetate, methyl methacrylate, or styrene or combinations thereof. Such copolymer is preferably produced using a single-site catalyst.

### C. Other components

**[0040]** In addition to the above components, the first and second polyolefin solutions can contain (a) additional polyolefin and/or (b) heat-resistant polymer resins having melting points or glass transition temperatures (Tg) of about 170°C or higher, in amounts not deteriorating the properties of the microporous membrane, for example 10% or less by mass based on the polyolefin composition.

(a) Additional polyolefins

**[0041]** The additional polyolefin can be at least one of (a) polybutene-1, polypentene-1, poly-4-methylpentene-1, polyhexene-1, polyoctene-1, polyvinyl acetate, polymethyl methacrylate, polystyrene and an ethylene/α-olefin copolymer, each of which may have an Mw of form1 x $10^4$ to 4 x $10^6$, and (b) a polyethylene wax having an Mw of form 1 x $10^3$ to 1 x $10^4$. Polybutene-1, polypentene-1, poly-4-methylpentene-1, polyhexene-1, polyoctene-1, polyvinyl acetate, polymethyl methacrylate and polystyrene are not restricted to homopolymers, but may be copolymers containing still other α-olefins.

(b) Heat-resistant resins

**[0042]** The heat-resistant resins can be, for example, (a) amorphous resins having melting points of about 170°C or higher, which may be partially crystalline, and (b) completely amorphous resins having Tg of about 170°C or higher and mixtures thereof. The melting point and Tg are determined by differential scanning calorimetry (DSC) according to method JIS K7121. Specific examples of the heat-resistant resins include polyesters such as polybutylene terephthalate (melting point: about 160-230°C), polyethylene terephthalate (melting point: about 250-270°C), etc., fluororesins, polyamides (melting point: 215-265°C), polyarylene sulfide, polyimides (Tg: 280°C or higher), polyamide imides (Tg: 280°C), polyether sulfone (Tg: 223°C), polyetheretherketone (melting point: 334°C), polycarbonates (melting point: 220-240°C), cellulose acetate (melting point: 220°C), cellulose triacetate (melting point: 300°C), polysulfone (Tg: 190°C), polyetherimide (melting point: 216°C), etc.

## [3] Manufacturing method

**[0043]** In an embodiment, the multi-layer microporous membrane of the present invention is a two-layer membrane. In another embodiment, the multi-layer microporous membrane has at least three layers. For the sake of brevity, the production of the microporous membrane will be mainly described in terms of two-layer and three-layer membranes, although those skilled in the art will recognize that the same techniques can be applied for production of membranes of the present invention having at least three layers. Non-limiting examples of such multi-layer membranes would include, looking from top to bottom of the membrane: a first material layer, a second material layer; a first material layer, a second material layer, a first material layer; etc.

**[0044]** In an embodiment, the three-layer microporous membrane comprises a second material layer with a first material layer on each surface of and in planar contact with the second material layer. In an embodiment, the second layer is produced from the second polyolefin solution and the first layers are produced from first polyolefin solutions.

**[0045]** The total amount of the polyethylene in the multi-layer microporous membrane of the present invention should be, and preferably is at least about 47.5 wt. %, based on the weight of the multi-layer microporous membrane. There are a number of options for manufacturing the present multi-layer microporous membrane.

**[0046]** A method for producing the multi-layer microporous membrane of the present invention comprises layering, such as for example by coextrusion, one or more layers comprising the first layer material with one or more layers comprising the second layer material, the layers comprising the first layer material being on one or both sides of the layers comprising the second layer material. The first layer material can be produced by (1) combining a first polyolefin composition and at least one diluent to form a first mixture, (2) extruding the first mixture through a die to form an extrudate, (3) cooling the extrudate to form a cooled extrudate, (4) stretching the cooled extrudate in at least one direction to form a stretched sheet, (5) removing at least a portion of the diluent from the stretched sheet to form a membrane, (6) stretching the membrane to form a stretched membrane, and (7) heat-setting the stretched membrane product of step (6) to form the first microporous layer material. The second layer material can be produced by steps comprising (1) combining a second polyolefin composition and at least one second diluent to form a second mixture, (2) extruding the second mixture through a die to form a second extrudate, (3) cooling the second extrudate to form a cooled second extrudate, (4) stretching the cooled second extrudate in at least one direction to form a stretched sheet, (5) removing at least a portion of the diluent or solvent from the stretched sheet to form a membrane, (6) stretching the membrane to a high magnification to form a stretched membrane, and (7) heat-setting the stretched membrane product of step (6) to form the second microporous layer material. The layers comprising the first microporous layer material and the layers comprising the second layer material can be layered with each other downstream of the above step (7), or may be layered with each other at any of steps (3) through (7), or may be coextruded, i.e. extruded simultaneously through separate dies, at step (2). The ratio of the sum of the thicknesses of the layer(s) comprising the first layer material to the sum of the thicknesses of the layer(s) comprising the second layer material can be in the range of, e.g., about 10/90 to about 75/25, for example from about 20/80 to about 50/50. This ratio can be calculated, e.g., from the amount (by weight) of the first polyolefin solution extruded through the extruder compared to the amount of the second polyolefin solution extruded through the extruder during coextrusion.

**[0047]** When the layers comprising the first and second layer materials are layered with each other by coextrusion, the multi-layer microporous membrane of the present invention is produced by (1a) combining a first polyolefin composition and at least one diluent to form a first mixture (e.g., a polyolefin solution), (1b) combining a second polyolefin composition and at least one diluent to form a second mixture (e.g., a second polyolefin solution), (2) simultaneously extruding the first and second mixtures through dies to form first and second extrudates such that they are in planar contact one with the other, (3) simultaneously cooling the first and second extrudates to form cooled extrudates, (4) simultaneously stretching the cooled extrudates in at least one direction to form a stretched sheet comprising a first layer material and a second layer material, (5) removing at least a portion of the diluents from the stretched sheet to form a membrane comprising a first layer comprising layer material and a second layer comprising the second material, (6) stretching the membrane in at least one direction to form a stretched membrane comprising a first layer material and a second layer material, and (7) heat-setting the stretched membrane product of step (6) to form the coextruded microporous membrane comprising a first layer comprising the first layer material and a second layer comprising the second layer material.

**[0048]** Of course, coextrusion may comprise more than one layer comprising the first layer material and more that one layer comprising the second layer material by way of extruding any number of polyolefin solutions comprising respective polyolefin compositions such that step (2) of the method of the invention results in simultaneously extruding the various polyolefin solutions through dies to form respective extrudates such that they are in planar contact one with the other. For example, the extrudates in planar contact one with the other may comprise a first layer and a second layer; a first layer, a second layer, and a first layer; a first layer, a second layer, a first layer, and a second layer; etc.

### 1a. Preparation of first mixture

**[0049]** The first polyolefin composition comprises polyolefin resins as described above that can be combined, for example by dry mixing or melt blending, with an appropriate first diluent or solvent, for example a membrane-forming solvent, to produce the first mixture. Optionally, the first mixture can contain various additives such as one or more antioxidants, fine silicate powder (pore-forming material), etc., provided these are used in a concentration range that does not significantly degrade the desired properties of the multi-layer microporous membrane.

**[0050]** The first diluent is preferably one that is liquid at room temperature. While not wishing to be bound by any theory or model, it is believed that the use of a liquid diluent or solvent to form the first polyolefin solution makes it possible to conduct stretching of the gel-like sheet at a relatively high stretching magnification. In an embodiment, the first diluent or solvent can be at least one of aliphatic, alicyclic or aromatic hydrocarbons such as nonane, decane, decalin, p-xylene, undecane, dodecane, liquid paraffin, etc.; mineral oil distillates having boiling points comparable to those of the above hydrocarbons; and phthalates which are liquid at room temperature such as dibutyl phthalate, dioctyl phthalate, etc. In an embodiment where it is desired to obtain a multi-layer, gel-like sheet having a stable liquid solvent content, non-volatile liquid solvents such as liquid paraffin can be used, either alone or in combination with other solvents. Optionally, a solvent which is miscible with polyethylene in a melt blended state but solid at room temperature can be used, either alone or in combination with a liquid solvent. Such solid solvent can include, for example stearyl alcohol, ceryl alcohol, paraffin waxes, etc. Although it is not critical, it can be more difficult to evenly stretch the gel-like sheet or resulting membrane when the solution contains no liquid solvent.

**[0051]** The viscosity of the liquid solvent is not critical. For example, the viscosity of the liquid solvent can range from about 30 cSt to about 500 cSt, or from about 30 cSt to about 200 cSt, at 25°C. When the viscosity at 25°C is less than about 30 cSt, it can be more difficult to prevent foaming the polyolefin solution, which can lead to difficulty in blending. On the other hand, when the viscosity is greater than about 500 cSt, it can be more difficult to remove the liquid solvent from the multi-layer microporous polyolefin membrane.

**[0052]** In an embodiment, the resins, etc., used to produce to the first polyolefin composition are melt-blended in, for example, a double screw extruder or mixer. For example, a conventional extruder (or mixer or mixer-extruder) such as a double-screw extruder can be used to combine the resins, etc., to form the first polyolefin composition. The diluent or solvent can be added to the polyolefin composition (or alternatively to the resins used to produce the polyolefin composition) at any convenient point in this step of the process. For example, in an embodiment where the first polyolefin composition and the first diluent or solvent are melt-blended, the diluent or solvent can be added to the polyolefin composition (or its components) at any of (i) before starting melt-blending, (ii) during melt-blending of the first polyolefin composition, or (iii) after melt-blending, for example by supplying the first diluent or solvent to the melt-blended or partially melt-blended polyolefin composition in a second extruder or extruder zone located downstream of the extruder zone used to melt-blend the polyolefin composition.

**[0053]** When melt-blending is used, the melt-blending temperature is not critical. For example, the melt-blending temperature of the first polyolefin solution can range from about 10°C higher than the melting point $Tm_1$ of the polyethylene resins in the first polyolefin composition to about 120°C higher than $Tm_1$. For brevity, such a range can be represented as $Tm_1 + 10°C$ to $Tm_1 + 120°C$. In an embodiment where the polyethylene resins in the first polyolefin composition have a melting point of about 130°C to about 140°C, the melt-blending temperature can range from about 140°C to about 250°C, or from about 170°C to about 240°C.

**[0054]** When an extruder such as a double-screw extruder is used for melt-blending, the screw parameters are not critical. For example, the screw can be characterized by a ratio L/D of the screw length L to the screw diameter D in the double-screw extruder, which can range, for example, from about 20 to about 100, or from about 35 to about 70. Although this parameter is not critical, when L/D is less than about 20, melt-blending can be more difficult, and when L/D is more than about 100, faster extruder speeds might be needed to prevent excessive residence time of the polyolefin solution in the double-screw extruder (which can lead to undesirable molecular weight degradation). The cylinder (or bore) of the double-screw extruder can have an inner diameter of in the range of about 40 mm to about 100 mm, for example.

**[0055]** In an embodiment, the amount of first polyolefin composition in the first mixture can range from about 1 to about 75 wt.%, based on the weight of the mixture, for example from about 20 to about 70 wt.%. Although the amount of first polyolefin composition in the first mixture is not critical, when the amount is less than about 1 wt.%, it can be more difficult to produce the multi-layer microporous polyolefin membrane at an acceptably efficient rate. Moreover, when the amount is less than 1 wt.%, it can be more difficult to prevent swelling or neck-in at the die exit during extrusion, which can make it more difficult to form and support the multi-layer, gel-like sheet, which is a precursor of the membrane formed during the manufacturing process. On the other hand, when the amount of first polyolefin composition solution is greater than about 75 wt.%, it can be more difficult to form the multi-layer, gel-like sheet.

### 1b. Preparation of second mixture

**[0056]** The second mixture can be prepared by the same methods used to prepare the first mixture. For example, the second mixture can be prepared by melt-blending a second polyolefin composition with a second diluent. The second diluent can be selected from among the same solvents as the first diluent or solvent. While the second diluent or solvent can be selected independently of the first diluent or solvent, the second diluent or solvent can be the same as the first diluent or solvent, and can be used in the same relative concentration as the first diluent or solvent is used in the first mixture. Optionally, the second mixture can contain various additives such as one or more antioxidants, fine silicate powder (pore-forming material), etc., provided these are used in a concentration range that does not significantly degrade the desired properties of the multi-layer microporous membrane.

**[0057]** The second polyolefin composition is selected independently of the first polyolefin composition. The second polyolefin composition comprises the first and second polyethylene resins. Since the first and second microporous layer materials do not have the same composition, the resins and the relative amounts of polyethylene resins used to produce the second polyolefin composition are different from the amount of the first polyethylene resin used to produce the first polyolefin composition.

**[0058]** Although it is not critical, the melt-blending conditions for the second polyolefin solution likely differ from the conditions described for producing the first polyolefin composition in that the melt-blending temperature of the second polyolefin solution can range from about the melting point $Tm_2$ of the polyethylene resins in the second polyolefin composition + 10°C to $Tm_2$ + 120°C.

## 2. Extrusion

**[0059]** In an embodiment, the first mixture is conducted from a first extruder to a first die and the second mixture is conducted from a second extruder to a second die. A layered extrudate in sheet form ( i.e., a body significantly larger in the lateral directions than in the thickness direction) can be extruded from the first and second die. Optionally, the first and second mixtures are co-extruded from the first and second die with a planar surface of a first extrudate layer formed from the first mixture in contact with a planar surface of a second extrudate layer formed from the second mixture. A planar surface of the extrudate can be defined by a first vector in the machine direction of the extrudate and a second vector in the transverse direction of the extrudate.

**[0060]** In an embodiment, a die assembly is used where the die assembly comprises the first and second die, as for example when the first die and the second die share a common partition between a region in the die assembly containing the first mixture and a second region in the die assembly containing the second mixture.

**[0061]** In another embodiment, a plurality of dies is used, with each die connected to an extruder for conducting either the first or second mixture to the respective die. For example, in one embodiment, the first extruder containing the first mixture is connected to a first die and a third die, and a second extruder containing the second mixture is connected to a second die. As is the case in the preceding embodiment, the resulting layered extrudate can be simultaneously coextruded from the first, second, and third die to form a three-layer extrudate comprising a first and a third layer constituting surface layers (e.g., top and bottom layers) produced from the first mixture; and a second layer constituting a middle or intermediate layer of the extrudate situated between and in planar contact with both surface layers, where the second layer is produced from the second mixture.

**[0062]** In yet another embodiment, the same die assembly is used but with the mixtures reversed, i.e., the second extruder containing the second mixture is connected to the first die and the third die, and the first extruder containing the first mixture is connected to the second die.

**[0063]** In any of the preceding embodiments, die extrusion can be conducted using conventional die extrusion equipment. For example, extrusion can be conducted by a flat die or an inflation die. In one embodiment useful for co-extrusion of multi-layer gel-like sheets, multi-manifold extrusion can be used, in which the first and second mixtures are conducted to separate manifolds in a multi-layer extrusion die and laminated at a die lip inlet. In another such embodiment, block extrusion can be used, in which the first and second mixtures are first combined into a laminar flow (i.e., in advance), with the laminar flow then connected to a die. Because multi-manifold and block processes are known to those skilled in the art of processing polyolefin films (for example as disclosed in JP06-122142 A, JP06-106599A), they are considered conventional, and therefore their operation will be not described in detail.

**[0064]** Die selection is not critical, and a conventional multi-layer sheet-forming, flat or inflation die can be used. Die gap is not critical. For example, the multi-layer sheet-forming flat die can have a die gap of from about 0.1 mm to about 5 mm. Die temperature and extruding speed are also non-critical parameters. For example, the die can be heated to a die temperature ranging from about 140°C to about 250°C during extrusion. The extruding speed can range, for example, from about 0.2 m/minute to about 15 m/minute. The thickness of the layers of the layered extrudate can be independently selected. While the extrusion has been described in terms of embodiments producing two and three-layer extrudates, the extrusion step is not limited thereto. For example, a plurality of dies and/or die assemblies can be used to produce multi-layer extrudates having four or more layers using the extrusion methods of the preceding embodiments. In such a layered extrudate, each surface or intermediate layer can be produced using either the first mixture and/or the second mixture.

### 3. Formation of a multi-layer extrudate

**[0065]** The multi-layer extrudate can be formed into a high polyolefin content multi-layer, extrudate (generally in the form of a gel-like sheet) by cooling, for example. Cooling rate and cooling temperature are not particularly critical. For example, the multi-layer, gel-like sheet can be cooled at a cooling rate of at least about 50°C/minute until the temperature of the multi-layer, gel-like sheet (the cooling temperature) is approximately equal to the multi-layer, gel-like sheet's gelatin temperature (or lower). In an embodiment, the extrudate is cooled to a temperature of about 25°C or lower in order to form the multi-layer gel-like sheet. While not wishing to be bound by any theory or model, it is believed that cooling the layered extrudate sets the polyolefin micro-phases of the first and second polyolefin solutions for separation by the diluent or solvent. It has been observed that in general a slower cooling rate (e.g., less than 50°C/minute) provides the multi-layer, gel-like sheet with larger pseudo-cell units, resulting in a coarser higher-order structure. On the other hand, a relatively faster cooling rate (e.g., 80°C/minute) results in denser cell units. Although it is not a critical parameter, when the cooling rate of the extrudate is less than 50°C/minute, increased polyolefin crystallinity in the layer can result, which can make it more difficult to process the multi-layer, gel-like sheet in subsequent stretching steps. The choice of cooling method is not critical. For example conventional sheet cooling methods can be used. In an embodiment, the cooling method comprises contacting the layered extrudate with a cooling medium such as cooling air, cooling water, etc. Alternatively, the extrudate can be cooled via contact with rollers cooled by a cooling medium, etc.

**[0066]** The term "high polyolefin content" means the cooled extrudate comprises at least about 15%, for example from about 15 to about 50%, polyolefin derived from the resins of the polyolefin compositions, based on the mass of the cooled extrudate. It is believed that a polyolefin content of less than about 15 % of the cooled extrudate makes it more difficult to form a microporous membrane structure of the present invention exhibiting the excellent set of properties. A polyolefin content of more than about 50% can lead to higher viscosity which makes it more difficult to form the desired membrane structure. The cooled extrudate preferably has a polyolefin content at least as high as that of the polyolefin solution.

### 4. Stretching the cooled extrudate

**[0067]** The cooled extrudate, generally in the form of a high polyolefin content gel-like molding or sheet, is then stretched in at least one direction. While not wishing to be bound by any theory or model, it is believed that the gel-like sheet can be uniformly stretched because the sheet contains the diluent or solvent. The gel-like sheet is preferably stretched to a predetermined magnification after heating by, for example, a tenter method, a roll method, an inflation method or a combination thereof. The stretching may be conducted monoaxially or biaxially, though the biaxial stretching is preferable. In the case of biaxial stretching, any of simultaneous biaxial stretching, sequential stretching or multi-stage stretching (for instance, a combination of the simultaneous biaxial stretching and the sequential stretching) may be used, though the simultaneous biaxial stretching is preferable. The amount of stretch in either direction need not be the same.

**[0068]** The stretching magnification of this first stretching step can be, for example, 2 fold or more, preferably 3 to 30 fold in the case of monoaxial stretching. In the case of biaxial stretching, the stretching magnification can be, for example, 3 fold or more in any direction, namely 9 fold or more, preferably 16 fold or more, more preferably 25 fold or more, e.g. 49 fold or more, in area magnification. An example for this first stretching step would include stretching from about 9 fold to about 400 fold. A further example would be stretching from about 16 to about 49 fold. Again, the amount of stretch in either direction need not be the same. With the area magnification of 9 fold or more, the pin puncture strength of the microporous membrane is improved. When the area magnification is more than 400 fold, stretching apparatuses, stretching operations, etc., involve large-sized stretching apparatuses, which can be difficult to operate.

**[0069]** To obtain a good microporous structure for the present multi-layer membrane, the stretching temperature of this first stretching step is relatively high, preferably from about the crystal dispersion temperature ("Tcd") of the combined polyethylene content of the cooled extrudate to about Tcd + 30°C, e.g. in a range of Tcd of the combined polyethylene content to Tcd + 25°C, more specifically in a range of Tcd + 10°C to Tcd + 25°C, most specifically in a range of Tcd + 15°C to Tcd + 25°C. When the stretching temperature is lower than Tcd, it is believed that the combined polyethylene content is so insufficiently softened that the gel-like sheet is easily broken by stretching, failing to achieve high-magnification stretching.

**[0070]** The crystal dispersion temperature is determined by measuring the temperature characteristics of dynamic viscoelasticity according to ASTM D 4065. Because the combined polyethylene content herein has a crystal dispersion temperature of about 90 to 100°C, the stretching temperature is from about 90 to 130°C; for example from about 100 to 125°C, more specifically from 105 to 125°C.

**[0071]** The above stretching causes cleavage between polyolefin, e.g. polyethylene, lamellas, making the polyolefin phases finer and forming large numbers of fibrils. The fibrils form a three-dimensional network structure. The stretching is believed to improve the mechanical strength of the microporous membrane and expands its pores, making the microporous membrane suitable for use as a battery separator.

**[0072]** Depending on the desired properties, stretching may be conducted with a temperature distribution in a thickness direction, to provide the microporous membrane with further improved mechanical strength. The detailed description of this method is given by Japanese Patent 3347854.

## 5. Removal of the diluent or solvent

**[0073]** The first and second diluents are removed (or displaced) at least in part from the multi-layer gel-like sheet in order to form a solvent-removed gel-like sheet. A displacing (or "washing") solvent can be used to remove (wash away, or displace) at least a portion of the first and second diluents or solvents. While not wishing to be bound by any theory or model, it is believed that because the polyolefin phases in the multi-layer gel-like sheet produced from the first polyolefin solution and the second polyolefin solution are separated from the diluent or solvent phase, the removal of the diluent or solvent provides a porous membrane constituted by fibrils forming a fine three-dimensional network structure and having pores communicating three-dimensionally and irregularly. The choice of washing solvent is not critical provided it is capable of dissolving or displacing at least a portion of the first and/or second diluent or solvent. Suitable washing solvents include, for example, one or more of volatile solvents such as saturated hydrocarbons exemplified by pentane, hexane, heptane, etc.; chlorinated hydrocarbons exemplified by methylene chloride, carbon tetrachloride, etc.; ethers exemplified by diethyl ether, dioxane, etc.; ketones exemplified by methyl ethyl ketone, etc.; linear fluorocarbons exemplified by trifluoroethane, $C_6F_{14}$, $C_7F_{16}$, etc.; cyclic hydrofluorocarbons exemplified by $C_5H_3F_7$, etc.; hydrofluoroethers exemplified by $C_4F_9OCH_3$, $C_4F_9OC_2H_5$, etc.; and perfluoroethers exemplified by $C_4F_9OCF_3$, $C_4F_9OC_2F_5$, etc.

**[0074]** The method for removing the diluent is not critical, and any method capable of removing a significant amount of diluent can be used, including conventional methods. For example, the multi-layer, gel-like sheet can be washed by immersing the sheet in the washing solvent and/or showering the sheet with the washing solvent. The amount of washing solvent used is not critical, and will generally depend on the method selected for removal of the diluent. For example, the amount of washing solvent used can range from about 300 to about 30,000 parts by mass, based on the mass of the gel-like sheet. While the amount of diluent or solvent removed is not particularly critical, generally a higher quality (more porous) membrane will result when at least a major amount of first and second diluent is removed from the gel-like sheet. In an embodiment, the diluent is removed from the gel-like sheet (e.g., by washing) until the amount of the remaining diluent in the multi-layer gel-like sheet becomes less than 1 wt.%, based on the weight of the gel-like sheet.

**[0075]** The multi-layer microporous membrane deprived of the diluent or solvent can be dried by a heat-drying method, a wind-drying (e.g., air drying using moving air) method, etc., to remove remaining volatile components from the membrane, e.g. washing solvent. Any drying method capable of removing a significant amount of the washing solvent can be used. Preferably, substantially all of the washing solvent is removed during drying. The drying temperature is preferably equal to or lower than Tcd, more preferably 5°C or more lower than Tcd. Drying is conducted until the remaining washing solvent becomes preferably 5% or less by mass, more preferably 3% or less by mass, per 100% by mass (on a dry basis) of the microporous membrane. Insufficient drying undesirably can lead to decrease in the porosity of the microporous membrane by the subsequent heat treatment, resulting in poor permeability.

### 6. Stretching the solvent-deprived and/or dried membrane

**[0076]** The diluent-deprived and/or dried multi-layer membrane is stretched in a second stretching step (re-stretched) at least monoaxially at high magnification. The re-stretching of the membrane can be conducted, for example, while heating, by a tenter method, etc., as in the first stretching step. The re-stretching may be monoaxial or biaxial. In the case of biaxial stretching, any one of simultaneous biaxial stretching or sequential stretching may be used, though the simultaneous biaxial stretching is preferable. Because the re-stretching is usually conducted on the membrane in a long sheet form, which is obtained from the stretched gel-like sheet, the directions of MD and TD (where MD means "machine direction", i.e., the direction of membrane travel during processing, and TD means "transverse direction", i.e., a direction orthogonal to both the MD and the horizontal surface of the membrane) in the re-stretching is usually the same as those in the stretching of the cooled extrudate. In the present invention, however, the re-stretching is actually somewhat greater than that used in the stretching of the cooled extrudate. Stretching magnification in this step is from about 1.1 to about 1.8 fold in at least one direction, for example from about 1.2 to about 1.6 fold. Stretching need not be the same magnification in each direction. If stretching in step (4) of the present method is lower in the range of from about 9 to about 400, then stretching in step (6) of the present method should be higher in the range of from about 1.1 to about 1.8. Likewise, if stretching in step (4) of the present method is higher in the range of from about 9 to about 400, then stretching in step (6) of the present method should be lower in the range of from about 1.1 to about 1.8.

**[0077]** The second stretching or re-stretching is conducted at a second temperature preferably equal to Tm or lower, more preferably in a range of Tcd to Tm. When the second stretching temperature is higher than Tm, it is believed that the melt viscosity is generally too low to conduct good stretching, resulting in low permeability. When the second stretching temperature is lower than Tcd, it is believed that the polyolefin is insufficiently softened so that the membrane might be broken by stretching, i.e., a failure to achieve uniform stretching. In an embodiment, the second stretching temperature is usually from about 90 to about 135°C, for example from about 95 to about 130°C.

**[0078]** The monoaxial stretching magnification of the membrane in this step, as mentioned above, is preferably from about 1.1 to about 1.8 fold. A magnification of 1.1 to 1.8 fold generally provides the membrane of the present invention with a structure having a large average pore size. In the case of monoaxial stretching, the magnification can be form 1.1 to 1.8 fold in a longitudinal or transverse direction. In the case of biaxial stretching, the membrane may be stretched at the same or different magnifications in each stretching direction, though preferably the same, as long as the stretching magnifications in both directions are within 1.1 to 1.8 fold.

**[0079]** When the second stretching magnification of the membrane is less than 1.1 fold, it is believed that the membrane structure of the present invention has poorer permeability, electrolytic solution absorption and compression resistance in the membrane. When the second stretching magnification is more than 1.8 fold, the fibrils formed are too fine, and it is believed that the heat shrinkage resistance and the electrolytic solution absorption characteristics of the membrane are reduced. This second stretching magnification is more preferably from 1.2 to 1.6 fold.

**[0080]** The stretching rate is preferably 3%/second or more in a stretching direction.

In the case of monoaxial stretching, stretching rate is 3%/second or more in a longitudinal or transverse direction. In the case of biaxial stretching, stretching rate is 3%/second or more in both longitudinal and transverse directions. A stretching rate of less than 3%/second decreases the membrane's permeability, and provides the membrane with large unevenness in properties (particularly, air permeability) in a width direction when stretched in a transverse direction. The stretching rate is preferably 5%/second or more, more preferably 10 %/second or more. Though not particularly critical, the upper limit of the stretching rate is preferably 50%/second to prevent rupture of the membrane.

### 7. Heat treatment

**[0081]** The membrane product of step (6) of the present method is thermally treated (heat-set) to stabilize crystals and make uniform lamellas in the membrane. The heat-setting is preferably conducted by a tenter method or a roll method. The heat-setting temperature is preferably in a range of Tcd to Tm. It is believed that too low a heat-setting temperature deteriorates the membrane's pin puncture strength, tensile rupture strength, tensile rupture elongation and heat shrinkage resistance, while too high a heat-setting temperature deteriorates membrane permeability.

**[0082]** An annealing treatment can be conducted after the heat-setting step. The annealing is a heat treatment with no load applied to the multi-layer microporous membrane, and may be conducted by using, e.g., a heating chamber with a belt conveyer or an air-floating-type heating chamber. The annealing may also be conducted continuously after the heat-setting with the tenter slackened. The annealing temperature is preferably Tm or lower, more preferably in a range from about 60°C to about Tm -5°C. Annealing is believed to provide the multi-layer microporous membrane with high permeability and strength. Optionally, the multi-layer membrane is annealed without prior heat-setting. In an embodiment, the heat-setting of step (7) is optional.

### 8. Heat-setting treatment of stretched sheet

**[0083]** The stretched sheet between steps (4) and (5) may be heat-set, provided this heat setting does not deteriorate the properties of the multi-layer microporous membrane. The heat-setting method may be conducted the same way as described above for step (7).

### 9. Heat roller treatment

**[0084]** At least one surface of the stretched sheet from step (4) may be brought into contact with one or more heat rollers following any of steps (4) to (7). The roller temperature is preferably in a range of from Tcd +10°C to Tm. The contact time of the heat roll with the stretched sheet is preferably from about 0.5 second to about 1 minute. The heat roll may have a flat or rough surface. The heat roll may have a suction functionality to remove the solvent. Though not particularly critical, one example of a roller-heating system may comprise holding heated oil in contact with a roller surface.

### 10. Hot solvent treatment

**[0085]** The stretched sheet may be contacted with a hot solvent between steps (4) and (5). A hot solvent treatment turns fibrils formed by stretching to a leaf vein form with relatively thick fiber trunks, providing the multi-layer microporous membrane with large pore size and suitable strength and permeability. The term "leaf vein form" means that the fibrils have thick fiber trunks, and thin fibers extending in a complicated network structure from the trunks. The details of the hot solvent treatment method are described in WO 2000/20493.

### 11. Heat-setting of membrane containing washing solvent

**[0086]** The microporous membrane containing a washing solvent between steps (5) and (6) may be heat-set to a degree that does not deteriorate the properties of the multi-layer microporous membrane. The heat-setting method may be the same as described above in step (7).

### 12. Cross-linking

**[0087]** The heat-set multi-layer microporous membrane may be cross-linked by ionizing radiation rays such as α-rays, β-rays, γ-rays, electron beams, etc. In the case of irradiating electron beams, the amount of electron beams is preferably from about 0.1 to about 100 Mrad, and the accelerating voltage is preferably form about 100 to about 300 kV. The cross-linking treatment elevates the melt down temperature of the multi-layer microporous membrane.

### 13. Hydrophilizing treatment

**[0088]** The heat-set multi-layer microporous membrane may be subjected to a hydrophilizing treatment (a treatment that makes the membrane more hydrophilic). The hydrophilizing treatment may be a monomer-grafting treatment, a surfactant treatment, a corona-discharging treatment, etc. The monomer-grafting treatment is preferably conducted after the cross-linking treatment.

**[0089]** In the case of surfactant treatment hydrophilizing the heat-set microporous membrane, any of nonionic surfactants, cationic surfactants, anionic surfactants and amphoteric surfactants may be used, and the nonionic surfactants are preferred. The microporous membrane can be dipped in a solution of the surfactant in water or a lower alcohol such as methanol, ethanol, isopropyl alcohol, etc., or coated with the solution by a doctor blade method.

### 14. Surface-coating treatment

**[0090]** While not required, the heat-set microporous membrane resulting from step (7) can be coated with porous polypropylene, porous fluororesins such as polyvinylidene fluoride and polytetrafluoroethylene, porous polyimides, porous polyphenylene sulfide, etc., to improve melt down properties when the membrane is used as a battery separator. The polypropylene used for the coating preferably has Mw of form about 5,000 to about 500,000, and a solubility of about 0.5 grams or more in 100 grams of toluene at 25°C. Such polypropylene more preferably has a racemic diade fraction of from about 0.12 to about 0.88, the racemic diade being a structural unit in which two adjacent monomer units are mirror-image isomers to each other. The surface-coating layer may be applied, for instance, by applying a solution of the above coating resin in a good solvent to the microporous membrane, removing part of the solvent to increase a resin concentration, thereby forming a structure in which a resin phase and a solvent phase are separated, and removing the remainder of the solvent. Examples of good solvents for this purpose include aromatic compounds, such as toluene or xylene.

### [4] Lamination

**[0091]** The choice of lamination technique or method is not particularly critical, and conventional lamination methods such as heat-induced lamination can be used to laminate the multi-layer gel-like sheet. Other suitable lamination methods include, for example, heat-sealing, impulse-sealing, ultrasonic-bonding, etc., either alone or in combination. Heat-sealing can be conducted using, e.g., one or more pair of heated rollers where the gel-like sheets are conducted through at least one pair of the heated rollers. Although the heat-sealing temperature and pressure are not particularly critical, sufficient heating and pressure should be applied for a sufficient time to ensure that the gel-like sheets are appropriately bonded to provide a multi-layer, microporous membrane with relatively uniform properties and little tendency toward delamination. In an embodiment, the heat-sealing temperature can be, for instance, about 90°C to about 135°C, or from about 90°C to about 115°C. In an embodiment, the heat-sealing pressure can be from about 0.01 MPa to about 50 MPa.

**[0092]** The thickness of the layers formed from the first and second mixtures (i.e., the layers comprising the first and second microporous layer materials) can be controlled by adjusting the thickness of the first and second gel-like sheets and by the amount of stretching (stretching magnification and dry stretching magnification), when one or more stretching steps are used. Optionally, the lamination step can be combined with a stretching step by passing the gel-like sheets through multi-stages of heated rollers.

## [5] Properties of the multi-layer microporous membrane

**[0093]** The final microporous membrane generally comprises the polymer used to produce the extrudate. A small amount of diluent or other species introduced during processing can also be present, generally in amounts less than 1 wt. % based on the weight of the microporous polyolefin membrane. A small amount of polymer molecular weight degradation might occur during processing, but this is acceptable. In an embodiment, molecular weight degradation during processing, if any, causes the value of MWD of the polymer in the membrane to differ from the MWD of the polymers used to produce the membrane by no more than, e.g., about 10%, or no more than about 1%, or no more than about 0.1%.

**[0094]** The thickness of the final membrane is generally in the range of 3 μm to 200 μm. For example, the membrane can have a thickness in the range of from about 5 μm to about 50 μm, e.g., from about 15 μm to about 30 μm. The thickness of the microporous membrane can be measured, e.g., by a contact thickness meter at 1 cm longitudinal intervals over the width of 10 cm, and then averaged to yield the membrane thickness. Thickness meters such as the Litematic available from Mitsutoyo Corporation are suitable. Non-contact thickness measurement methods are also suitable, e.g. optical thickness measurement methods. Optionally, the multi-layer microporous membrane has one or more of the following characteristics.

(a) Air permeability of ≤ 400 seconds/100cm$^3$ (converted to the value at 20 μm thickness)

**[0095]** The membrane's air permeability is measured according to JIS P8117. In an embodiment, the membrane air permeability is in the range of form 20 to 400 seconds/100 cm$^3$. If desired, air permeability $P_1$ measured on a microporous membrane having a thickness $T_1$ according to JIS P8117 can be converted to air permeability $P_2$ at a thickness of 20μm by the equation of $P_2 = (P_1 \times 20)/T_1$. In an embodiment, the membrane's air permeability is in the range of 50 seconds/100cm$^3$ to 400 seconds/100cm$^3$, or 100 seconds/100cm$^3$ to 350 seconds/100cm$^3$.

(b) Porosity of from about 25 to about 80%

**[0096]** The membrane's porosity is measured conventionally by comparing the membrane's actual weight to the weight of an equivalent non-porous membrane of 100% polyethylene (equivalent in the sense of having the same length, width, and thickness). Porosity is then determined using the formula: Porosity % = 100 x (w2-w1)/w2, wherein "w1" is the actual weight of the microporous membrane and "w2" is the weight of an equivalent non-porous membrane of 100% polyethylene having the same size and thickness.

(c) Pin puncture strength of ≥ 3500 mN (converted to the equivalent value for a membrane having a 20μm thickness)

**[0097]** The membrane's pin puncture strength (converted to the value at membrane thickness of 20μm) is represented by the maximum load measured when the microporous membrane is pricked with a needle of 1 mm in diameter with a spherical end surface (radius R of curvature: 0.5 mm) at a speed of 2 mm/second. In an embodiment, the membrane's pin puncture strength (converted to 20μm) is in the range of 3600mN to 5,000mN.

**[0098]** The maximum load is measured when each microporous membrane having a thickness of $T_1$ is pricked with a needle of 1 mm in diameter with a spherical end surface (radius R of curvature: 0.5 mm) at a speed of 2 mm/second. The measured maximum load $L_1$ is converted to the maximum load $L_2$ at a thickness of 20μm by the equation of $L_2 = (L_1 \times 20)/T_1$, and defined as pin puncture strength.

(d) MD and TD tensile strength of ≥ 40,000 kPa

**[0099]** A tensile strength of 40,000 kPa or more in both longitudinal and transverse directions (measured using a 10mm wide test piece according to ASTM D-882), is characteristic of suitable durable microporous membranes, particularly when used as battery separators. MD tensile strength is, e.g., in the range of about 80,000 to 150,000kPa, and TD tensile strength is, e.g., in the range of 90,000 to 150,000kPa.

(e) Tensile elongation ≥ 100%

**[00100]** A tensile elongation of 100% or more in both longitudinal and transverse directions (measured according to ASTM D-882), is characteristic of suitably durable microporous membranes, particularly when used as battery separators. In an embodiment, MD TE is ≥ 130%, e.g., 135% to 150%, and TD TE is ≥ 130%, e.g., 140% to 155%.

(f) TD heat shrinkage ratio at 105°C of less than 12% and MD heat shrinkage ratio at 105°C of less than 12%

**[00101]** The shrinkage ratio of the microporous membrane orthogonal planar directions (e.g., machine direction or transverse direction) at 105°C is measured as follows: (i) Measure the size of a test piece of microporous membrane at ambient temperature in both the machine direction and transverse direction, (ii) equilibrate the test piece of the microporous membrane at a temperature of 105°C for 8 hours with no applied load, and then (iii) measure the size of the membrane in both the machine and transverse directions. The heat (or "thermal") shrinkage ratio in either the machine or transverse directions can be obtained by dividing the result of measurement (i) by the result of measurement (ii) and expressing the resulting quotient as a percent.

**[00102]** In an embodiment, the microporous membrane has a TD heat shrinkage ratio at 105°C ≤ 10%, e.g., in the range of 2.0% to 9%, and an MD heat shrinkage ratio at 105°C ≤ 10%, e.g., in the range of 2% to 6%.

(g) Thickness variation ratio of 20% or less after heat compression (expressed as an absolute value)

**[00103]** The thickness variation ratio after heat compression at 90°C under pressure of 2.2 MPa for 5 minutes is generally 20% or less per 100% of the thickness before compression. Batteries comprising microporous membrane separators with a thickness variation ratio of 20% or less have suitably large capacity and good cyclability. In an embodiment, the membrane's thickness variation ratio is ≤ 10%, e.g., in the range of 5% to 10%.

**[00104]** To measure the thickness variation ratio after heat compression, a microporous membrane sample is situated between a pair of highly flat plates, and heat-compressed by a press machine under a pressure of 2.2 MPa (22 kgf/cm$^2$) at 90°C for 5 minutes, to determine an average thickness. A thickness variation ratio is calculated by the formula of (average thickness after compression - average thickness before compression) / (average thickness before compression) x 100.

(h) Air permeability after heat compression ≤ 1000 sec/100 $cm^3$

**[00105]** The microporous polyolefin membrane when heat-compressed under the above conditions generally has an air permeability (Gurley value) of 1000 sec/100 $cm^3$ or less. Batteries using such membranes have suitably large capacity and cyclability. The air permeability is preferably 700 sec/100 $cm^3$ or less, e.g., in the range of 200 sec/100$cm^3$ to 620 sec/$cm^3$.

**[00106]** Air permeability after heat compression is measured according to JIS P8117.

(i) Surface roughness ≥ 3 x $10^2$ nm

**[00107]** The surface roughness of the membrane measured by an atomic force microscope (AFM) in a dynamic force mode is generally 3 x $10^2$ nm or more (measured as the average maximum height difference across the membrane). The membrane's surface roughness is preferably 3.1 x $10^2$ nm or more, e.g., in the range of 10 nm to 700 nm.

(j) Electrolytic solution absorption speed ≥ 3.5

**[00108]** Using a dynamic surface tension measuring apparatus (DCAT21 with high-precision electronic balance, available from Eko Instruments Co., ltd.), a microporous membrane sample is immersed in an electrolytic solution for 600 seconds (electrolyte: 1 mol/L of $LiPF_6$, solvent: ethylene carbonate/dimethyl carbonate at a volume ratio of 3/7) kept at 18°C, to determine an electrolytic solution absorption speed by the formula of [weight (in grams) of microporous membrane after immersion / weight (in grams) of microporous membrane before immersion]. The electrolytic solution absorption speed is expressed by a relative value, assuming that the electrolytic solution absorption rate in the microporous membrane of Comparative Example 8 is 1. In an embodiment, the membrane's electrolytic solution absorption speed is in the range of 3.5 to 10, or 3.6 to 6.

(k) Shutdown Temperature of 140°C or less

**[00109]** The membrane's shutdown temperature is ≤ 140°C, e.g., in the range of 130°C to 139°C. The shut down temperature of the microporous membrane is measured by a thermomechanical analyzer (TMA/SS6000 available from Seiko Instruments, Inc.) as follows: A rectangular sample of 3 mm x 50 mm is cut out of the microporous membrane such that the long axis of the sample is aligned with the transverse direction of the microporous membrane and the short axis is aligned with the machine direction. The sample is set in the thermomechanical analyzer at a chuck distance of 10 mm, i.e., the distance from the upper chuck to the lower chuck is 10mm. The lower chuck is fixed and a load of 19.6mN applied to the sample at the upper chuck. The chucks and sample are enclosed in a tube which can be heated. Starting at 30°C, the temperature inside the tube is elevated at a rate of 5°C/minute, and sample length change under the 19.6mN load is measured at intervals of 0.5 second and recorded as temperature is increased. The temperature is increased to 200°C. "Shut down temperature" is defined as the temperature of the inflection point observed at approximately the melting point of the polymer having the lowest melting point among the polymers used to produce the membrane.

(l) Melt down temperature of 150°C or higher

**[00110]** Melt down temperature is measured by the following procedure: A rectangular sample of 3 mm x 50 mm is cut out of the microporous membrane such that the long axis of the sample is aligned with the transverse direction of the microporous membrane as it is produced in the process and the short axis is aligned with the machine direction. The sample is set in the thermomechanical analyzer (TMA/SS6000 available from Seiko Instruments, Inc.) at a chuck distance of 10 mm, i.e., the distance from the upper chuck to the lower chuck is 10mm. The lower chuck is fixed and a load of 19.6mN applied to the sample at the upper chuck. The chucks and sample are enclosed in a tube which can be heated. Starting at 30°C, the temperature inside the tube is elevated at a rate of 5°C/minute, and sample length change under the 19.6mN load is measured at intervals of 0.5 second and recorded as temperature is increased. The temperature is increased to 200°C. The melt down temperature of the sample is defined as the temperature at which the sample breaks, generally at a temperature in the range of about 145°C to about 200°C.

**[00111]** In an embodiment, the meltdown temperature is in the range of from 168°C to 180°C, e.g., 170°C to 178°C.

(m) Maximum TD shrinkage in molten state ≤ 20%

**[00112]** Maximum shrinkage in the molten state is measured by the following procedure: Using the TMA procedure described for the measurement of melt down temperature, the sample length measured in the temperature range of from 135°C to 145°C are recorded. The membrane shrinks, and the distance between the chucks decreases as the membrane shrinks. The maximum shrinkage in the molten state is defined as the sample length between the chucks measured at 23°C (L1 equal to 10mm) minus the minimum length measured generally in the range of about 135°C to about 145°C (equal to L2) divided by L1, i.e., [L1-L2]/L1*100%. The rectangular sample of 3 mm x 50 mm used is cut out of the microporous membrane such that the long axis of the sample is aligned with the transverse direction of the microporous membrane as it is produced in the process and the short axis is aligned with the machine direction.

**[00113]** In an embodiment, the membrane's maximum TD shrinkage in the molten state is observed to occur (TMA method above) at about 140°C. In an embodiment, the maximum TD shrinkage in the molten state is in the range of 1% to 15%, or 5% to 13%.

(n) Capacity Recovery Ratio ≥ 70%

**[00114]** Capacity Recovery Ratio is a property of the membrane that is related to the membrane's electrochemical stability when the membrane is used as a battery separator in a lithium ion battery. Capacity Recovery Ratio is expressed as a percent and is related to the amount of battery storage capacity that is lost after storing the battery at an elevated temperature for thirty days. For automotive batteries, such as those used for starting or powering motor means for moving an electric vehicle or hybrid electric vehicle, and for power tool batteries, a Capacity Recovery Ratio ≥ 70% is desired since those relatively high-power, high capacity applications are particularly sensitive to any loss in the battery's ability to store electric charge. The term "high-capacity" batteries generally means batteries capable of supplying 1 Ampere hour (1 Ah) or more, e.g., 2.0 Ah to 3.6 Ah.

**[00115]** To measure the membrane's Capacity Recovery Ratio, a membrane having a length (MD) of 70mm and a width (TD) of 60mm is located between and anode and cathode having the same planar dimensions as the membrane. The anode is made of natural graphite and the cathode is made of $LiCoO_2$. An electrolyte is prepared by dissolving $LiPF_6$ into a mixture of ethylene carbonate (EC) and methylethyl carbonate (EMC) (4/6, V/V) as 1 M solution. The electrolyte is impregnated into the membrane in the region between the anode and the cathode to complete the battery.

**[00116]** The charge capacity recovery ratio is measured by charging and then discharging the battery at a temperature of 23°C and recording the amount of charge supplied by the battery during discharge ("initial charge capacity"). The battery is then exposed to a temperature of 80°C for thirty days, and then cooled to 23°C. After cooling, the charge capacity is re-measured (final charge capacity"). The Capacity Recovery Ratio is defined as the final charge capacity divided by the initial charge capacity times 100%.

**[00117]** In an embodiment, the membrane's Capacity Recovery Ratio ≥ 70%, e.g., in the range of 75% to 100%, or 78 to 85%.

### [6] Battery separator

**[00118]** In an embodiment, the battery separator formed from any of the above multi-layer microporous membranes of the present invention has a thickness of form about 3 to about 200 μm, or from about 5 to about 50 μm, or from about 7 to about 35 μm, though the most suitable thickness is properly selected depending on the type of battery to be manufactured.

### [7] Battery

**[00119]** In an embodiment, the multi-layer microporous membrane of the present invention can be used as a separator for primary and secondary batteries such as lithium ion batteries, lithium-polymer secondary batteries, nickel-hydrogen secondary batteries, nickel-cadmium secondary batteries, nickel-zinc secondary batteries, silver-zinc secondary batteries, and particularly for lithium ion secondary batteries. Explanations will be made below on the lithium ion secondary batteries.

**[00120]** The lithium ion secondary battery comprises a cathode, an anode, and a separator located between the anode and the cathode. The separator generally contains an electrolytic solution (electrolyte). The electrode structure is not critical, and conventional electrode structures can be used. The electrode structure may be, for instance, a coin type in which a disc-shaped cathode and anode are opposing, a laminate type in which a planar cathode and anode are alternately laminated with at least one separator situated between the anode and the cathode, a toroidal type in which ribbon-shaped cathode and anode are wound, etc.

**[00121]** The cathode generally comprises a current collector, and a cathodic-active material layer capable of absorbing and discharging lithium ions, which is formed on the current collector. The cathodic-active materials can be, for example, inorganic compounds such as transition metal oxides, composite oxides of lithium and transition metals (lithium composite oxides), transition metal sulfides, etc. The transition metals can be, for example, V, Mn, Fe, Co, Ni, etc. In an embodiment, the lithium composite oxides are lithium nickelate, lithium cobaltate, lithium manganate, laminar lithium composite oxides based on $\alpha$-$NaFeO_2$, etc. The anode generally comprises a current collector, and a negative-electrode active material layer formed on the current collector.

The negative-electrode active materials can be, for example, carbonaceous materials such as natural graphite, artificial graphite, cokes, carbon black, etc.

**[00122]** The electrolytic solutions can be obtained by dissolving lithium salts in organic solvents. The choice of solvent and/or lithium salt is not critical, and conventional solvents and salts can be used. The lithium salts can be, for example, $LiClO_4$, $LiPF_6$, $LiAsF_6$, $LiSbF_6$, $LiBF_4$, $LiCF_3SO_3$, $LiN(CF_3SO_2)_2$, $LiC(CF_3SO_2)_3$, $Li_2B_{10}Cl_{10}$, $LiN(C_2F_5SO_2)_2$, $LiPF_4(CF_3)_2$, $LiPF_3(C_2F_5)_3$, lower aliphatic carboxylates of lithium, $LiAlCl_4$, etc. The lithium salts may be used alone or in combination. The organic solvents can be organic solvents having relatively high boiling points (compared to the battery's shut-down temperature) and high dielectric constants. Suitable organic solvents include ethylene carbonate, propylene carbonate, ethylmethyl carbonate, γ-butyrolactone, etc.; organic solvents having low boiling points and low viscosity such as tetrahydrofuran, 2-methyltetrahydrofuran, dimethoxyethane, dioxolane, dimethyl carbonate, diethyl carbonate, and the like, including mixtures thereof. Because the organic solvents generally having high dielectric constants generally also have a high viscosity, and vice versa, mixtures of high- and low-viscosity solvents can be used.

**[00123]** When the battery is assembled, the separator is generally impregnated with the electrolytic solution, so that the separator (multi-layer microporous membrane) is provided with ion permeability. The choice of impregnation method is not critical, and conventional impregnation methods can be used. For example, the impregnation treatment can be conducted by immersing the multi-layer microporous membrane in an electrolytic solution at room temperature.

**[00124]** The method selected for assembling the battery is not critical, and conventional battery assembly methods can be used. For example, when a cylindrical battery is assembled, a cathode sheet, a separator formed by the multi-layer microporous membrane and an anode sheet are laminated in this order, and the resultant laminate is wound to a toroidal-type electrode assembly. A second separator might be needed to prevent short-circuiting of the toroidal windings. The resultant electrode assembly can be deposited into a battery can and then impregnated with the above electrolytic solution, and the battery lid acting as a cathode terminal provided with a safety valve can be caulked to the battery can via a gasket to produce a battery. The battery can be used as a source or sink of electric charge.

## [8] Examples

**[00125]** The present invention will be explained in more detail referring to Examples below without intention of restricting the scope of the present invention.

### Example 1

(1) Preparation of first polyolefin solution

**[00126]** A first polyolefin composition comprising (a) 50% first polyethylene resin having an Mw of 5.6 x $10^5$ and an MWD of 4.05, (b) 37.5 % first polypropylene resin having an Mw of 1.1 x $10^6$, a heat of fusion of 114 J/g and an MWD of 5, (c) 12.5% second polypropylene resin having an Mw of 6.6 x $10^5$, a heat of fusion of 103.3 J/g and an MWD of 11.4, is prepared by dry-blending, the percentages being based by weight of the first polyolefin composition. The polyethylene resin in the composition has a melting point of 135°C and a crystal dispersion temperature of 100°C.

**[00127]** Twenty-five parts by weight of the resultant first polyolefin composition is charged into a strong-blending double-screw extruder having an inner diameter of 58 mm and L/D of 42, and 75 parts by mass of liquid paraffin (50 cst at 40°C) is supplied to the double-screw extruder via a side feeder. Melt-blending is conducted at 210°C and 200 rpm to prepare a first polyolefin solution.

(2) Preparation of second polyolefin solution

**[00128]** A second polyolefin solution is prepared in the same manner as above except as follows. A second polyolefin composition comprising (a) 80% first polyethylene resin having an Mw of 5.6 x $10^5$ and an MWD of 4.05, and (a') 20% of a second polyethylene resin having an Mw of 1.9 x $10^6$ and an MWD of 5.09, is prepared by dry-blending, the percentages being based by weight of the second polyolefin composition. The polyethylene resin in the composition has a melting point of 135°C and a crystal dispersion temperature of 100°C.

**[00129]** Thirty parts by weight of the resultant second polyolefin composition is charged into a strong-blending double-screw extruder having an inner diameter of 58 mm and L/D of 42, and 70 parts by mass of liquid paraffin (50 cst at 40°C) is supplied to the double-screw extruder via a side feeder. Melt-blending is conducted at 210°C and 200 rpm to prepare a second polyolefin solution.

(3) Production of membrane

**[00130]** The first and second polyolefin solutions are supplied from their double-screw extruders to a three-layer-extruding T-die, and extruded therefrom to form an extrudate (also called a laminate) of first polyolefin solution layer/second polyolefin solution layer/first polyolefin solution layer at a layer thickness ratio of 10/80/10. The extrudate is cooled while passing through cooling rollers controlled at 0°C, to form a three-layer gel-like sheet, which is simultaneously biaxially stretched at 115°C to a magnification of 5 fold in both machine (longitudinal) and transverse directions by a tenter-stretching machine. The stretched three-layer gel-like sheet is fixed to an aluminum frame of 20 cm x 20 cm, immersed in a bath of methylene chloride controlled at 25°C to remove liquid paraffin with vibration of 100 rpm for 3 minutes, and dried by air flow at room temperature. The dried membrane is re-stretched by a batch-stretching machine to a magnification of 1.4 fold in a transverse direction at 129°C. The re-stretched membrane, which remains fixed to the batch-stretching machine, is heat-set at 125°C for 10 minutes to produce a three-layer microporous membrane.

**Example 2**

**[00131]** Example 1 is repeated except the first and second microporous polyolefin membranes were separately extruded and then laminated in an order of first microporous membrane/second microporous membrane/first microporous membrane at a layer thickness ratio of 25/50/25.

**Example 3**

**[00132]** Example 1 is repeated except the first polyolefin composition of the first polyolefin solution comprises 25 % first polypropylene resin and 25 % second polypropylene resin along with the 50 % first polyethylene resin, the percentages being based on the weight of the first polyolefin composition.

**Example 4**

**[00133]** Example 1 is repeated except the first polyolefin composition of the first polyolefin solution comprises 60 % first polyethylene resin, 25 % first polypropylene resin, and 15 % second polypropylene resin, the percentages being based by weight of the first polyolefin composition.

**Example 5**

**[00134]** Example 4 is repeated except the dried membrane is re-stretched by a batch-stretching machine to a magnification of 1.4 fold in the transverse direction and 1.2 fold in the machine direction at 129°C.

**Example 6**

**[00135]** Example 1 is repeated except the second polypropylene resin in the first polyolefin composition has a weight average molecular weight of $5.7 \times 10^5$, a heat of fusion of 94.6 J/g and an MWD of 5.9.

**Example 7**

**[00136]** Example 1 is repeated except the first polypropylene resin in the first polyolefin composition has a weight average molecular weight of $0.9 \times 10^6$, a heat of fusion of 106 J/g and a molecular weight distribution of 4.5.

**Comparative Example 1**

**[00137]** Example 1 is repeated except the first and second microporous polyolefin membranes are separately extruded and then laminated in an order of first microporous membrane/second microporous membrane/first microporous membrane at a layer thickness ratio of 40/20/40.

**Comparative Example 2**

**[00138]** Example 1 is repeated except the first and second microporous polyolefin membranes are laminated in an order of second microporous membrane/first microporous membrane/second microporous membrane at a layer thickness ratio of 10/80/10.

**Comparative Example 3**

**[00139]** Example 1 is repeated except that there is no re-stretching of the dried membrane.

**Comparative Example 4**

**[00140]** Example 1 is repeated except the first polyolefin composition of the first polyolefin solution comprises 50% first polyethylene resin and 50% first polypropylene resin, the percentages being based by weight of the first polyolefin composition. There is no second polypropylene resin in this first polyolefin composition.

**Comparative Example 5**

**[00141]** Example 1 is repeated except the first polyolefin composition of the first polyolefin solution comprises 50% first polyethylene resin and 50% second polypropylene resin, the percentages being based by weight of the first polyolefin composition. There is no first polypropylene resin in this first polyolefin composition.

**Comparative Example 6**

**[00142]** Example 1 is repeated except the first polyolefin composition of the first polyolefin solution comprises 12.5% first polypropylene resin and 37.5% second polypropylene resin along with the 50% first polyethylene resin, the percentages being based by weight of the first polyolefin composition.

**Comparative Example 7**

**[00143]** Example 1 is repeated except the first polyolefin composition of the first polyolefin solution comprises 25% first polyethylene resin and 25% second polyethylene resin having an Mw of 2 x $10^6$ and an MWD of 8, the percentages being based by weight of the first polyolefin composition.

**Comparative Example 8**

**[00144]** Example 1 is repeated except with the first polyolefin composition of the first polyolefin solution comprising 80% first polyethylene resin and 20% second polyethylene resin having a weight average molecular weight of 2 x $10^6$ and a molecular weight distribution of 8, the percentages being based by weight of the first polyolefin composition. There are no first or second polypropylene resins in this first polyolefin composition, and no re-stretching of the dried three-layer membrane.

**PROPERTIES**

**[00145]** The properties of the multi-layer microporous membranes of Examples 1-8 and Comparative Examples 1-8 are shown in Tables 1 and 2.

**[00146]**

**Table 1**

| PROPERTIES | Ex 1 | Ex 2 | Ex 3 | Ex 4 | Ex 5 | Ex 6 | Ex 7 | |
|---|---|---|---|---|---|---|---|---|
| Thickness μm | 17.9 | 18.0 | 18.1 | 18.2 | 18.0 | 18.3 | 18.2 | |
| Air Perm. | 260 | 310 | 240 | 250 | 270 | 260 | 240 | |
| Porosity % | 53.1 | 56.3 | 57.8 | 52.1 | 51.8 | 52.8 | 54.6 | |
| Punct. Strength | 4116 | 3626 | 3920 | 4410 | 4508 | 4018 | 4214 | |
| Tensile Strength MD//TD | 116620<br>117600 | 89180<br>90160 | 110740<br>111720 | 122500<br>117600 | 119560<br>115640 | 115640<br>116620 | 117600<br>116620 | |
| Tensile Elongation MD//TD | 145<br>140 | 135<br>140 | 140<br>140 | 150<br>155 | 145<br>150 | 145<br>140 | 145<br>140 | |
| Heat Shrinkage MD//TD | 5.8<br>8.7 | 5.6<br>8.5 | 5.5<br>8.4 | 5.3<br>8.3 | 5.7<br>2.3 | 5.9<br>8.8 | 5.6<br>8.5 | |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Surface Roughness ($x10^2$ nm) | 3.4 | 3.4 | 3.2 | 3.3 | 3.4 | 3.8 | 3.5 | |
| Elec. Soln. Absorp. Speed | 3.7 | 4 | 4.5 | 3.6 | 3.5 | 3.7 | 3.8 | |
| Thick. Var. Aft. Heat Comp. % | -9 | -7 | -6 | -8 | -7 | -10 | -10 | |
| Air Perm. Aft. Heat Comp. | 520 | 610 | 480 | 490 | 530 | 530 | 490 | |
| Meltdown Temp. °C | 176 | 178 | 174 | 172 | 171 | 175 | 177 | |
| Max. Shrinkage % * | 11.8 | 11.5 | 9.9 | 12.3 | 7.8 | 11.6 | 11.7 | |
| Cap. Recovery Ratio % | 81 | 82 | 80 | 78 | 78 | 80 | 81 | |
| Shutdown Temp. °C | 135 | 135 | 135 | 135 | 135 | 135 | 135 | |

*Maximum Shrinkage in Molten State (% at about 140 °C)

### Table 2

| **PROPERTIES** | **Comp Ex 1** | **Comp Ex 2** | **Comp Ex 3** | **Comp Ex 4** | **Comp Ex 5** | **Comp Ex 6** | **Comp Ex 7** | **Comp Ex 8** |
|---|---|---|---|---|---|---|---|---|
| Thickness µm | 17.8 | 18.2 | 18.3 | 18.4 | 18.2 | 18.0 | 18.1 | 18.2 |
| Air Perm. | 420 | 440 | 360 | 280 | 230 | 250 | 270 | 490 |
| Porosity % | 56.7 | 57.3 | 45.2 | 50.3 | 55.2 | 54.8 | 54.2 | 38.3 |
| Punct. Strength | 2842 | 2646 | 3724 | 4214 | 2842 | 3136 | 3724 | 5292 |
| Tensile Strength MD//TD | 72520<br>73500 | 68600<br>69580 | 78400<br>116620 | 117600<br>118580 | 73500<br>74480 | 75460<br>77420 | 98000<br>98980 | 179340<br>141120 |
| Tensile Elongation MD//TD | 125<br>125 | 125<br>125 | 190<br>140 | 150<br>145 | 130<br>130 | 130<br>130 | 140<br>140 | 140<br>240 |
| Heat Shrinkage MD//TD | 5.3<br>8.2 | 3.3<br>5.9 | 8.0<br>5.0 | 7.1<br>10.1 | 6.2<br>8.9 | 6.5<br>8.7 | 6.3<br>9.4 | 6.0<br>5.5 |
| Surface Roughness ($x10^2$ nm) | 3.3 | 2.3 | 3.3 | 3.2 | 33 | 15 | 3.4 | 2.2 |
| Elec. Soln. Absorp. Speed | 4 | 1.1 | 2.9 | 2.3 | 4.8 | 4.6 | 3.4 | 1 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Thick. Var. Aft. Heat Comp. % | -6 | -15 | -15 | -8 | -16 | -8 | -8 | -20 |
| Air Perm. Aft. Heat Comp. | 800 | 1210 | 1010 | 780 | 550 | 630 | 520 | 1020 |
| Meltdown Temp. °C | 179 | 175 | 173 | 179 | 162 | 169 | 177 | 148 |
| Max. Shrinkage % * | 11.1 | 8.8 | 4.8 | 15.8 | 4.3 | 5.2 | 35.1 | 32.0 |
| Cap. Recovery Ratio % | 81 | 70 | 79 | 79 | 80 | 80 | 77 | 63 |
| Shutdown Temp. °C | 135 | 135 | 135 | 135 | 135 | 135 | 135 | 135 |

*Maximum Shrinkage in Molten State (% at about 140 °C)

**[00147]** It is noted from Table 1 that the multi-layer microporous membrane of the present invention has well-balanced properties, including air permeability, pin puncture strength, tensile strength, tensile elongation, shut down temperature and melt down temperature, as well as excellent electrolytic solution absorption, with little variation of thickness and air permeability after heat compression. Lithium ion secondary batteries comprising the multi-layer microporous membranes of the present invention have capacity recovery ratios of 70% or more, indicating desirable high temperature retention properties.

**[00148]** On the other hand, the microporous membrane products of the Comparative Examples exhibit a poorer balance of properties.

**[00149]** The multi-layer microporous membrane of the present invention has well-balanced properties and use of such multi-layer microporous membrane as a battery separator provides batteries having excellent safety, heat resistance, retention properties and productivity.

**[00150]** All patents, test procedures, and other documents cited herein, including priority documents, are fully incorporated by reference to the extent such disclosure is not inconsistent and for all jurisdictions in which such incorporation is permitted.

**[00151]** While the illustrative forms disclosed herein have been described with particularity, it will be understood that various other modifications will be apparent to and can be readily made by those skilled in the art without departing from the spirit and scope of the disclosure. Accordingly, it is not intended that the scope of the claims appended hereto be limited to the examples and descriptions set forth herein but rather that the claims be construed as encompassing all the features of patentable novelty which reside herein, including all features which would be treated as equivalents thereof by those skilled in the art to which this disclosure pertains.

**[00152]** When numerical lower limits and numerical upper limits are listed herein, ranges from any lower limit to any upper limit are contemplated.

## CLAIMS

1. A multi-layer microporous membrane comprising polyethylene and polypropylene and having a pin puncture strength $\geq$ 3500 mN, an electrolytic solution absorption speed $\geq$ 3.5 and air permeability after heat compression $\leq$ 1000 seconds/cm$^3$.

2. The membrane of claim 1, wherein the membrane comprises at least one first microporous membrane layer and at least one second microporous membrane layer in planar contact one with the other, wherein the first microporous membrane layer comprises a first polyethylene, a first polypropylene, and a second polypropylene different from the first polypropylene; and wherein the second microporous membrane layer comprises a first polyethylene and a second polyethylene.

3. The membrane of claim 2 wherein

the first layer comprises (a) from 30 to 70% of a first polyethylene, the first polyethylene having a weight average molecular weight Mw < 1.0 x 10$^6$, (b) from 20 to 40% of a first polypropylene, the first polypropylene having an Mw $\geq$ 0.8 x 10$^6$and a $\Delta$Hm $\geq$ 80 J/g, and (c) from 10 to 30% of a second polypropylene, the second polypropylene having an Mw < 0.8 x 10$^6$ and a $\Delta$Hm $\geq$ 80 J/g, the percentages being based on the weight of the first microporous membrane layer; and

wherein the second layer comprises (a) from 60 to 90% of a first polyethylene, the first polyethylene of the second layer having an Mw < 1.0 x 10$^6$, and (a') from 10 to 40% of a second polyethylene, the second polyethylene having an Mw $\geq$ 1.0 x 10$^6$, the percentages being based on the weight of the second microporous membrane layer.

4. The multi-layer microporous membrane of claim 3 wherein the first microporous membrane layer comprises (a) from 40 to 60% of the first polyethylene, the first polyethylene having an Mw in the range of from 4.5 x 10$^5$ to 6.5 x 10$^5$ and an MWD in the range of 2 to 10, (b) from 25 to 40% of the first polypropylene, the first polypropylene having an Mw in the range of from 0.9 x 10$^6$ to 2 x 10$^6$, an MWD in the range of 1.5 to 10, and a $\Delta$Hm in the range of 105 $\leq$ $\Delta$Hm $\leq$ 125, and (c) from 10 to 25% of a second polypropylene, the second polypropylene having an Mw in the range of from 4 x 10$^5$ to 7.5 x 10$^5$, an MWD in the range of from 2 to 20, and a $\Delta$Hm in the range of 90 $\leq$ $\Delta$Hm < 105, the percentages being based on the weight of the first microporous membrane layer; and

the second microporous membrane layer comprises (a) from 70 to 85% of the first polyethylene, the first polyethylene of the second layer having an Mw in the range of from $4.5 \times 10^5$ to $6.5 \times 10^5$ and an MWD in the range of 2 to 10, and (a') from 15 to 30% of the second polyethylene, the second polyethylene having an Mw in the ranged of from $1.1 \times 10^6$ to $5 \times 10^6$ and an MWD in the range of 2 to 10, the percentages being based on the weight of the second microporous membrane layer.

5. The multi-layer microporous membrane of claims 3 or 4, wherein the membrane further comprises a third microporous layer comprising (a) from 30 to 70% of a first polyethylene, the first polyethylene having a weight average molecular weight $Mw < 1.0 \times 10^6$, (b) from 20 to 40% of a first polypropylene, the first polypropylene having an $Mw \geq 0.8 \times 10^6$ and a $\Delta Hm \geq 80$ J/g, and (c) from 10 to 30% of a second polypropylene, the second polypropylene having an $Mw < 0.8 \times 10^6$ and a $\Delta Hm \geq 80$ J/g, the percentages being based on the weight of the first microporous membrane layer; the second microporous layer being located between the first and third microporous layers.

6. The multi-layer microporous membrane of any of claims 3-5, the membrane having a thickness ≥ 3μm and having one or more of a melt down temperature ≥ 150°C, a maximum shrinkage in the molten state ≤ of 20%, an air permeability ranging ≤ 400 seconds/100 $cm^3$, a porosity in the range of from 25 to 80%, a tensile strength ≥ 40,000 kPa in at least one planar direction, a tensile elongation ≥ 100%, a heat shrinkage ≤ 12% in at least one planar direction, a thickness variation ratio after heat compression ≤ 20%, a surface roughness $\geq 3 \times 10^2$ nm or more, or a maximum TD shrinkage in the molten state ≤ 20%.

7. The multi-layer microporous membrane of any of claims 3-6, wherein the membrane is a two-layer or three-layer membrane.

8. The multi-layer microporous membrane of claim 7, wherein the first microporous membrane layer and the second microporous membrane layer are in planar contact one with the other in the following order: first/second; first/second/first; first/second/first/second; or first/second/first/second/first.

9. The multi-layer microporous membrane of claim 8, wherein the second microporous membrane layer contains a greater amount of the first polyethylene than the first microporous membrane layer and the total amount of first polyethylene in the multi-layer microporous membrane is at least 37.5 wt. % based on the weight of the

multi-layer microporous membrane.

10. A battery comprising at least one anode, at least one cathode, an electrolyte, and a battery separator located between the anode and the cathode, the battery separator comprising a multi-layer microporous membrane comprising polyethylene and polypropylene and having a pin puncture strength ≥ 3500 mN, an electrolytic solution absorption speed ≥ 3.5, and an air permeability after heat compression ≤ 1000 seconds/cm$^3$.

11. A method for producing a multi-layer microporous membrane, comprising: (1a) combining a first polyolefin composition and at least one diluent to form a first mixture, the first polyolefin composition comprising (a) from 30 to 70% of a first polyethylene resin having an Mw < 1.0 x $10^6$, (b) from 20 to 40% of a first polypropylene resin having an Mw ≥ 0.8 x $10^6$ and a ΔHm ≥ 80 J/g, and (c) from 10 to 30 % of a second polypropylene resin having an Mw < 0.8 x $10^6$ and a ΔHm ≥ 80 J/g, the percentages being based on the weight of the first polyolefin composition, (1b) combining a second polyolefin composition and at least one diluent to form a second mixture, the second polyolefin composition comprising (a) from 60 to 90 % of a first polyethylene resin having an Mw < 1.0 x $10^6$, and (a') from 10 to 40% of a second polyethylene resin having an Mw ≥ 1.0 x $10^6$, the percentages being based on the weight of the second polyolefin composition, (2) extruding the first and second mixtures through die or dies to produce a layered extrudate having at least a first layer comprising the first mixture and a second layer comprising the second mixture that is in planar contact with he first layer, (3) cooling the extrudate to form a cooled extrudate, (4) stretching the cooled extrudate in at least one direction at a high stretching temperature to form a stretched sheet, (5) removing at least a portion of the diluent from the stretched sheet to form a membrane, (6) stretching the membrane in at least one direction to form a stretched membrane, and (7) heat-setting the stretched membrane product of step (6) to form the multilayer microporous membrane.

12. The method of claim 11 further comprising a heat-setting treatment step (4i) between steps (4) and (5) wherein the stretched sheet is heat-set at a temperature of the stretching temperature ±5°C, a heat roll treatment step (4ii) following step (4i) and before step (5) wherein the stretched sheet contacts a heated roller at a temperature from the crystal dispersion temperature of the polyolefin composition to the melting point +10°C of the polyolefin composition, and a hot solvent treatment step (4iii) following step (4ii) and

before step (5) wherein the stretched sheet is contacted with a hot solvent.

13. The method of claims 11 or 12, further comprising a heat-setting treatment step (5i) following step (5) wherein the membrane is heat-set at a temperature of the stretching temperature ±5°C, and a cross-linking step (5ii) following step (5i) wherein the heat-set membrane is cross-linked by ionizing radiation rays selected from one or more of α-rays, β-rays, γ-rays, and electron beams.

14. The method of any of claims 11-13, further comprising a hydrophilizing treatment step (7i) following step (7) wherein the heat-set microporous membrane is made more hydrophilic by one or more of a monomer-grafting treatment, a surfactant treatment, and a corona-discharging treatment and/or a surface-coating treatment step (8) following step (7) wherein the heat-set microporous membrane is coated with one or more of a porous polypropylene, a porous fluororesin, a porous polyimide, and a porous polyphenylene sulfide.

15. The method of any of claims 11-14, wherein (a) the first polyethylene is one or more of ethylene homopolymer or ethylene/α-olefin copolymer having an Mw in the range of from $4.5 \times 10^5$ to $6.5 \times 10^5$ and an MWD in the range of 2 to 10, (b) the first polypropylene is one or more of propylene homopolymer or propylene/α-olefin copolymer having an Mw in the range of from $0.9 \times 10^6$ to $2 \times 10^6$, an MWD in the range of 1.5 to 10, and a ΔHm in the range of $105 \leq \Delta Hm \leq 125$, and (c) the second polypropylene is one or more of propylene homopolymer or propylene/α-olefin copolymer having an Mw in the range of from $4 \times 10^5$ to $7.5 \times 10^5$, an MWD in the range of from 2 to 20, and a ΔHm in the range of $90 \leq \Delta Hm < 105$.

16. The method of any of claims 11-15, wherein the multi-layer microporous membrane comprises a first layer having a first thickness and a second layer having a second thickness, the ratio of the first thickness to the second thickness being in the range of from 10/90 to 75/25.

17. The method of any of claims 11-16, wherein the multi-layer microporous membrane comprises three or more layers, a first layer having a first thickness T1, a second layer having a second thickness T2, and a third layer produced from the first mixture and having a thickness T3, wherein the second layer is located between the first and third layers, and wherein $\frac{T1+T3}{T2}$ is in the range of $\frac{10}{90}$ to $\frac{75}{25}$.

18. The method of any of claim 17, wherein the first and third layers are surface layers of the membrane and wherein the second layer is in planar contact with the first and third layers.

19. The multi-layer microporous membrane produced by any of claims 11- 18.

20. The multi-layer microporous membrane of claim 19, wherein the membrane has a pin puncture strength ≥ 3500 mN, an electrolytic solution absorption speed ≥ 3.5, and an air permeability after heat compression ≤ 1000 seconds/cm$^3$.

# INTERNATIONAL SEARCH REPORT

International application No
PCT/JP2008/068911

A. CLASSIFICATION OF SUBJECT MATTER
INV. H01M2/16 H01M10/40

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)
H01M

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

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

EPO-Internal, IBM-TDB, FSTA, COMPENDEX, INSPEC, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
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| P,L,<br>X | WO 2008/026780 A (TONEN SEKIYUKAGAKU KK [JP]; OZAKI HIROYUKI [JP]; KIMISHIMA KOTARO [JP]) 6 March 2008 (2008-03-06)<br>pages 1,37,52,, column 118<br>claims 1-812<br>----- | 1,2,10,<br>19,20 |
| A | US 2007/221568 A1 (NAGASHIKI YUSUKE [JP] ET AL) 27 September 2007 (2007-09-27)<br>the whole document<br>-----<br>-/-- | 13,14 |

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

☒ See patent family annex.

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

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|---|---|
| Date of the actual completion of the international search<br>9 March 2009 | Date of mailing of the international search report<br>16/03/2009 |
| Name and mailing address of the ISA/<br>European Patent Office, P.B. 5818 Patentlaan 2<br>NL – 2280 HV Rijswijk<br>Tel. (+31-70) 340-2040,<br>Fax: (+31-70) 340-3016 | Authorized officer<br>Götz, Heide |

## INTERNATIONAL SEARCH REPORT

International application No
PCT/JP2008/068911

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
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