Patent Document 2 discloses a nonaqueous electrolyte secondary battery separator obtained by laminating a porous layer comprising 591 g of ion-exchanged water, 9 g of water-soluble polymer CMC, and 45 g of alumina fine particles on a porous polyethylene film. This separator has dimensional stability and load characteristics.

[0009]

Patent Document 3 discloses that a laminated film comprising a heat-resistant layer composed mainly of a porous polyolefin layer and filler, which is excellent in heat-shrinkable properties and shape retention can be obtained if the overall basis weight of the heat-resistant layer is at least 0.5 times the overall basis weight of the porous polyolefin layer.

[0010]

Further, Patent Document 4 discloses a polyolefin porous membrane comprising a polyethylene resin and having (a) a shutdown temperature of 135°C or lower, (b) a rate of air resistance change of 1×10^4 sec/100 cc/°C or more, and (c) a transverse shrinkage rate at 130°C of not more than 20%, and discloses that the polyolefin porous membrane has excellent shutdown properties.

Patent Document 1: JP 2013-46998 A

Patent Document 2: JP 2004-227972 A

Patent Document 3: JP 2012-226921 A

Patent Document 4: WO 2007/60991

Summary ~~of the Invention~~

Problems to be Solved by the Invention

[0011]

In the laminated microporous membranes disclosed in Patent Documents 1 to 3, it is difficult to maintain the properties of a substrate porous membrane because of infiltration of a water-soluble resin into pores of the membrane, and in particular, the

problem is deterioration of shutdown properties at low temperatures. Further, in Patent Document 1, it is intended to maintain the properties of the substrate even in the case where the modifying porous layer comprising a water-soluble resin and particles is laminated on a polyolefin porous membrane, but it is necessary, in applying a slurry, to adjust the contact angle between the slurry and the substrate porous membrane.

[0012]

On the other hand, the polyolefin microporous membrane disclosed in Patent Document 4 provides a limited improvement in heat resistance and physical strength, and, for example, one possible method is to laminate the modifying porous layer of Patent Documents 1 to 3 on the polyolefin porous membrane of Patent Document 4, but deterioration of shutdown properties cannot be avoided by simple lamination.

[0013]

In other words, hitherto there has been no laminated polyolefin microporous membrane that is satisfactory in heat resistance and physical strength while utilizing the shutdown properties of a polyolefin microporous membrane.

[0014]

An object of the present ~~invention~~ disclosure is to provide a battery separator comprising a laminated polyolefin microporous membrane composed of a polyolefin microporous membrane and a modifying porous layer having adhesion to the polyolefin microporous membrane, the polyolefin microporous membrane being provided with physical strength and heat resistance with shutdown properties not being significantly reduced, and a method of producing the battery separator.

Means for Solving the Problems

[0015]

To solve the problems described above, the battery separator of the present ~~invention~~ disclosure has the following constitution:

In a first aspect, there is provided ~~A~~a battery separator which is a laminated polyolefin microporous membrane, comprising a polyolefin microporous membrane, and a modifying porous layer comprising a water-soluble resin or water-dispersible resin, and fine particles, the modifying porous layer being laminated on at least one surface of the polyolefin microporous membrane, wherein the polyolefin microporous membrane comprises a polyethylene resin and has (a) a shutdown temperature (a temperature at which an air resistance measured while heating the polyolefin microporous membrane at a temperature rise rate of 5°C/min reaches 1×10^5 sec/100 cc) of 135°C or lower, (b) a rate of air resistance change (a gradient of a curve representing dependency of the air resistance on temperature at an air resistance of 1×10^4 sec/100 cc) of 1×10^4 sec/100 cc/°C or more, (c) a transverse shrinkage rate at 130°C (measured by thermomechanical analysis under a load of 2 gf at a temperature rise rate of 5°C/min) of 20% or less, and a thickness of 16 μm or less, the shutdown temperature difference between the polyolefin microporous membrane and the laminated polyolefin microporous membrane being 4.0°C or less.

[0016]

In the battery separator of the present ~~invention~~disclosure, the water-soluble resin or water-dispersible resin preferably comprises at least one of carboxymethylcellulose and an acrylic resin.

[0017]

In the battery separator of the present ~~invention~~disclosure, the fine particles are preferably at least one selected from titanium dioxide, alumina, and boehmite.

[0018]

In the battery separator of the present ~~invention~~disclosure, the polyethylene resin preferably has a $\Delta Hm_{\leq 125°C}$, a cumulative endotherm up to 125°C relative to a heat of crystal melting measured by differential scanning calorimetry at a temperature rise

rate of 10°C/min, of not more than 20% and a $T_{50\%}$, a temperature at the time when the endotherm reaches 50% of the heat of crystal melting, of 135°C or lower.

[0019]

In the battery separator of the present ~~invention~~disclosure, the polyethylene resin preferably comprises a copolymer of ethylene and any other α-olefin.

[0020]

In the battery separator of the present disclosure~~invention~~, preferably, the polyethylene resin comprises a copolymer of ethylene and any other α-olefin, and the copolymer is produced using a single-site catalyst and has a mass average molecular weight of not less than 1×10^4 but less than 7×10^6.

[0021]

To solve the problems described above, the method of producing the battery separator of the present ~~invention~~ disclosure has the following constitution in a second aspect:

A method of producing the battery separator according to any one of the above, comprising the steps of:

(a) preparing a polyolefin resin solution by melt-kneading a polyolefin resin comprising a polyethylene resin with a membrane-forming solvent in a twin-screw extruder such that the ratio of a feed rate Q (kg/h) of the polyolefin resin to a screw speed Ns (rpm) (Q/Ns) is 0.1 to 0.55 Kg/h/rpm, the polyethylene resin having ~~a $\Delta Hm_{\leq 125°C}$,~~ a cumulative endotherm up to 125°C relative to a heat of crystal melting measured by differential scanning calorimetry at a temperature rise rate of 10°C/min, of not more than 20% and ~~a $T_{50\%}$,~~ a temperature at the time when the endotherm reaches 50% of the heat of crystal melting, of 135°C or lower;

(b) forming a gel-like sheet by extruding the polyolefin resin solution through a die and cooling the extrudate;

(c) stretching the gel-like sheet at a rate of 1 to 80%/sec relative to 100% of the length before stretching;

(d) removing the membrane-forming solvent to obtain a polyolefin microporous membrane; and

(e) applying a coating solution comprising a water-soluble resin or water-dispersible resin, and fine particles to at least one surface of the polyolefin microporous membrane obtained above, followed by drying, wherein the volume ratio of the water-soluble resin or water-dispersible resin to the fine particles is 2 to 8% and the concentration of the water-soluble resin or water-dispersible resin is 0.8 to 5%.

Effects of the Invention

[0022]

The present ~~invention~~ disclosure provides a laminated polyolefin microporous membrane having excellent shutdown properties, physical strength, and heat resistance as well as adhesion between a polyolefin microporous membrane and a modifying porous layer. "Modifying porous layer" as used herein refers to a layer comprising a resin that provides or improves at least one properties such as heat resistance, adhesion to electrode material, and electrolyte permeability.

Brief Description of the Drawings

[0023]

FIG. 1 shows a typical example of a melting endotherm curve;

FIG. 2 shows the same melting endotherm curve as in FIG. 1 showing a total endotherm at 125°C;

FIG. 3 shows the same melting endotherm curve as in FIG. 1 showing a $T_{50\%}$, a temperature at the time when the endotherm reaches 50% of a heat of crystal melting;

FIG. 4 shows a typical example of a temperature T/(air resistance p)$^{-1}$ curve for determining a shutdown start temperature; and

FIG. 5 shows a typical example of a temperature T/air resistance p curve for

CLAIMS

1. A battery separator which is a laminated polyolefin microporous membrane, comprising:

a polyolefin microporous membrane; and

a modifying porous layer comprising a water-soluble resin or water-dispersible resin, and fine particles, the modifying porous layer being laminated on at least one surface of the polyolefin microporous membrane, wherein the polyolefin microporous membrane comprises a polyethylene resin and has (a) a shutdown temperature (a temperature at which an air resistance measured while heating the polyolefin microporous membrane at a temperature rise rate of 5°C/min reaches 1×10^5 sec/100 cc) of 135°C or lower, (b) a rate of air resistance change (a gradient of a curve representing dependency of the air resistance on temperature at an air resistance of 1×10^4 sec/100 cc) of 1×10^4 sec/100 cc/°C or more, (c) a transverse shrinkage rate at 130°C (measured by thermomechanical analysis under a load of 2 gf at a temperature rise rate of 5°C/min) of 20% or less, and a thickness of 16 μm or less, the shutdown temperature difference between the polyolefin microporous membrane and the laminated polyolefin microporous membrane being 4.0°C or less.

2. The battery separator according to claim 1, wherein the water-soluble resin or water-dispersible resin comprises at least one of carboxymethylcellulose (CMC) and an acrylic resin.

3. The battery separator according to claim 1 or 2, wherein the fine particles are at least one selected from titanium dioxide, alumina, and boehmite.

4. The battery separator according to any one of claims 1 to 3, wherein the polyethylene resin has ~~a $\Delta Hm_{\leq 125°C}$~~ a cumulative endotherm up to 125°C relative to a heat of crystal melting measured by differential scanning calorimetry at a temperature rise rate of 10°C/min, of not more than 20% and ~~a $T_{50\%}$~~ a temperature at

the time when the endotherm reaches 50% of the heat of crystal melting, of 135°C or lower.

5. The battery separator according to any one of claims 1 to 4, wherein the polyethylene resin comprises a copolymer of ethylene and any other α-olefin.

6. The battery separator according to any one of claims 1 to 5, wherein the polyethylene resin comprises a copolymer of ethylene and any other α-olefin, and the copolymer is produced using a single-site catalyst and has a mass average molecular weight of not less than 1×10^4 but less than 7×10^6.

7. A method of producing the battery separator according to any one of claims 1 to 6, comprising the steps of:

(a) preparing a polyolefin resin solution by melt-kneading a polyolefin resin comprising a polyethylene resin with a membrane-forming solvent in a twin-screw extruder such that the ratio of a feed rate Q (kg/h) of the polyolefin resin to a screw speed Ns (rpm) (Q/Ns) is 0.1 to 0.55 Kg/h/rpm, the polyethylene resin having ~~a~~ $\Delta Hm_{\leq 125°C}$, ~~a~~ a cumulative endotherm up to 125°C relative to a heat of crystal melting measured by differential scanning calorimetry at a temperature rise rate of 10°C/min, of not more than 20% and ~~a~~ $T_{50\%}$, ~~a~~ a temperature at the time when the endotherm reaches 50% of the heat of crystal melting, of 135°C or lower;

(b) forming a gel-like sheet by extruding the polyolefin resin solution through a die and cooling the extrudate;

(c) stretching the gel-like sheet at a rate of 1 to 80%/sec relative to 100% of the length before stretching;

(d) removing the membrane-forming solvent to obtain a polyolefin microporous membrane; and

(e) applying a coating solution comprising a water-soluble resin or water-dispersible resin, and fine particles to at least one surface of the polyolefin microporous membrane obtained above, followed by drying, wherein the volume