

ABSORBENT ARTICLES

TECHNICAL FIELD

This invention relates to an absorbent article. More particularly, it relates to an absorbent article comprising a porous sheet which exhibits excellent tensile strength and high molding productivity as well as excellent moisture permeability and resistance to water pressure.

BACKGROUND ART

Porous sheets for absorbent articles have conventionally been produced by a process comprising molding a molten mixture of a polyolefin, such as polyethylene or polypropylene, and 40% by weight or more of an inorganic filler into a sheet and monoaxially or biaxially stretching the resulting sheet.

Porous sheets obtained by the above process are excellent in air- and moisture-permeability and cause no moisture condensation and are therefore useful as wall paper and wrapping paper. Addition of softness to these excellent properties makes the porous sheet suitable for use as an element of absorbent articles such as a back sheet of disposable diapers. In order to obtain soft porous sheets, it has been proposed to use linear low-density polyethylene as a polyolefin.

However, the conventional porous sheet has the following disadvantages for use as an element of absorbent articles such as disposal diapers.

For example, commonly employed disposal diapers are fabricated from an absorbent member for absorbing excreta such as urine, a topsheet which covers the surface of the absorbent member and is directly applied to the skin, and a back sheet which covers the back side of the absorbent member and prevents leakage, these three parts being adhered together into a unitary body. The top and bottom ends and side edges of the diaper corresponding to the waist portion and a crotch portion are made stretchable for tight-fit to prevent leakage. The disposable diapers also have a fastening means such as tapes, with which the diaper is fitted to a wearer's body in use. The above-mentioned porous sheet is used as the back sheet.

The above-mentioned tapes provided for fastening (so-called fastening tapes) mostly have a width of about 25 to 35 mm for convenience of handling. However, when the fastening tape is unfastened to adjust the position of the diaper for a better fit or to see if urine has been discharged or not, the tape cannot be peeled without tearing the soft back sheet due to lack of strength. This being the case, the diaper must be

changed with a new one. In order to avoid this, it has been proposed to provide wide tapes having a release surface (so-called landing tapes or target tapes) on the front side back sheet, on which fastening tapes may be removably adhered.

However, many problems are posed by the use of landing tapes. That is, the kinds of diaper constituting members and processes of production of diapers increase. A landing tape is more costly than any other diaper constituting members, so that use of the landing tape with a sufficient width increases the cost. In addition, even with a wide landing tape, cases are sometimes met with depending on the body size of a wearer, in which a fastening tape is adhered to the back sheet outside the landing tape area and cannot be stripped off.

Japanese Patent Application Laid-open 5-98057 discloses a high strength porous sheet obtained by blow molding a composition comprising a specific polyolefin, a filler, a specific plasticizer and a radical generator, and monoaxially stretching the blown film in the machine direction.

Although the sheet disclosed has nearly twice as much strength as a porous sheet obtained by a conventional process (a molten mixture of a polyolefin and

an inorganic filler is molded into a sheet followed by stretching), such a degree of improvement is still insufficient for eliminating the necessity of landing tapes. In addition, since the use of the radical generator makes melt flow properties of the molded resin composition different from those of the composition before molding, it is difficult to recycle inevitably produced in the course of the production, resulting in reduced productivity.

Further, Japanese Patent Application Laid-open 5-38011 (corresponding to USP 4,539,256) discloses a microporous sheet obtained by a process comprising melt-blending a specific crystallizable polymer and a specific compound miscible with that polymer, molding the mixture into a sheet, causing phase separation to occur during a cooling step, and stretching the resulting sheeting.

Although the microporous sheet disclosed has two or three times as high strength as a sheet obtained by the conventional process (a molten mixture of a polyolefin and an inorganic filler is molded into a sheet followed by stretching), the strength still does not reach a sufficient level for making landing tapes needless. According to the present inventors' study, a porous sheet withstanding removal of a fastening tape

This Sheet Has Been Replaced



THIS SHEET HAS BEEN
REPLACED

therefrom is required to have at least 4 times, preferably 5 times, as high strength as a porous sheet obtained by the conventional process.

Besides, compared with the above-described conventional process for producing a porous sheet, the process for producing a microporous sheet as disclosed in the above patent involves problems that scattering of the compound miscible with the crystallizable polymer causes pollution of the working environment, and that wear of a screw and scorching of the polymer are likely to occur, so that the molding should be suspended occasionally for the molding machine to be taken apart and cleaned, resulting in poor industrial productivity.

DISCLOSURE OF THE INVENTION

An object of the present invention is to provide an absorbent article such as a disposable diaper comprising a porous sheet as a back sheet, in which the porous sheet exhibits markedly excellent tensile strength as well as moisture permeability and resistance to water pressure and can be produced at high productivity so that the diaper is inexpensive and easy to use. That is, the diaper can be fastened by adhering a fastening tape to any position of the back sheet regardless of the body size of a wearer with no need of

providing a landing tape.

As a result of extensive investigations, the present inventors have found that the above object is accomplished by using a porous sheet made of specific polypropylene as a back sheet of an absorbent article. The present invention has been reached based on this finding.

The present invention provides an absorbent article comprising a liquid permeable topsheet, a liquid impermeable back sheet and an absorbent member interposed between said topsheet and said back sheet, said absorbent article being characterized in that:

said back sheet comprises a porous sheet obtainable by preparing, by melt blending, a melt blended solution comprising 30 to 90 parts by weight of a crystalline polyolefin and 10 to 70 parts by weight of a compound with which said crystalline polyolefin is miscible and in which said crystalline polyolefin will dissolve at or above the melting point of said crystalline polyolefin but which will phase separate below the melting point of said crystalline polyolefin, molding said melt blended solution into a sheet, and stretching said sheet at least in one direction; and

said crystalline polyolefin is a polypropylene having a weight average molecular weight (Mw) to number

average molecular weight (Mn) ratio (Mw/Mn) of more than 6.0.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a perspective view of a disposable diaper as one embodiment of the absorbent article of the present invention.

Fig. 2 is a perspective view of the disposable diaper shown in Fig. 1 in an unfolded condition and having a part thereof cut away.

DETAILED DESCRIPTION OF THE INVENTION

The absorbent article according to the present invention will be described below in detail.

The absorbent article of the present invention is characterized by having the above-described porous sheet as a back sheet.

The crystalline polyolefin which is used in the porous sheet is polypropylene having a weight average molecular weight (Mw) to number average molecular weight (Mn) ratio (Mw/Mn) of more than 6.0, preferably more than 6.3.

An Mw/Mn ratio is a measure of molecular weight distribution. As long as the Mw/Mn ratio of the polypropylene is more than 6.0, when the polypropylene is melt-blended with, for example, not less than 20% by weight of the above-mentioned compound such as mineral

oil, the mineral oil rapidly dissolves in the polypropylene so that they can be mixed in a stable manner.

If it is 6.0 or smaller, which means a narrow molecular weight distribution of the polypropylene, the polypropylene exhibits instable dissolving properties with respect to the aforesaid compound such as mineral oil. This being the case, it is difficult to mix the polypropylene and the mineral oil at a prescribed mixing ratio. Additionally, in using a twin-screw extruder, a vent-up phenomenon occurs, and mixing cannot be effected smoothly, failing to perform extrusion stably.

The polypropylene having the above-specified molecular weight distribution can easily be obtained by polymerizing propylene in multiple stages in the presence of a prescribed catalyst. In more detail, an organoaluminum compound or a reaction product of an organoaluminum compound and ethyl ether is reacted with titanium tetrachloride to obtain a solid reaction product, which is further reacted with ethyl ether and titanium tetrachloride to obtain a solid reaction product. The resulting solid reaction product is combined with an organoaluminum compound and an aromatic carboxylic acid ester (a) to prepare a catalyst system having an aromatic carboxylic acid ester (a) to

solid reaction product (b) molar ratio (a/b) of 0.1 to 10.0. The above-described polypropylene can easily be obtained by a multi-stage polymerization process in the presence of the thus prepared catalyst system in such a manner, for example, that 35 to 65% by weight of the total polymer is produced in the first stage and the balance, 35 to 65% by weight, is produced in the second and following stages.

The polypropylene preferably has a weight average molecular weight between 300,000 and 600,000 and a melting point between 155°C and 170°C.

The polypropylene may be any of a homopolymer, a block copolymer or a random copolymer, or a mixture of two or more thereof. As long as the effects of the present invention are not impaired, the polypropylene may be used in combination with other polymers such as polyethylene.

Beside to the above-mentioned Mw/Mn ratio, it is preferable that the polypropylene satisfies the relationship: $1.00 \geq P \geq 0.015 \log MI + 0.955$, wherein P is an isotactic pendant content; and MI is a melt index.

The isotactic pendant content (P) is indicative of crystallinity of polypropylene.

With P and MI satisfying the relationship

$1.00 \geq P \geq 0.015 \log MI + 0.955$, the polypropylene exhibits high crystallinity and improved rigidity. If P is less than $0.015 \log MI + 0.955$, the polypropylene has reduced rigidity so that the porous sheet may have to have a large thickness for assuring rigidity necessary as a back sheet, which leads to an increase of cost.

The MI of the polypropylene preferably ranges from 0.03 to 2.0 g/10 min.

If the MI is less than 0.03, the molten polymer needs increased power in granulation or molding because of its poor fluidity, which is not only uneconomical but hinders speeding up of production. If it exceeds 2.0, the molten resin has reduced tension. It follows that, for example, a tubular film of the polypropylene is hard to lift in blown film extrusion, and sheeting becomes instable.

The polypropylene satisfying the above relationship can be prepared by, for example, the process disclosed in Japanese Patent Publication 64-5051, p. 7, col. 13, l. 44 to p. 8, col. 15, l. 9.

The compound which is used in the porous sheet is a compound with which said crystalline polyolefin is miscible and in which said crystalline polyolefin will dissolve at or above the melting point of said crystal-



line polyolefin but which will phase separate below the melting point of said crystalline polyolefin.

The compound is not particularly limited as long as it possesses the above-mentioned characteristics. Suitable examples include mineral oils such as liquid paraffin, synthetic lubricating oils, dioctyl phthalate, diethyl phthalate, triethylene glycol, dibutyl phthalate, and esters of phthalic acid, trimellitic acid, pyromellitic acid and/or an aliphatic polybasic carboxylic acid and an alkyl alcohol.

The porous sheet to be used in the present invention is a porous sheet obtainable by preparing, by melt blending, a melt blended solution comprising 30 to 90 parts by weight, preferably 60 to 80 parts by weight, of a crystalline polyolefin and 10 to 70 parts by weight, preferably 20 to 40 parts by weight, of the compound, molding the melt blended solution into a sheet, and stretching the sheet at least in one direction.

If the proportion of the crystalline polyolefin is less than 30 parts by weight, the stretched sheet obtained has poor fabricability due to shortage of the matrix resin and, when rolled, undergoes collapse of fine pores or bleeding of the compound, such as mineral oil. If it exceeds 90 parts by weight, fine pores

affording moisture permeability cannot be formed by stretching.

The temperature suitable for melt blending is at or above the melting point of the crystalline polyolefin, preferably ranging from 180 to 250 °C. Melt blending for preparing a melt blended solution can be carried out in a twin-screw extruder. Polypropylene pellets are fed into a hopper in an constant amount, while the compound is fed into the vent of the twin-screw extruder.

In carrying out sheeting, the melt blended solution is preferably once cooled to prepare pellets of the blend. The pellets are blow molded by extrusion through a circular die of a single-screw extruder, or the pellets is blow molded by extrusion through a circular die connected to the tip of a twin-screw extruder via a gear pump.

In the sheeting, the following additives may be added to the melt blended solution in the amounts described below, all based on the total melt blended solution, if desired.

a) 0.5% by weight or less of a nucleating agent which controls the crystal size of polypropylene, such as aluminum p-tert-butylbenzoate, 1,2,3,4-dibenzylidene sorbitol or 1,2,3,4-di-(p-ethylbenzylidene)

sorbitol;

b) 1% by weight or less of an inorganic filler for tear prevention, such as anhydrous silica or zeolite;

c) 20% by weight or less of an opacifying inorganic filler, such as titanium oxide, barium sulfate, calcium carbonate or talc; and

d) 0.05% by weight or less of a colorant, such as Phthalocyanine Blue, Quinacridone Red, Dioxane Violet or Isoindolinone.

In using the nucleating agent, it is preferably added as a nucleating agent masterbatch. The nucleating agent masterbatch is a pelletized mixture prepared by mixing a nucleating agent and a resin, such as polypropylene or polyethylene, with a solvent.

Stretching of the sheet is preferably conducted at a stretching temperature of 10 to 80°C to a stretching ratio of 1.2 to 3 either monoaxially or biaxially.

The micro pores formed on stretching preferably have a pore size of 0.05 to 1 μm . The porous sheet preferably has a density of 0.7 to 0.85 g/cm^3 , a basis weight of 10 to 60 g/m^2 , and a thickness of 20 to 70 μm .

The method for obtaining the porous sheet of the present invention will be illustrated by way of a

specific example, molding method (1).

Molding Method (1):

The melt blended solution comprising polypropylene and the compound at a prescribed ratio and, if desired, various additives is extruded by a twin-screw extruder (diameter: 45 mm; L/D: 33.5) at 230 °C into strands, cooled in a water bath, and pelletized by a pelletizer to prepare compounded pellets. The polypropylene is fed into a hopper, while the compound is fed into the middle part of the extruder by means of a diaphragm pump.

The compounded pellets are fed into an air cooling type blown-film extrusion machine, extruded from a circular die having a diameter of 200 mm at 210 °C, and cooled by air at 20 °C blown from an air ring while being taken up at a take-up speed of 6 m/min to obtain a blown tube having a blow-up ratio of 2, a flat width of about 630 mm, and a thickness of about 50 μ m. When a nucleating agent is added, a nucleating agent masterbatch and polypropylene are previously dry blended at a prescribed ratio and fed into the blown-film extrusion machine.

The resulting sheet is monoaxially stretched in the machine direction at 50 °C at a stretching ratio of 1.5 by means of a roller stretcher and subjected to

annealing at 120 °C to obtain a porous sheet. The resulting porous sheet has a thickness of about 40 μm .

The thus obtained porous sheet preferably has a moisture permeability of 0.5 to 4.0 g/100 $\text{cm}^2 \cdot \text{hr}$. The porous sheet preferably has a yield strength (the stress at the yield point in the stress-strain curve in a tensile measurement) of 90 to 180 kgf/ cm^2 provided that the yield strength is measured in the direction (MD or CD) which exhibits lower yield strength.

The absorbent article according to the present invention will now be illustrated in greater detail by referring to Figs. 1 and 2.

Fig. 1 is a perspective view of a disposable diaper as one embodiment of the absorbent article of the present invention. Fig. 2 is a perspective view of the disposable diaper shown in Fig. 1 in an unfolded condition and having a part thereof cut away.

The disposable diaper shown in Figs. 1 and 2 comprises a liquid permeable topsheet 2, liquid impermeable back sheet 3 and an absorbent member 4 interposed between the topsheet 2 and the back sheet 3, in which back sheet 3 comprises the above-mentioned porous sheet.

In more detail, as shown in Figs. 1 and 2, rear waist area 5', front waist area 5, crotch area 9, and

side flaps 8 of the disposable diaper are fabricated from topsheet 2, back sheet 3, and absorbent member 4, each having an hourglass shape.

Elastic members 7 are provided between topsheet 2 and back sheet 3 in front waist area 5, rear waist area 5', and side flaps 8, respectively. A pair of tape fasteners 10 are provided on both edges of rear waist area 5', thereby enhancing the function and performance of the diaper.

As shown in Fig. 2, the disposable diaper is constituted such that it has longitudinal sides and that the topsheet 2 is almost the same as the back sheet in width and length.

The topsheet 2 is usually fabricated from nonwoven fabric having a basis weight of, for example, 15 to 40 g/m². As far as liquid permeable, a film, a net or the like may be used as the topsheet 2. The topsheet 2 with a hydrophilic central area and water-repellent peripheral area is particularly preferred.

The absorbent member 4 preferably comprises fluff (comminuted kraft pulp) covered with water-absorbing paper, preferably one containing superabsorbent polymer particles. The fluff usually weighs about 10 to 40 g. The superabsorbent polymer may be located in any of the upper, medium and lower layers of the

absorbent member or be mixed with pulp. Examples of suitable superabsorbent polymers include starch types, cellulose types and synthetic polymer types, such as a starch-acrylic acid (or a salt thereof) graft copolymer, a saponified starch-acrylonitrile copolymer, cross-linked sodium carboxymethyl cellulose, and an acrylic acid (or a salt thereof) polymer. Such a superabsorbent polymer is capable of absorbing and retaining 20 times as much liquid as its own weight and gels on liquid absorption.

The elastic member 7 preferably comprises at least 1 and more preferably up to about 5 strings or ribbons of polyurethane, natural rubber, etc. or strings which become elastic on being wetted with water. The elastic member 7 has a length of about 30 to about 60% of that of a diaper and is preferably extensible about 1.3 to 2.0 times the original length.

While the absorbent article of the present invention has been explained by referring to flat type disposable diapers, the present invention is not limited thereto and is applicable to other articles, such as sanitary napkins, pads for incontinence, panty diapers, and the like.

The present invention will be described in greater detail with reference to Examples, but it

should be understood that the present invention is not deemed to be limited thereto.

EXAMPLES 1 and 2

A porous sheet was obtained by the above-described molding method (1) using 70 parts by weight of the polypropylene shown in Table 1, 25 parts by weight of the compound shown in Table 2, and 5 parts by weight of a nucleating agent masterbatch [nucleating agent ("EC-1", a trade name produced by EC Kagaku K.K.; 2 wt%)]].

A disposable diaper shown in Figs. 1 and 2 was fabricated using the resulting porous sheet as a back sheet.

EXAMPLE 3

A porous sheet was obtained by the above-described molding method (1) using 65 parts by weight of the polypropylene shown in Table 1 and 35 parts by weight of the compound shown in Table 2.

A disposable diaper shown in Figs. 1 and 2 was fabricated using the resulting porous sheet as a back sheet.

EXAMPLES 4 TO 8

A porous sheet was obtained by the above-described molding method (1) using 70 parts by weight of the polypropylene shown in Table 1 and 30 parts by

weight of the compound shown in Table 2.

A disposable diaper shown in Figs. 1 and 2 was fabricated using the resulting porous sheet as a back sheet.

COMPARATIVE EXAMPLES 1 AND 2

A porous sheet was obtained by the above-described molding method (1) using 65 parts by weight of the polypropylene shown in Table 1, 30 parts by weight of the compound shown in Table 2, and 5 parts by weight of the same nucleating agent masterbatch as used in Example 1.

A disposable diaper shown in Figs. 1 and 2 was fabricated using the resulting porous sheet as a back sheet.

The polypropylene used in Examples 1 to 8 and Comparative Examples 1 and 2 were tested in terms of items (1) to (3) described below, and the porous sheets obtained in these examples were tested in terms of items (4) to (9) described below. The results of tests (1) to (3) are shown in Table 1, and those of tests (4) to (9) are shown in Table 3.

(1) Melt Index (MI): Measured according to ASTM D-1238 under a load of 2.16 kg.

(2) Isotactic Pendant Content (P): An isotactic content in the polypropylene molecular chain in terms

of pendant content unit was obtained by ^{13}C -NMR in accordance with *Macromolecules*, 8, 687 (1975).

(3) Mw/Mn: Determined from a weight average molecular weight (Mw) and a number average molecular weight (Mn) as measured by GPC (140 °C, in o-dichlorobenzene solution).

(4) Moisture Permeability: Measured in accordance with JIS Z0208.

(5) Resistance to Water Pressure: Measured in accordance with JIS L1093B.

(6) Yield Strength: A yield strength of a 10 mm wide strip slit out of the sheet in the direction perpendicular to the stretching direction was measured with a Tensilon tensile tester at a pulling speed of 300 mm/min and a distance of 50 mm between chucks.

(7) Tear Strength: A 30 mm wide and 60 mm long test piece was cut out of the sheet in such a manner that the longitudinal sides of the piece were parallel to the stretching direction of the sheet, and a cut was made with a blade from the center of one shorter side by 30 mm along the longitudinal center line. Each of the two divided ends of the shorter side was fixed to each chuck to make the test piece a T-shape and torn apart along the stretching direction at a pulling speed of 300 mm/min. An average load obtained from the

measurement chart was taken as a tear strength.

(8) Stability of Extrusion: The polypropylene and the compound was kneaded by feeding the compound into an open barrel in the middle of a twin-screw extruder. The stability of blending was evaluated according to the following standard.

E ... Extrusion can be conducted in a stable manner free from vent-up of the extrudate, pulsation of the motor load or pulsation of the extrusion output.

F ... Extrusion is possible while being accompanied by vent-up of the extrudate, pulsation of the motor load or pulsation of the extrusion output.

P ... Extrusion is impossible due to noticeable vent-up of the extrudate, pulsation of the motor load or pulsation of the extrusion output.

(9) Strippability of Tape: A fastening tape was adhered to the porous sheet (back sheet) of the disposable diaper obtained in Examples and Comparative Examples and then stripped off to evaluate the strippability according to the following standard.

The fastening tape used comprises a 80 μ m thick polyethylene sheet having coated thereon Panel

Master AM936 produced by Kanebo NSC Co., Ltd. by means of a bar coater and allowed to stand at room temperature for 24 hours to have a 30 μm thick adhesive layer and an adhesive area of 30 x 25 mm^2 .

E ... The fastening tape is strippable satisfactorily without causing a break or extension of the back sheet.

F ... Stripping causes a slight tear of the back sheet.

P ... Stripping causes a break of the back sheet.

TABLE 1

	Polyolefin		MI (g/10 min)	P	Mw/Mn
	Manufacturer	Trade Name			
Example 1	Chisso Sekiyu Kagaku K. K.	WT6061	0.5	0.94	6.5
Example 2	Chisso Sekiyu Kagaku K. K.	WT6048	0.6	0.97	7.5
Examples 3 to 8	Chisso Sekiyu Kagaku K. K.	XF1932	0.4	0.97	6.5
Comparative Example 1	Showa Denko K. K.	PA122	2.4	0.94	4.0
Comparative Example 2	Idemitsu Petrochemical Co., Ltd.	P400S	3.2	0.95	4.5

TABLE 2

	Compound	Manufacturer	Trade Name
Examples 1 to 3, Comparative Examples 1 and 2	Liquid Paraffin	Idemitsu Petrochemical Co., Ltd.	PW90
Example 4	Synthetic Lubricating Oil	Idemitsu Petrochemical Co., Ltd.	HC600
Example 5	Diethyl Phthalate	Kao Corp.	Vinysizer #80
Example 6	Diethyl Phthalate	—	—
Example 7	Triethylene Glycol	—	—
Example 8	Dibutyl Phthalate	—	—

TABLE 3

Results of Evaluation

	Moisture Permeability (g/100cm ² · hr)	Resistance to Water Pressure (mEq)	Yield Strength (Kgf/cm ²)	Tear Strength (gf)	Stability of Extrusion	Tape Strippability
Example 1	2.1	>2.0	104	21	E	E
Example 2	1.9	>2.0	147	23	E	E
Example 3	2.5	>2.0	107	16	E	F
Example 4	2.2	>2.0	130	17	E	E
Example 5	2.3	>2.0	128	19	E	E
Example 6	1.9	>2.0	128	18	E	E
Example 7	1.9	>2.0	125	19	E	E
Example 8	2.0	>2.0	129	17	E	E
Compara. Example 1	1.9	>2.0	82	13	F	P
Compara. Example 2	2.1	>2.0	79	11	F	P

INDUSTRIAL APPLICABILITY

The absorbent article according to the present invention comprises, as a back sheet, a porous sheet excellent in tensile strength, molding productivity as well as moisture permeability and water pressure resistance. Therefore, there is no need of providing a landing tape, and the absorbent article is inexpensive and is easy to use in that a fastening tape may be adhered to any position of the back sheet regardless of the body size of a wearer.

Many other variations and modifications of the invention will be apparent to those skilled in the art without departing from the spirit and scope of the invention. The above-described embodiments are, therefore, intended to be merely exemplary, and all such variations and modifications are intended to be included within the scope of the invention as defined in the appended claims.



CLAIMS

1. An absorbent article comprising a liquid permeable topsheet, a liquid impermeable back sheet and an absorbent member interposed between said topsheet and said back sheet, said absorbent article being characterized in that:

said back sheet comprises a porous sheet obtainable by preparing, by melt blending, a melt blended solution comprising 30 to 90 parts by weight of a crystalline polyolefin and 10 to 70 parts by weight of a compound with which said crystalline polyolefin is miscible and in which said crystalline polyolefin will dissolve at or above the melting point of said crystalline polyolefin but which will phase separate below the melting point of said crystalline polyolefin, molding said melt blended solution into a sheet, and stretching said sheet at least in one direction; and

said crystalline polyolefin is a polypropylene having a weight average molecular weight (Mw) to number average molecular weight (Mn) ratio (Mw/Mn) of more than 6.0.

2. The absorbent article as claimed in claim 1,

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herein said polypropylene has an isotactic pendant content (P) and a melt index (MI) satisfying the relationship:

$$1.00 \geq P \geq 0.015 \log MI + 0.955$$

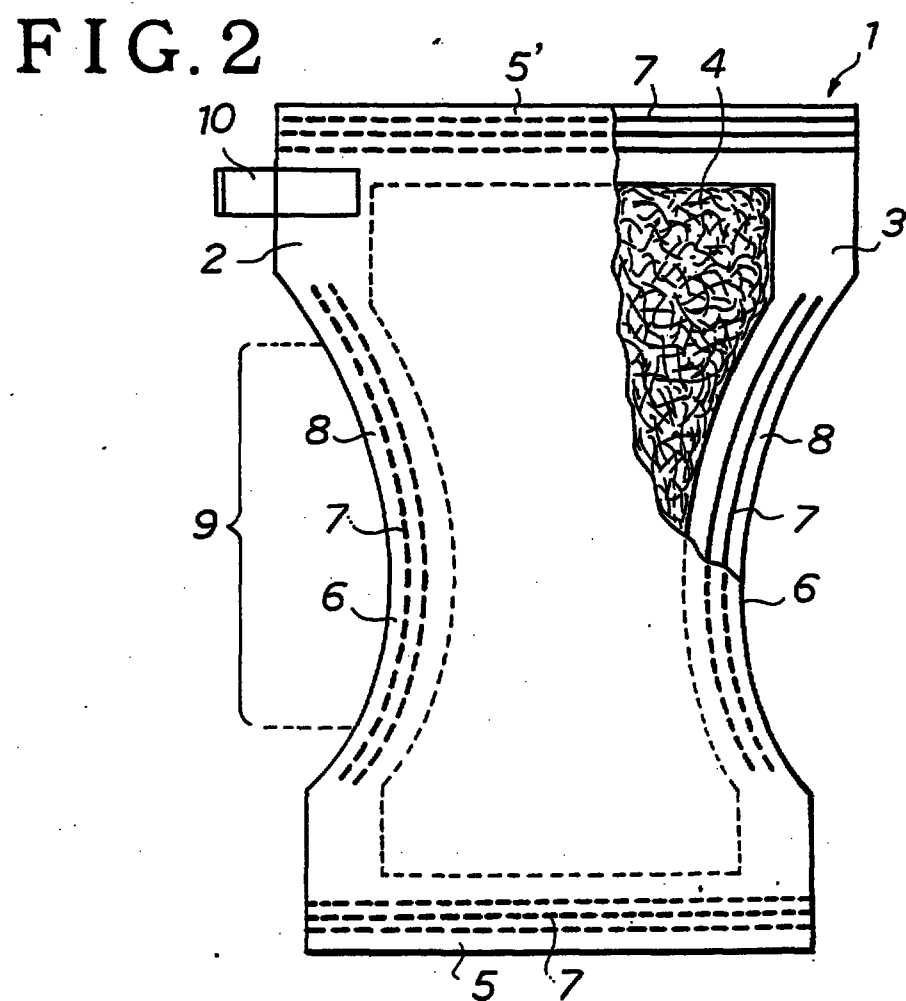
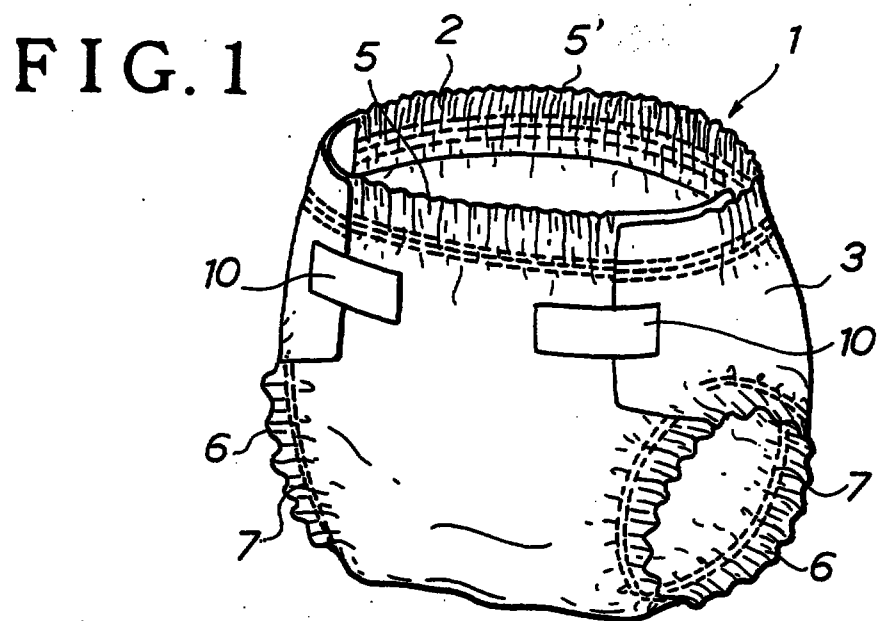
3. The absorbent article as claimed in claim 1, wherein said compound is at least one compound selected from the group consisting of a mineral oil, a synthetic lubricating oil, dioctyl phthalate, diethyl phthalate, triethylene glycol, dibutyl phthalate, and an ester of phthalic acid, trimellitic acid, pyromellitic acid and/or an aliphatic polybasic carboxylic acid and an alkyl alcohol.

4. The absorbent article as claimed in claim 1, wherein said porous sheet had a moisture permeability of 0.5 to 4.0 g/100 cm²·hr.



This Sheet Has Been Replaced





an inorganic filler is molded into a sheet followed by stretching), such a degree of improvement is still insufficient for eliminating the necessity of landing tapes. In addition, since the use of the radical generator makes melt flow properties of the molded resin composition different from those of the composition before molding, it is difficult to recycle inevitably produced discarded pieces in the course of the production, resulting in reduced productivity.

Further, Japanese Patent Application Laid-open 5-38011 (corresponding to USP 4,539,256) discloses a microporous sheet obtained by a process comprising melt-blending a specific crystallizable polymer and a specific compound miscible with that polymer, molding the mixture into a sheet, causing phase separation to occur during a cooling step, and stretching the resulting sheet.

Although the microporous sheet disclosed has two or three times as high strength as a sheet obtained by the conventional process (a molten mixture of a polyolefin and an inorganic filler is molded into a sheet followed by stretching), the strength still does not reach a sufficient level for making landing tapes needless. According to the present inventors' study, a porous sheet withstanding removal of a fastening tape

This is the replacement sheet

Date: 05 SEP 1996

$1.00 \geq P \geq 0.015 \log MI + 0.955$, the polypropylene exhibits high crystallinity and improved rigidity. If P is less than $0.015 \log MI + 0.955$, the polypropylene has reduced rigidity so that the porous sheet may have to have a large thickness for assuring rigidity necessary as a back sheet, which leads to an increase of cost.

The MI of the polypropylene preferably ranges from 0.03 to 2.0 g/10 min.

If the MI is less than 0.03, the molten polymer needs increased power in granulation or molding because of its poor fluidity, which is not only uneconomical but hinders speeding up of production. If it exceeds 2.0, the molten resin has reduced tension. It follows that, for example, a tubular film of the polypropylene is hard to lift in blown film extrusion, and sheeting becomes instable.

The polypropylene satisfying the above relationship can be prepared by, for example, the process disclosed in Japanese Patent Publication 64-5051, p. 7, col. 13, 1.44 to p. 8, col. 15, 1.9.

The compound which is used in the porous sheet is a compound with which said crystalline polyolefin is miscible and in which said crystalline polyolefin will dissolve at above the melting point of said crystal-

DescriptionMicroporous Sheet Material, Method of Making
and Articles Made TherewithTechnical Field

5 The invention relates to microporous sheet material, methods of making the same, and articles made therewith.

Background Art

10 Microporous films or membranes have a structure that enables fluids to flow through them. The effective pore size is at least several times the mean free path of the flowing molecules, namely from several micrometers down to about 100 Angstroms. Such sheets are generally opaque, even when made of a transparent material, because the surfaces and the internal structure scatter visible light.

15 Microporous membranes or films have been utilized in a wide variety of applications such as for the filtration of solids, the ultra filtration of colloidal matter, as diffusion barriers or separators in electrochemical cells, or in the preparation of synthetic leather, and in cloth
20 laminates. The latter utilities require, of course, permeability to water vapor for the applications as
25 synthetic shoes, raincoats, outer wear, camping equipment such as tents, and the like. Microporous films or
 membranes are often utilized for filter cleaning
 antibiotics, beer, oils, bacteriological broths, as well as
 for the analysis of air, microbiological samples,
 interveneous fluids, vaccines and the like. Microporous
 membranes or films are also utilized to make surgical
30 dressings, bandages, and in other fluid transmissive
 medical applications. The microporous membrane or film may be laminated to other articles to make laminates having particular utility. Such laminations may include a microporous layer and an outer shell layer to provide a

particularly useful garment material. The microporous films or membranes may be utilized as a tape backing to provide products such as a fluid-transmissive, wound dressing or hair set tape.

5 The art of preparing microporous films or membranes is not restricted, but rather is replete with a wide variety of methods of producing such articles. Methods commonly used to provide microporous films or membranes are described in the following references:

10 U.K. Patent Application GB 2,026,381 A, published February 6, 1980, discloses the preparation of membranes having a porous surface by blending polymer with a liquid component to form a binary two-phase system which, in the liquid aggregate state, has a region of miscibility and a
15 region with miscibility gaps, forming a sheet of the blend in the former state, casting the film into a bath of the liquid component, and removing the liquid component to provide porosity. The resultant non-oriented porous sheet has a relatively low tensile strength.

20 Various patents assigned to W. L. Gore and Associates, Inc., including U.S. Patent Nos. 3,953,566; 3,962,153; 4,096,227; 4,110,392; 4,187,390 and 4,194,041, describe the preparation of porous articles, including microporous
25 sheets formed exclusively of polytetrafluoroethylene (PTFE), not a thermoplastic polymer, characterized by having polymer nodes connected by fibrils. Such articles are produced by extruding a paste comprised of PTFE particles and a lubricant, removing the lubricant and stretching and annealing the resultant product. The
30 resultant product is a sintered, oriented porous film of PTFE.

 U.S. Pat. No. 3,201,364, assigned to Monsanto Company, describes the preparation of a non-oriented, non-porous
35 packaging film comprised of a single phase blend of polypropylene and mineral oil.

 U.S. Pat. Nos. 4,100,238 and 4,197,148 describe the preparation of microporous films by extruding a two

component blend, solvent leaching one dispersed component and stretching the resultant leached film to obtain a desired porosity. The blend consists of polymer and a leachable, non-miscible substance. Once the leachable dispersed polymer phase is removed and the film oriented, a porous film results.

U.S. Pat. No. 3,679,540, assigned to Celanese Corporation, discloses a method for making a microporous polymer film by cold stretching an elastic polymer film until porous surface regions are formed by film failure, hot stretching the cold stretched film until fibrils and pores or open cells are formed and then heat setting the resultant film. Controlled porosity is generally not attained in such films because they do not always uniformly fibrillate to a specific pore size.

Certain U.S. patents disclose the preparation of porous polymer films by blending into the polymer a non-miscible leachable particulate substance such as starch, salts, etc. forming a sheet and leaching the particulate substance from the polymer sheet. Such U.S. patents include Nos. 3,214,501 and 3,640,829. U.S. Pat. No. 3,870,593 discloses the preparation of a microporous polymer sheet by blending non-miscible, non-leachable filler into the polymer, forming a sheet of the blend and stretching the sheet to form pores which are initiated at the sites of the filler particles.

Disclosure of Invention

Microporous sheet materials according to the present invention are made by the following method steps:

- 30 (a) melt blending to form a solution of 30 to 80 parts by weight of a crystallizable thermoplastic polymer with correspondingly 70 to 20 parts by weight of a compound with which the thermoplastic polymer is miscible and in which the thermoplastic polymer will dissolve at the
35 melting temperature of the thermoplastic polymer but which is immiscible below the melting temperature of the

thermoplastic polymer and from which the thermoplastic polymer will phase separate on cooling to a temperature below the melting temperature of the thermoplastic polymer;

- 5 (b) forming a sheet of the melt blended solution;
- (c) cooling the sheet to a temperature at which the compound becomes immiscible with the thermoplastic polymer to cause phase separation to occur between the thermoplastic polymer and the compound thereby to provide a sheet
- 10 comprising an aggregate of a first phase comprising particles of the thermoplastic polymer in a second phase comprising the compound with adjacent thermoplastic polymer particles being distinct but having a plurality of zones of continuity; and
- 15 (d) orienting said sheet at least in one direction to separate adjacent particles of thermoplastic polymer from one another to provide a network of interconnected micropores therebetween and to permanently attenuate the thermoplastic polymeric material in the zones of continuity to
- 20 form fibrils.

The compound may be removed from the sheet, e.g., by solvent extraction.

The formed sheet, before orientation, is a solid, generally transparent sheet comprising an aggregate of a

25 first phase of particles of thermoplastic polymer in a second phase of the additive compound. The particles, may be described as lamellae, spherulites and aggregates of spherulites of the polymer with additive compound occupying the space between particles. Adjacent particles of polymer

30 are distinct but they have a plurality of zones of continuity. That is, the polymer particles are generally surrounded or coated by the compound but not completely. There are areas of contact between adjacent polymer particles where phase separation has not occurred and there

35 is a continuum of polymer from one particle to the next adjacent particle in such zones of continuity.

On orienting or stretching, the polymer particles are pulled apart, permanently attenuating the polymer in the zones of continuity thereby forming the fibrils and forming minute voids between coated particles, creating a network of interconnected micropores, thereby rendering the sheet permanently translucent. The size of the micropores is easily controlled by varying the degree of stretching, percent of additive compound, melt-quench conditions, compound removal and heat-stabilization procedures. The microfibrils for the most part do not appear to be broken by stretching but they are permanently stretched beyond their elastic limit so that they do not elastically recover to their original position when the stretching force is released. As used herein, "orienting" means such stretching beyond the elastic limit so as to introduce permanent set or elongation of the sheet. By contrast, assignee's U.S. Pat. No. 4,206,980 discloses similar films but having fibrils not stretched beyond the elastic limit in order to preserve the reversibly transparent-translucent feature of the films described in the patent.

The sheet of the invention has a microporous structure characterized by a multiplicity of spaced (i.e. separated from one another), randomly dispersed, non-uniform shaped, equiaxed, nonporous particles of thermoplastic polymer coated with the compound and connected by fibrils. (Equiaxed means having approximately equal dimensions in all directions.)

Brief Description of Drawings

The invention will be further understood by reference to the drawings, wherein:

FIG. 1 is a diagrammatical view of an apparatus that may be used in the process of the invention to produce the microporous film of the invention;

FIG. 2 is a photomicrograph of the internal structure of a 50% machine direction oriented polypropylene microporous sheet according to the present invention at a magnification of 1000 X; and

FIGS. 3 and 4 are photomicrographs of the same subject as FIG. 2 except at higher magnifications of 5000 X and 10,000 X, respectively, to show more detail; and

FIG. 5 is a photomicrograph of the same subject as FIG. 2 showing the left half at a magnification of 5,000 X and having a portion of the left half (identified by a small rectangular border within the left half) further enlarged to a magnification of 25,000 X presented as the right half of this FIGURE to show further detail of the fibrils between particles in the sheet material.

FIG. 6 is a photomicrograph of the surface of a polyethylene biaxially oriented microporous sheet material according to the present invention at a magnification of 5000 X.

15 Detailed Description of the Invention

Crystallizable polymers suitable for use in the preparation of microporous sheet materials of the invention are well known and readily commercially available.

Crystallizable polymers, upon cooling their melt under controlled conditions, spontaneously form geometrically regular and ordered chemical structures. Preferred crystallizable polymers for use in the present invention have a high degree of crystallinity and also possess a tensile strength of at least about 70 kg/cm² (1000 psi).

Examples of suitable crystallizable polymers include addition polymers such as polyolefins and condensation polymers such as polyesters and polyamides. Useful polyolefins preferably include the polymers of ethylene and propylene but also may include isobutylene, 1-octene, styrene, isoprene, and the like, and copolymers of two or more such olefins that may be polymerized to contain crystalline and amorphous segments and mixtures of stereo-specific modification of such polymers e.g., mixtures of isotactic polypropylene and atactic polypropylene, isotactic polystyrene and atactic polypropylene. Useful polyesters include polyethylene-terephthalate,

polybutylene-terephthalate, polyhexamethylenedipate, polyhexamethylenesuccinate, and polyester copolymers. Useful polyamides include polyhexamethylenedipamide, polyhexamethylenesecbacamide and polycaprolactam. Another
5 useful polymer is polyvinylidene fluoride.

Compounds suitable for blending with the crystallizable polymer to make the microporous sheet materials of the invention are liquids or solids at room temperature and in which the crystallizable polymer will dissolve to form a
10 solution at or near the melting temperature of the crystallizable polymer but will become immiscible on cooling and from which the crystallizable polymer will phase separate on cooling below the melting temperature of the crystallizable polymer. Preferably, these compounds have a
15 boiling point at atmospheric pressure at least as high as the melting temperature of the crystallizable polymer. Compounds having lower boiling points may be used in those instances where superatmospheric pressure may be employed to elevate the boiling point of the compound to a
20 temperature at least as high as the melting temperature of the crystallizable polymer. Generally, suitable compounds have a solubility parameter and a hydrogen bonding parameter within a few units of the values of these parameters for the crystallizable polymer.

25 Some examples of blends of crystallizable polymers and blending compounds which are useful in preparing microporous sheet materials according to the present invention include: polypropylene with mineral oil, dioctylphthalate or mineral spirits; polypropylene-
30 polyethylene copolymer with mineral oil; polyethylene with mineral oil or mineral spirits; polyethylene terephthalate and polybutylene terephthalate with diethylphthalate; polyester elastomer with dioctylphthalate, nylon 6 (polycaprolactam) with triethylene glycol; and
35 polyvinylidene fluoride with dibutyl phthalate.

The melt is prepared by mixing 30 to 80% by weight of crystallizable thermoplastic polymer and correspondingly 70

to 20% by weight of blending compound and heating the mixture to at least the melting point of the crystallizable polymer. For ease of handling the melt and in its casting, it is convenient to initiate the formation of the melt-blend solution by heating the mixture to 25°C. to about 100°C. above the melting point of the crystallizable polymer.

The microporous sheet materials of the invention are prepared by casting a layer of a melt-blend solution comprising a crystallizable polymer and a blending compound and, depending on the particular polymer, cooling the layer in a quench bath at an appropriate temperature preferably between about 90°C and 225°C. below the melting temperature of the crystallizable polymer to provide a proper cooling rate. (For example for polypropylene having a melting point of 176°C., a cooling temperature between about 40°C. and 60°C. is employed.) Some minor degree of experimentation may be required to identify the appropriate temperature range which produces optimum phase separation for a particular polymer-blending compound system, this being well within the capability of one skilled in the art once apprised of the present disclosure.

The attainment of the films of the invention is dependent on the rate of cooling. During cooling, heat is removed from the melt-blend solution until the melting temperature of the crystallizable polymer is reached and solidification and phase separation of the polymer can begin. Cooling temperatures greater than about 225°C. below the melting point of the crystallizable polymer causes too rapid quenching of the melt and can result in single phase films which, although strong and transparent (as taught in the prior art), are substantially incapable of being rendered uniformly microporous by stretching. Cooling at temperatures of less than about 90°C. below the melting point of the crystallizable polymer allows for a too slow phase separation (crystallization) of the crystallizable polymer with formation of large spherulites

that results in films which are weak. Casting films which are too thick, i.e., thicker than 1,000 micrometers, to achieve the proper cooling rate as described above also allows for a too slow crystallization.

5 As shown in FIG. 1, generally, the melt-blend solution is obtained by feeding into the hopper 12 of an extruder 10 a mixture of crystallizable polymer and blending compound through the extruder which is heated, preferably with 3 zones 14, 15, 16, respectively heated at increasing temperatures toward the extruder exit 17 to a slot die 19 that has a slit gap of 25 to 1,000 micrometers. Preferably, the crystallizable polymer is fed into the hopper of the extruder and the blending compound is fed by a suitable device 13 into the extruder via a port 11 in the extruder wall intermediate the hopper and the extruder exit 17. It is also preferable to utilize a suitable mixing device such as a static mixer 18 between the extruder exit 17 and the slot die 19. In passing through the extruder, and, where used, the static mixer, the mixture of polymer and blending compound is heated to a temperature at or at least about 25°C. above the melting point of the crystallizable polymer (but below the thermal degradation temperature of the polymer) and mixed to form a melt-blend solution that is extruded through the slot die 19 as a layer 25 into a liquid quench bath 20 maintained at a suitable temperature below the melting temperature of the crystallizable polymer using a suitable coolant, e.g., water. In some instances, e.g., for nylon and polyester, it is necessary to cool the solution in the extruder before it reaches the die to a temperature as much as 50°C cooler than the melting temperature of the polymer in order to obtain phase separation in the sheet. The cooled film is then led from the quench bath 20, to machine-direction orienting device 21, transverse direction orienting device 22 and then to take-up roller 23. Orienting in two directions is, of course, optional.

The films of the invention possess a tensile strength of at least about 10 kg/cm², more often 50 kg/cm² or higher depending on the tensile strength of the crystallizable polymer used and the extent of orientation.

5 The films are rendered microporous by stretching until micropores are permanently developed or formed in the film, typically to at least obtain an increase in length (elongation) of about 10%. Stretching to provide an elongation of about 10% to about 1,000% is typical. The actual amount of
10 stretching required will depend on the particular composition of the film and the degree of porosity desired. Stretching may be provided by any suitable device which can provide stretching in at least one direction and may provide stretching both in that direction and in the trans-
15 verse direction. Stretching should be uniform to obtain uniform and controlled porosity. Stretching in one direction typically causes the film to narrow or "neck" in the cross direction so stretching to provide an elongation of 50%, for example, does not produce a 50% increase in the
20 surface area of the film.

 The microporous sheet materials of the present invention are preferably dimensionally stabilized according to conventional well known techniques by heating the oriented sheet while it is restrained at a heat stabilizing
25 temperature.

 As shown in photomicrographs FIGS. 2-6, the microporous sheet material of the invention is composed of randomly dispersed, equiaxed, irregularly shaped, nonporous particles of thermoplastic polymer. It should be noted
30 that the blending compound had been removed prior to taking photomicrographs 2-6. Particles are spaced from one another to provide a network of micropores therebetween. Particles are connected to each other by fibrils, shown in detail in FIG. 5, which radiate from each particle to the
35 next adjacent particles. The porous structure appearing on the face of some of the particles in photomicrographs 2-5 is not an indication that the particles are porous but

instead shows the residue of the fibrils as they retract to the particle once the sheet material is ruptured to reveal the internal structure.

The blending compound may be removed from the micro-
5 porous sheet to provide a unique microporous sheet material formed of the polymeric material per se. Removal may be by solvent extraction, volatilization, or any other convenient method. Once the blending compound has been removed, the resultant microporous sheet may be imbibed with various
10 materials to provide any of a variety of specific functions, thereby providing unique articles. For example, the imbibing material may be a liquid, solvent solution, solvent dispersion or solid. Such materials may be imbibed by any of a number of known methods which results in the
15 deposition of such materials within the porous structure of the microporous sheet. Some imbibing materials are merely physically placed within the microporous sheet. In some instances, the use of two or more reactive components as the imbibing materials permits the reaction within the
20 microporous sheet structure. Examples of imbibing material include medicaments, fragrances, antistatic agents, surfactants, pesticides and solid particulate material such as activated carbon and pigments. Certain materials, such as antistat or surfactants, may be imbibed without removal
25 of the blending compound.

The microporous sheet material, either both before or after removal of the blending compound, may be further modified by the deposition thereon of any of a variety of compositions by any of a variety of known coating or
30 deposition techniques. For example, the microporous sheet material may be coated with metal by vapor deposition or sputtering techniques or it may be coated with adhesives, aqueous or solvent-based coating compositions or dyes. Coating may be accomplished by such other conventional
35 coating techniques as roll coating, spray coating, dip coating or any other known coating techniques.

The microporous sheet materials of the present invention may be laminated to any of a variety of other structures such as other sheet materials to provide a composite structure which includes the microporous sheet material of the present invention. Lamination can be accomplished by conventional techniques.

The microporous sheet materials of the invention may be employed in any of a wide variety of situations where their microporous structures may be utilized. They may be used in the ultrafiltration of colloidal matter, as diffusion barriers or separators in electrochemical cells. They may be laminated to other materials and the laminate may be utilized in many ways, such as to form raincoats or other outer wear, camping equipment such as tents and sleeping bags. The microporous sheet materials may be utilized as filtering material for cleaning antibiotics, beer, oils, bacteriological broths and for sample collection in air analysis and to collect microbiological specimens. They may be utilized to make surgical dressings, bandages and in other medical applications. Many other uses for microporous sheets can be found in the literature.

EXAMPLES

The invention is further illustrated by the following examples, wherein all parts are by weight, unless otherwise specified.

EXAMPLE 1

Crystallizable polypropylene (available under the trade designation "Profax" type 6723 from Hercules, Inc.) having a density of 0.903 g/cc, a melt flow index of 0.8 and a melting point of about 176°C. was introduced into the hopper of a 2.5 cm extruder fitted with a 10.16 cm by 0.076 cm slit gap sheeting die positioned above a water quench tank. The polypropylene was fed into the extruder and the extruder operated at a 60 cc/min throughput rate

to produce a polypropylene sheet collected at the rate of 7.6 meters per minute. Mineral oil (available under the trade designation "Nujol" from Plough, Inc.) having a boiling point of 200°C. and a standard Saybolt viscosity of 360-390 at 38°C. (about 80 centistokes) was introduced into the extruder through an injection port at a rate to provide a blend of 70% by weight polypropylene and 30% by weight mineral oil. The mixture was cast as a transparent film into the water quench bath which was maintained at 49°C., producing a quenched film at the rate of 7.6 meters per minute. The melt in the extruder and the sheet die was maintained at approximately 245°C. during extrusion. The resulting film was then oriented at room temperature in the machine direction to obtain varying degrees of elongation. The porosity of each film was measured according to ASTM-D-726-58, Method A, by using a Gurley densometer to measure the time in seconds to pass 50 cc of air through the film. Porosity measurement results are reported in Table I.

20

EXAMPLE 2

A blend of 80% polypropylene and 20% mineral oil (of the same polymer and oil described in Example 1) was extruded as described in Example 1 into a water bath maintained at 49°C. collected at the rate of 7.6 meters per minute while maintaining the melt temperature at 245°C. and the film die at the same temperature. Stretching versus porosity results are shown in Table I.

EXAMPLE 3

The system described in Example 1 was used to extrude a blend as described in Example 2 except the quench bath was maintained at 60°C. to produce a film. Evaluation results of the film are shown in Table I.

EXAMPLE 4

Following the conditions described in Example 1, a 60:40 blend of polypropylene:mineral oil was prepared and stretched but found to be unsuitable because the film broke at a lengthwise stretch of less than 10%. The unstretched film had poor integrity and crumbled easily with touch.

EXAMPLE 5

A 70:30 polypropylene:mineral oil blend was extruded as described in Example 1 (except the film die was maintained at 260°C.) into a quench bath at 40°C. The film was stretched and its porosity determined. Results are shown in Table I.

EXAMPLE 6

The experiment of Example 5 was repeated except the film die was heated at 275°C. and the water bath maintained at 40°C. The resultant film was stretched and evaluated for porosity with results shown in Table I.

EXAMPLE 7

The experiment of Example 6 was repeated. The porosity was measured after stretching to 35%. The 35% stretched film was then restrained and heat set in an oven for 5 minutes at 107°C. and its porosity was then measured. The film was given another 5 minutes under restraint in the oven at 107°C. and its porosity was measured again. The film was then washed with toluene while restrained to remove mineral oil and dried in an oven at 107°C. and its porosity measured again. The result of each of the measurements is shown in Table I as Examples 7, 7a, 7b, and 7c, respectively.

EXAMPLE 8

A 60:40 blend of high density polyethylene having a density of 0.946 g/cc and a melt-flow index of 3.0 (available under the trade designation "Marlex" 6030 from

Phillips Petroleum Company) and mineral oil ("Nujol") was extruded in the same manner as described in Example 1 to produce a film which was in line lengthwise stretched 50% and collected. The resultant film was further machine
5 direction stretched while in a stretching apparatus and its porosity measured with results being shown in Table I as Example 8.

This film was then washed while under restraint with toluene to remove the mineral oil, air dried and its
10 porosity measured. The results, identified under Example 8a are shown in Table I.

The film of Example 8a was heat annealed for 10 minutes at 93°C. and then, after cooling, the air permeability measured. Results are shown in Table I under Example 8b.

15 The film described in Example 8b was cross stretched approximately 30% and the porosity measured with results shown in Table I under Example 8c.

EXAMPLE 9

A film was prepared from a melt blend of 70 parts
20 polyethylene-polypropylene copolymer (available under the trade designation "Shell" copoly P 6313) and 30 parts mineral oil as described in Example 1 under the same conditions. The resultant transparent film was mounted in a stretching apparatus, stretched 50% in the lengthwise
25 direction, washed with toluene while restrained at ambient temperature and heat set at 107°C. for 10 minutes. The porosity before stretching, solvent washing and annealing was too high to measure. The porosity after this treatment was 415.8 seconds.

30

EXAMPLE 10

The microporous films of Examples 1, 2, 5, 6 and 8c were tested for moisture vapor transmission by comparing the moisture evaporation or transmission rate of water from an open jar and with each of the tests samples applied over
35 the jar opening. The open jar was considered to have a

100% moisture transmission rate and the relative transmission rate of each of the film samples is compared to the transmission rate of the open jar. Ambient conditions were used, i.e., approximately 21°C. at 50% relative humidity.

5 Results are shown in Table II. The moisture vapor transmission rate of two commercially available microporous films available under the trade designation "Celgard" from the Celanese Company were also evaluated and the results are also reported in Table II.

10

EXAMPLE 11

A film as described in Example 1 was prepared with the exception that it was stretched 50% in line lengthwise and its width stretched 50% in line. The film was measured for porosity and moisture vapor transmission, as in Example 10 and without the mineral oil removed and with the oil removed by washing with toluene as in Example 11a. Results are:

Ex. No.	MVT% (g/m ² /24 hrs.)	MVT%	Porosity (seconds to pass 50 cc of air)
11	1102.8	76	48.1
20 11a	1131.8	78	25.8

EXAMPLE 12

A 70:30 blend of polypropylene:diethyl phthalate was extruded to form a film as described in Example 1 except the melt temperature was 260°C. and the water quench temperature was maintained at 60°C. The film was lengthwise stretched 65% in a stretching apparatus and found to have an air porosity of 1155.3 seconds.

The stretched film described above was washed with methylethyl ketone solvent to remove the diethyl phthalate and air dried. This film had an air porosity of 840.4 seconds.

The film described above was annealed for 10 minutes at 107°C. under restraint and its air porosity found to be 713.9 seconds.

EXAMPLE 13

The 70:30 blend of polypropylene:mineral oil described in Example 1 was formed into a sheet as described except the molten blend was cast onto a casting wheel maintained at 30°C. The resultant transparent film was in line length stretched 50% resulting in an opaque film which was measured for air porosity and moisture transmission. The film had no apparent air porosity and had a moisture vapor transmission of 330 g/m²/24 hrs. or 23%. This film had a unique physical structure, unlike the films of the previous examples which have an open or porous structure on both surfaces and throughout the film. This film had a porous structure on one side and approximately 75% through the thickness of the film, whereas the other side and the remaining 25% of the thickness had a fused or compressed structure. This fused or sealed side of the film had contacted the casting wheel upon exiting the film die. The porous side of the film could be marked with a felt-tipped marking pen whereas the smooth opposite side could not easily be marked and, when markings were placed on the smooth side, they smeared or wiped off easily. Films with such properties can be used as protective films or tapes, either for the resistance to marking or, by reversing the film to use the opposite side, for ready markability.

EXAMPLE 14

A 70:30 blend of polyester copolymer (available under the trade designation "Hytrel" 6346) and dioctyl phthalate was pelletized using a Baker Perkins twin screw compounder. ("Hytrel" is the trade designation of a polyester elastomeric block copolymer of short chain diol terephthalate and long chain polyester diol terephthalate manufactured by the E. I. DuPont Company.) The pellets were extruded as described in Example 1, except that no other dioctyl phthalate was injected into the system and the melt temperature was maintained at 274°C. and the water quench bath was maintained at 55°C. The resulting transparent film

film was mounted in a length stretching apparatus and stretched 40%. The stretched film was washed with methyl-ethyl ketone solvent to remove the dioctyl phthalate and its air porosity measured, after drying. The air porosity was 15,350 seconds. The film was biaxially stretched 40% and then found to have a porosity of 7,255 seconds.

EXAMPLE 15

Nylon 6 (available from the Foster Grant Company under the trade designation "FOSTA" Number 471) was extruded on the 2.5 cm extruder while triethylene glycol was injected into the extruder barrel to provide a 60:40 nylon 6:triethylene glycol blend which was cast from a 10.16 cm by 0.076 cm slit gap sheeting die heated at 220°C. and cast into a water quench bath at the rate of 5.2 meters per minute with the water bath being maintained at 44°C. The extruder melt temperature of the blend was maintained at 220°C. The film usually cast as transparent although, as some of the triethylene glycol was removed by the water in the quench bath, the film assumed a slightly opaque appearance on drying. As the glycol dissipated, the film became completely opaque. The dried film was stretched lengthwise 30% and the air porosity found to be 350 seconds.

EXAMPLE 16

A film was prepared of the blend described in Example 8, length stretched 35% in a stretching apparatus, and found to have a porosity of 848.1 seconds. The film was then solvent washed while restrained in isopropanol to remove oil, air dried and found to have a porosity of 130.3 seconds. The film was heated to 93.3°C. for 5 minutes in the stretching apparatus and found to have an air porosity of 71.8 seconds. The film was then cross stretched 30% and found to have a porosity of 34 seconds.

A similar freshly formed film as described above was washed in isopropyl alcohol and, after drying, found to have a porosity of 835.7 seconds. The film was length

stretched 35% and found to have a porosity of 211.4 seconds. Upon heat treating the stretched film at 93.3°C. for 5 minutes, its porosity was found to be 111.8 seconds. The same film cross stretched 30% had an air porosity of 5 32.3 seconds.

EXAMPLE 17

A 60:40 blend of high density polyethylene available from Atlantic Richfield Co. under the trade designation "Arco" 8590 having a density of 0.955 and a melt (flow index 10 of 11.0 and mineral oil "Nujol" was melt mixed in an extruder, cast from a 10.16 cm by 0.06 cm slit gap sheeting die at a melt temperature of 126.7°C. (approximately 10°C. below its crystalline melting point) into a water quench bath maintained at 48°C. and collected at the rate of 7.6 15 meters per minute. The resulting transparent film was length stretched 25% and solvent extracted with isopropyl alcohol to remove mineral oil to produce a microporous film having a porosity of 595 seconds. The microporous film was cross stretched 25% and its air porosity found to be 193 20 seconds. After heat treatment at 93.3° for 5 minutes, the porosity was 192 seconds.

EXAMPLE 18

A 65:35 blend of polypropylene (available under the trade designation "Profax" 6330 having a density of 0.90 25 g/cc and a melt flow index of 12.0):mineral oil ("Nujol") was melt mixed in the extruder cast from a 10.06 cm by 0.06 cm slit gap sheeting die at a melt temperature of 164°C., approximately 10° below its crystalline melt point, into a water quench bath maintained at 45°C. and collected at 7.3 30 meters per minute. The resulting transparent film was cross stretched 30% and washed with isopropyl alcohol to remove mineral oil, producing a microporous film having a porosity of 1170 seconds.

EXAMPLE 19

A 55:45 blend of polyethylene terephthalate having an intrinsic viscosity of 0.6 and a density of 1.37 g/cc and diethyl phthalate was melt blended and extruded using the apparatus described in Example 1 except the extrusion orifice was 10.16 cm by 0.06 cm and the melt temperature was 215°C., approximately 50° below its crystalline melting point. The water quench bath was maintained at 40°C. and the film collected at 3.66 meters per minute. The resulting transparent film was stretched 20% in the lengthwise direction under ambient conditions and 20% in the cross direction, washed in isopropyl alcohol to remove the diethyl phthalate, dried and found to have a porosity of 7675 seconds.

EXAMPLE 20

A 70:30 blend of polybutylene terephthalate (available from Eastman Chemical Company under the trade designation "Tenite" 6-P4D) and diethyl phthalate was melt mixed in the extruder, cast from a 10.16 cm by 0.06 cm slit gap sheeting die at a melt temperature of 224°C., approximately at its crystalline melting point, into a water quench bath maintained at 60°C. and collected at 6.7 meters per minute. The resulting transparent film was stretched under ambient conditions in the length and cross directions 20% and washed in toluene to remove the diethyl phthalate. The resulting microporous film had a porosity of 2,735 seconds.

EXAMPLE 21

The 30:70 blend of high density polyethylene having a density of 0.955 and a melt flow index of 11.0 (available under the trade designation "Arco" 8590):mineral oil ("Nujol") was melt mixed in the extruder at 254°C. and cast from the 10.16 cm by 0.06 cm slit of the sheeting die at a melt temperature of 271°C. into quench water maintained at 54°C. and collected at the rate of 7.62 meters per minute. The resultant transparent film was washed with toluene to

remove the mineral oil and the film was stretched 35% in the machine direction and cross stretched 25%. The resultant stretched microporous film had a porosity of 4.8 seconds.

EXAMPLE 22

- 5 A 60:30 blend of polyvinylidene fluoride (having a density of 1.75 g/cc and being available from Pennwalt Chemicals Company under the trade designation "Kynar" 740) and dibutyl phthalate was melt mixed in a twin screw extruder at 250°C. and cast from a 0.06 cm by 15.24 cm slit
- 10 260°C. sheeting die into a 32° water bath to produce a film which was collected at the rate of 7.62 meters per minute. The resultant transparent film was washed with 1,1,1-trichloroethane, biaxially stretched 10% in each direction and its air porosity found to be 1,099
- 15 seconds. The moisture vapor transmission was found to be 25%.

POROSITY (SEC TO PASS 50 CC AIR)

Length Increase (%)	Example No.	POROSITY (SEC TO PASS 50 cc AIR)													
		1	2	3	4	5	6	7	7a	7b	7c	8	8a	8b	8c
0	*														
5.															
10.	3760.0					638.3	508.7	472.1							
15.															
20.															
25.	710.2			814.5		128.9	73.2	68.8							
30.	572.4					73.6									
35.	499.5					60.4	41.5	35.4	21.7	21.6	15.8				
40.	451.2			475.1		54.3	36.2								
45.	421.4					50.5	32.0					471.7			
50.	398.2			411.2		43.4	24.8								
55.							21.4					369.1			
60.	354.4			348.9			19.5								
65.	337.8						16.5					366.4	106.5	67.0	20.7
70.	350.5			333.6											
75.	277.1														
80.	324.2			326.4											
85.	376.5														
90.				298.1											
95.															

TABLE I

Length Increase Example (%)	POROSITY (SEC TO PASS 50 CC AIR)														
	No.	1	2	3	4	5	6	7	7a	7b	7c	8	8a	8b	8c
100:		406.7	10,000	311.2											
110.		465.9													
120.		416.8													
130.		493.7		317.4											
140.		443.1													
150.															
160.		620.9													

* No measurable air porosity by ASTM-D-726-58

TABLE II

	gm H ₂ O/m ² /24 hrs.	Moisture Vapor Transmission (%)	Length Increase (Machine direction) (%)	Length Increase (Transverse direction) (%)
Open jar H ₂ O	1451.0	100.0	—	—
Example 1	—	0.0	0.	—
Example 2	842	58.0	100.	—
Example 5	896.3	62.0	50.	—
Example 6	1023.0	70.5	65.	—
Example 8c	856.1	59.0	65.	30.
Example 11	1102.8	76.0	50.	50.
Example 11a	1131.8	78.0	50.	50.
"Celgard" 2400	972.1	67.0	—	—
"Celgard" 2500	1117.3	77.0	—	—

"Celgard" is a Celanese Corp. registered trademark for porous films

CLAIMS

1. A method of making a microporous sheet, characterized by including the following steps:
 - (a) melt blending to form a solution of 30 to 80 parts by weight of a crystallizable thermoplastic polymer with correspondingly 70 to 20 parts by weight of a compound with which said thermoplastic polymer is miscible and in which said thermoplastic polymer will dissolve at the melting temperature of said thermoplastic polymer but which is immiscible below the melting temperature of said thermoplastic polymer and from which said thermoplastic polymer will phase separate on cooling to a temperature below the melting temperature of said thermoplastic polymer;
 - (b) forming a sheet of the melt blended solution;
 - (c) cooling said sheet to a temperature at which said compound becomes immiscible with said thermoplastic polymer to cause phase separation to occur between said compound and said polymer thereby to provide a sheet comprising an aggregate of a first phase comprising particles of said thermoplastic polymer in a second phase comprising said compound with adjacent thermoplastic polymer particles being distinct but having a plurality of zones of continuity; and
 - (d) orienting said sheet at least in one direction to separate adjacent particles of thermoplastic polymer from one another to provide a network of interconnected micropores therebetween and to permanently attenuate the thermoplastic polymeric material in said zones of continuity to form fibrils.
2. The method of claim 1 further characterized by said orienting being biaxial orienting.

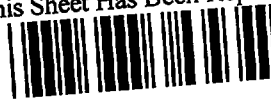


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3. The method of claim 1 further characterized by said orienting providing a length increase in said sheet of from about 10 to about 1,000 percent of the original length of said sheet.
- 5 4. The method of claim 1 further characterized by including the additional step of removing said compound.
- 10 5. The method of claim 1 further characterized by including the additional step of dimensionally stabilizing said sheet by heating the oriented sheet, while it is restrained, to a heat stabilizing temperature.
- 15 6. The method of claims 1, 3, 4 and 5 further characterized by including the additional step of laminating said microporous sheet to a second sheet.
- 20 7. The method of claim 1 further characterized by said thermoplastic polymer and said compound being selected from the group consisting of
 - (a) polypropylene with mineral oil, dioctylphthalate or mineral spirits;
 - (b) polyethylene with mineral oil or mineral spirits;
 - (c) polypropylene-polyethylene copolymer with mineral oil;
 - (d) polyethylene terephthalate with diethylphthalate;
 - 25 (e) polycaprolactam with triethylene glycol;
 - (f) polyvinylidene fluoride with dibutyl phthalate;
 - (g) polybutylene terephthalate with diethylphthalate; and
 - (h) polyester copolymer with dioctylphthalate.



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8. A microporous sheet material made according to the process of claim 1 characterized by comprising about 30 to 80 parts by weight of crystallizable thermoplastic polymer and correspondingly about 70 to 20 parts by weight of a compound with which said thermoplastic polymer is miscible and in which said thermoplastic polymer will dissolve at the melting temperature of said thermoplastic polymer but with which said thermoplastic polymer is immiscible below said melting temperature and from which said thermoplastic polymer will phase separate on cooling to a temperature below said melting temperature of said thermoplastic polymer, said microporous sheet having an internal structure characterized by a multiplicity of spaced, randomly dispersed, non-uniform shaped, equiaxed, non-porous particles of said thermoplastic polymer coated with said compound, adjacent coated particles throughout said sheet being separated from one another to provide said sheet with a network of interconnected micropores and said adjacent thermoplastic polymer particles being connected to each other by a plurality of fibrils consisting of said thermoplastic polymer.
9. A laminated structure further characterized by including the microporous sheet material of claim 8 and at least one other sheet material.
10. The microporous sheet material of claim 8 further characterized by said thermoplastic polymer and said compound being selected from the group consisting of
- (a) polypropylene with mineral oil, dioctylphthalate or mineral spirits;
 - (b) polyethylene with mineral oil or mineral spirits;
 - (c) polypropylene-polyethylene copolymer with mineral oil;
 - (d) polyethylene terephthalate with diethylphthalate;
 - (e) polycaprolactam with triethylene glycol;



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- (f) polyvinylidene fluoride with dibutyl phthalate;
- (g) polybutylene terephthalate with diethylphthalate;
and
- (h) polyester copolymer with dioctylphthalate.

- 5 11. A microporous sheet material made according to the
process of claim 5 characterized by comprising
crystallizable thermoplastic polymer, said microporous
sheet having an internal structure characterized by a
multiplicity of spaced, randomly disposed, non-uniform
10 shaped, equiaxed, non-porous particles of said
thermoplastic polymer, adjacent particles throughout
said sheet being separated from one another to provide
said sheet with a network of interconnected micropores
and being connected to each other by a plurality of
15 fibrils consisting of said thermoplastic polymer.
12. A laminated structure further characterized by
including the microporous sheet of claim 18 and at
least one other sheet material.
13. The method of claims 1 and 4 further characterized by
20 including the additional step of imbibing the
microporous sheet material with an imbibing material.
14. The method of claims 1 and 4 further characterized by
including the additional step of coating the resultant
microporous sheet material.

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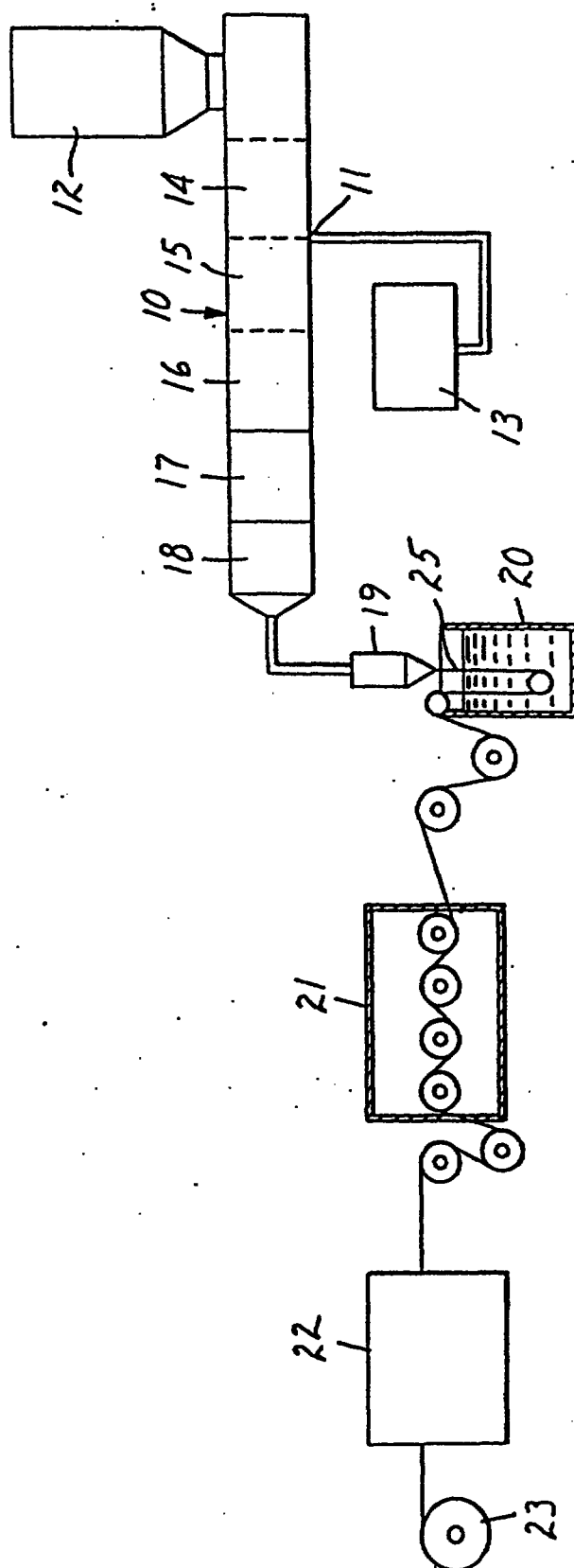
1/4*FIG. 1*



FIG. 2



FIG. 3



FIG. 4



FIG. 5

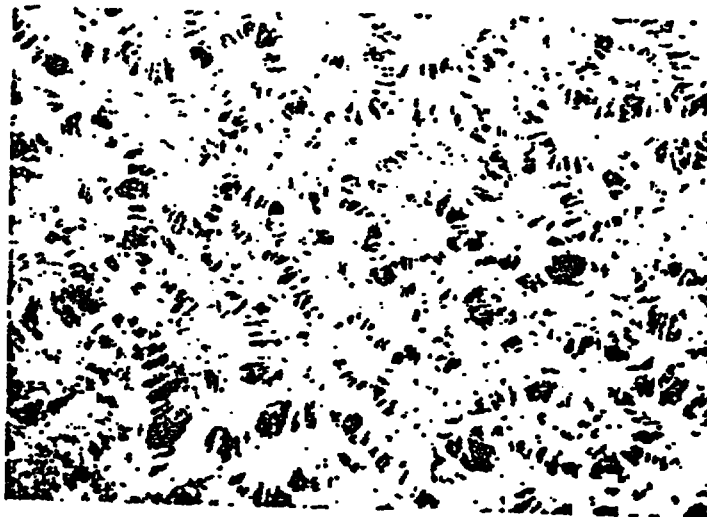


FIG. 6

an inorganic filler is molded into a sheet followed by stretching), such a degree of improvement is still insufficient for eliminating the necessity of landing tapes. In addition, since the use of the radical generator makes melt flow properties of the molded resin composition different from those of the composition before molding, it is difficult to recycle inevitably produced discarded pieces in the course of the production, resulting in reduced productivity.

Further, Japanese Patent Application Laid-open 5-38011 (corresponding to USP 4,539,256) discloses a microporous sheet obtained by a process comprising melt-blending a specific crystallizable polymer and a specific compound miscible with that polymer, molding the mixture into a sheet, causing phase separation to occur during a cooling step, and stretching the resulting sheet.

Although the microporous sheet disclosed has two or three times as high strength as a sheet obtained by the conventional process (a molten mixture of a polyolefin and an inorganic filler is molded into a sheet followed by stretching), the strength still does not reach a sufficient level for making landing tapes needless. According to the present inventors' study, a porous sheet withstanding removal of a fastening tape

$1.00 \geq P \geq 0.015 \log MI + 0.955$, the polypropylene exhibits high crystallinity and improved rigidity. If P is less than $0.015 \log MI + 0.955$, the polypropylene has reduced rigidity so that the porous sheet may have to have a large thickness for assuring rigidity necessary as a back sheet, which leads to an increase of cost.

The MI of the polypropylene preferably ranges from 0.03 to 2.0 g/10 min.

If the MI is less than 0.03, the molten polymer needs increased power in granulation or molding because of its poor fluidity, which is not only uneconomical but hinders speeding up of production. If it exceeds 2.0, the molten resin has reduced tension. It follows that, for example, a tubular film of the polypropylene is hard to lift in blown film extrusion, and sheeting becomes instable.

The polypropylene satisfying the above relationship can be prepared by, for example, the process disclosed in Japanese Patent Publication 64-5051, p. 7, col. 13, 1.44 to p. 8, col. 15, 1.9.

The compound which is used in the porous sheet is a compound with which said crystalline polyolefin is miscible and in which said crystalline polyolefin will dissolve at above the melting point of said crystal-



7 lodged under cover
of SG 9501694-S.
Arthur Loke 9/5/97
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CLAIMS

1. A method of making a microporous sheet, characterized by including the following steps:
 - (a) melt blending to form a solution of 30 to 80 parts by weight of a crystallizable thermoplastic polymer with correspondingly 70 to 20 parts by weight of a compound with which said thermoplastic polymer is miscible and in which said thermoplastic polymer will dissolve at the melting temperature of said thermoplastic polymer but which is immiscible below the melting temperature of said thermoplastic polymer and from which said thermoplastic polymer will phase separate on cooling to a temperature below the melting temperature of said thermoplastic polymer;
 - (b) forming a sheet of the melt blended solution;
 - (c) cooling said sheet to a temperature at which said compound becomes immiscible with said thermoplastic polymer to cause phase separation to occur between said compound and said polymer thereby to provide a sheet comprising an aggregate of a first phase comprising particles of said thermoplastic polymer in a second phase comprising said compound with adjacent thermoplastic polymer particles being distinct but having a plurality of zones of continuity; and
 - (d) orienting said sheet at least in one direction to separate adjacent particles of thermoplastic polymer from one another to provide a network of interconnected micropores therebetween and to permanently attenuate the thermoplastic polymeric material in said zones of continuity to form fibrils.

2. The method of claim 1 further characterized by said orienting being biaxial orienting.

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3. The method of claim 1 further characterized by said orienting providing a length increase in said sheet of from about 10 to about 1,000 percent of the original length of said sheet.
- 5 4. The method of claim 1 further characterized by including the additional step of removing said compound.
- 10 5. The method of claim 1 further characterized by including the additional step of dimensionally stabilizing said sheet by heating the oriented sheet, while it is restrained, to a heat stabilizing temperature.
- 15 6. The method of claims 1, 3, 4 and 5 further characterized by including the additional step of laminating said microporous sheet to a second sheet.
- 20 7. The method of claim 1 further characterized by said thermoplastic polymer and said compound being selected from the group consisting of
 - (a) polypropylene with mineral oil, dioctylphthalate or mineral spirits;
 - (b) polyethylene with mineral oil or mineral spirits;
 - (c) polypropylene-polyethylene copolymer with mineral oil;
 - (d) polyethylene terephthalate with diethylphthalate;
 - 25 (e) polycaprolactam with triethylene glycol;
 - (f) polyvinylidene fluoride with dibutyl phthalate;
 - (g) polybutylene terephthalate with diethylphthalate; and
 - (h) polyester copolymer with dioctylphthalate.

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8. A microporous sheet material made according to the process of claim 1 characterized by comprising about 30 to 80 parts by weight of crystallizable thermoplastic polymer and correspondingly about 70 to 20 parts by weight of a compound with which said thermoplastic polymer is miscible and in which said thermoplastic polymer will dissolve at the melting temperature of said thermoplastic polymer but with which said thermoplastic polymer is immiscible below said melting temperature and from which said thermoplastic polymer will phase separate on cooling to a temperature below said melting temperature of said thermoplastic polymer, said microporous sheet having an internal structure characterized by a multiplicity of spaced, randomly dispersed, non-uniform shaped, equiaxed, non-porous particles of said thermoplastic polymer coated with said compound, adjacent coated particles throughout said sheet being separated from one another to provide said sheet with a network of interconnected micropores and said adjacent thermoplastic polymer particles being connected to each other by a plurality of fibrils consisting of said thermoplastic polymer.
9. A laminated structure further characterized by including the microporous sheet material of claim 8 and at least one other sheet material.
10. The microporous sheet material of claim 8 further characterized by said thermoplastic polymer and said compound being selected from the group consisting of
- (a) polypropylene with mineral oil, dioctylphthalate or mineral spirits;
 - (b) polyethylene with mineral oil or mineral spirits;
 - (c) polypropylene-polyethylene copolymer with mineral oil;
 - (d) polyethylene terephthalate with diethylphthalate;
 - (e) polycaprolactam with triethylene glycol;



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- (f) polyvinylidene fluoride with dibutyl phthalate;
- (g) polybutylene terephthalate with diethylphthalate;
and
- (h) polyester copolymer with dioctylphthalate.

- 5 11. A microporous sheet material made according to the
process of claim 5 characterized by comprising
crystallizable thermoplastic polymer, said microporous
sheet having an internal structure characterized by a
multiplicity of spaced, randomly disposed, non-uniform
10 shaped, equiaxed, non-porous particles of said
thermoplastic polymer, adjacent particles throughout
said sheet being separated from one another to provide
said sheet with a network of interconnected micropores
and being connected to each other by a plurality of
15 fibrils consisting of said thermoplastic polymer.
12. A laminated structure further characterized by
including the microporous sheet of claim 18 and at
least one other sheet material.
- 20 13. The method of claims 1 and 4 further characterized by
including the additional step of imbibing the
microporous sheet material with an imbibing material.
14. The method of claims 1 and 4 further characterized by
including the additional step of coating the resultant
microporous sheet material.

This is the replacement sheet

Date:

09 JUN 1997



CLAIMS

1. A method of making a microporous sheet, characterized by including the following steps:
 - (a) melt blending to form a solution of 30 to 80 parts by weight of a crystallizable thermoplastic polymer with correspondingly 70 to 20 parts by weight of a compound with which said thermoplastic polymer is miscible and in which said thermoplastic polymer will dissolve at the melting temperature of said thermoplastic polymer but which is immiscible below the melting temperature of said thermoplastic polymer and from which said thermoplastic polymer will phase separate on cooling to a temperature below the melting temperature of said thermoplastic polymer;
 - (b) forming a sheet of the melt blended solution;
 - (c) cooling said sheet to a temperature at which said compound becomes immiscible with said thermoplastic polymer to cause phase separation to occur between said compound and said polymer thereby to provide a sheet comprising an aggregate of a first phase comprising particles of said thermoplastic polymer in a second phase comprising said compound with adjacent thermoplastic polymer particles being distinct but having a plurality of zones of continuity; and
 - (d) orienting said sheet at least in one direction to separate adjacent particles of thermoplastic polymer from one another to provide a network of interconnected micropores therebetween and to permanently attenuate the thermoplastic polymeric material in said zones of continuity to form fibrils.
2. The method of claim 1 further characterized by said orienting being biaxial orienting.

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3. The method of claim 1 further characterized by said orienting providing a length increase in said sheet of from about 10 to about 1,000 percent of the original length of said sheet.
- 5 4. The method of claim 1 further characterized by including the additional step of removing said compound.
- 10 5. The method of claim 1 further characterized by including the additional step of dimensionally stabilizing said sheet by heating the oriented sheet, while it is restrained, to a heat stabilizing temperature.
- 15 6. The method of claims 1, 3, 4 and 5 further characterized by including the additional step of laminating said microporous sheet to a second sheet.
- 20 7. The method of claim 1 further characterized by said thermoplastic polymer and said compound being selected from the group consisting of
 - (a) polypropylene with mineral oil, dioctylphthalate or mineral spirits;
 - (b) polyethylene with mineral oil or mineral spirits;
 - (c) polypropylene-polyethylene copolymer with mineral oil;
 - (d) polyethylene terephthalate with diethylphthalate;
 - 25 (e) polycaprolactam with triethylene glycol;
 - (f) polyvinylidene fluoride with dibutyl phthalate;
 - (g) polybutylene terephthalate with diethylphthalate; and
 - (h) polyester copolymer with dioctylphthalate.

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8. A microporous sheet material made according to the process of claim 1 characterized by comprising about 30 to 80 parts by weight of crystallizable thermoplastic polymer and correspondingly about 70 to 20 parts by weight of a compound with which said thermoplastic polymer is miscible and in which said thermoplastic polymer will dissolve at the melting temperature of said thermoplastic polymer but with which said thermoplastic polymer is immiscible below said melting temperature and from which said thermoplastic polymer will phase separate on cooling to a temperature below said melting temperature of said thermoplastic polymer, said microporous sheet having an internal structure characterized by a multiplicity of spaced, randomly dispersed, non-uniform shaped, equiaxed, non-porous particles of said thermoplastic polymer coated with said compound, adjacent coated particles throughout said sheet being separated from one another to provide said sheet with a network of interconnected micropores and said adjacent thermoplastic polymer particles being connected to each other by a plurality of fibrils consisting of said thermoplastic polymer.
9. A laminated structure further characterized by including the microporous sheet material of claim 8 and at least one other sheet material.
10. The microporous sheet material of claim 8 further characterized by said thermoplastic polymer and said compound being selected from the group consisting of
- (a) polypropylene with mineral oil, dioctylphthalate or mineral spirits;
 - (b) polyethylene with mineral oil or mineral spirits;
 - (c) polypropylene-polyethylene copolymer with mineral oil;
 - (d) polyethylene terephthalate with diethylphthalate;
 - (e) polycaprolactam with triethylene glycol;

- (f) polyvinylidene fluoride with dibutyl phthalate;
- (g) polybutylene terephthalate with diethylphthalate;
and
- (h) polyester copolymer with dioctylphthalate.

- 5 11. A microporous sheet material made according to the
process of claim 5 characterized by comprising
crystallizable thermoplastic polymer, said microporous
sheet having an internal structure characterized by a
multiplicity of spaced, randomly disposed, non-uniform
10 shaped, equiaxed, non-porous particles of said
thermoplastic polymer, adjacent particles throughout
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said sheet with a network of interconnected micropores
and being connected to each other by a plurality of
15 fibrils consisting of said thermoplastic polymer.
12. A laminated structure further characterized by
including the microporous sheet of claim 18 and at
least one other sheet material.
13. The method of claims 1 and 4 further characterized by
20 including the additional step of imbibing the
microporous sheet material with an imbibing material.
14. The method of claims 1 and 4 further characterized by
including the additional step of coating the resultant
microporous sheet material.



* C L M S *

This is the replacement sheet

Date:

21 JUL 1997

an inorganic filler is molded into a sheet followed by stretching), such a degree of improvement is still insufficient for eliminating the necessity of landing tapes. In addition, since the use of the radical generator makes melt flow properties of the molded resin composition different from those of the composition before molding, it is difficult to recycle inevitably produced discarded pieces in the course of the production, resulting in reduced productivity.

Further, Japanese Patent Application Laid-open 5-38011 (corresponding to USP 4,539,256) discloses a microporous sheet obtained by a process comprising melt-bending a specific crystallizable polymer and a specific compound miscible with that polymer, molding the mixture into a sheet, causing phase separation to occur during a cooling step, and stretching the resulting sheeting.

Although the microporous sheet disclosed has two or three times as high strength as a sheet obtained by the conventional process (a molten mixture of a polyolefin and an inorganic filler is molded into a sheet followed by stretching), the strength still does not reach a sufficient level for making landing tapes needless. According to the present inventors' study, a porous sheet withstanding removal of a fastening tape

herein said polypropylene has an isotactic pendant content (P) and a melt index (MI) satisfying the relationship:

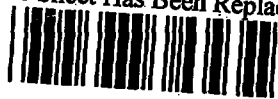
$$1.00 \geq P \geq 0.015 \log MI + 0.955$$

3. The absorbent article as claimed in claim 1, wherein said compound is at least one compound selected from the group consisting of a mineral oil, a synthetic lubricating oil, dioctyl phthalate, diethyl phthalate, triethylene glycol, dibutyl phthalate, and an ester of phthalic acid, trimellitic acid, pyromellitic acid or an aliphatic polybasic carboxylic acid and an alkyl alcohol.

4. The absorbent article as claimed in claim 1, wherein said porous sheet had a moisture permeability of 0.5 to 4.0 g/100 cm²·hr.

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Date: 31 JUL 1997

herein said polypropylene has an isotactic pendant content (P) and a melt index (MI) satisfying the relationship:

$$1.00 \geq P \geq 0.015 \log MI + 0.955$$

3. The absorbent article as claimed in claim 1, wherein said compound is at least one compound selected from the group consisting of a mineral oil, a synthetic lubricating oil, dioctyl phthalate, diethyl phthalate, triethylene glycol, dibutyl phthalate, and an ester of phthalic acid, trimellitic acid, pyromellitic acid or an aliphatic polybasic carboxylic acid and an alkyl alcohol.

4. The absorbent article as claimed in claim 1, wherein said porous sheet had a moisture permeability of 0.5 to 4.0 g/100 cm²·hr.

This is the replacement sheet

Date:

01 SEP 1997

