

Clarke, Modet & C^o
COLOMBIA

SEÑORES
DIVISIÓN DE NUEVAS CREACIONES
SUPERINTENDENCIA DE INDUSTRIA Y COM
E. S. D.

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO



No. 04-022977-00008-0000

Fecha: 2008-02-07 16:01:13 Dep: 2020 NUECREACIONE
Tra: 11 PATENTE/II Lvs: 379 FASENACIONALII
Act: 444 RESPUESTA/REQUE Folios: 19

COD: 008

RE.: SOLICITUD DE PATENTE EN COLOMBIA
EXPEDIENTE N° 04.022.977
TITULO: PELICULAS MULTICAPA MICROPOROSAS Y
METODOS PARA FABRICARLAS
SOLICITANTE: CLOPAY PLASTIC PRODUCTS COMPANY,
INC.
FECHA SOLICITUD: MARZO 12 DE 2004

ASUNTO: CONTESTACIÓN A REQUERIMIENTO OFICIAL

DILIA RODRIGUEZ D'ALEMAN, en mi condición de apoderada de la sociedad solicitante, por el presente escrito doy respuesta a su auto notificado por estado de 28 de septiembre de 2007, para el cual se solicitó prórroga y que vence el día 7 de febrero de 2008 y me permito presentar las siguientes aclaraciones:

CLARIDAD

Como respuesta a las objeciones realizadas en la acción oficial, que objetan la claridad de la invención reclamada, el solicitante presenta nuevo capítulo reivindicatorio, que reemplaza el original que obra en la solicitud, y que ha sido redactado para remediar las incongruencias presentes en las reivindicaciones anexadas anteriormente y de acuerdo con las recomendaciones efectuadas por ese Despacho.

El nuevo capítulo reivindicatorio se ajusta a las disposiciones del artículo 34, toda vez que las modificaciones realizadas limitan la invención y no implican una ampliación de la protección.

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En este sentido, es necesario señalar que las composiciones con olefinas alfa de 4 a 8 átomos de carbono tiene su sustento en la página 26, desde la línea 10 hasta la página 27, línea 19 de la memoria descriptiva. No obstante, es deseo del solicitante restringir el alcance a los componentes homopolímeros de polipropileno, copolímeros de etileno y propileno, poli(etileno-buteno), poli(etileno-hexeno), poli(etileno-octeno), dentro de la reivindicación 2.

Adicionalmente, la mezcla de dos o más de estos polímeros se encuentra debidamente sustentada desde la antigua página 17, línea 27 hasta la página 19, línea 3 de la memoria descriptiva.

En consecuencia, el presente capítulo reivindicatorio **SI** tiene sustento dentro de la descripción de la solicitud en estudio.

Además, el solicitante también le aclara a ese Despacho con relación a la objeción planteada en el punto 1) a) iii) de la acción oficial, que el aparte de "resumen de la invención" **SI** hace mención a películas multicapas, contrario a lo establecido por el señor examinador. En dicho aparte, la presente solicitud menciona que "En una modalidad, la invención se dirige a películas multicapa microporosas que comprenden una primera y una segunda capa microporosa... En una modalidad más específica, la invención se dirige a películas multicapa microporosas que comprenden una primera, segunda y tercera capas microporosas".

Como se puede observar en el párrafo anterior, este aparte no se relaciona únicamente con películas de dos capas, sino que también se mencionan películas multicapas como es el caso de las películas de tres capas.

Adicionalmente, como respuesta a las objeciones realizadas por el señor examinador que se relacionan con los dibujos de la presente solicitud, el solicitante presenta nuevamente dichos dibujos que corresponden con los presentados inicialmente con la solicitud de patente y se presentan tanto de modo electrónico como físico para una mejor visión de los mismos.

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ACERCA DEL EXAMEN DE FONDO

Dado que ahora la solicitud ha sido modificada y un nuevo capítulo reivindicatorio ha sido presentado, se solicita a ese Despacho proceder con el estudio de patentabilidad basado en el último capítulo reivindicatorio anexado.

Agradezco continuar con el presente trámite.

Señor Jefe,

Handwritten signature of Dilia Rodriguez D'Aleman

DILIA RODRIGUEZ D'ALEMAN
ADP/MRO/srch
P-54504

FORMULARIO ÚNICO DE CORRECCIONES Y MODIFICACIONES
2000-10

1) SOLICITUD DE:

☐ Corrección de error material

☒ Modificación a una solicitud

2) SOLICITANTE

Nombre: CLOPAY PLASTIC
PRODUCTS COMPANY

Dirección: 8585 Duke
Boulevard Mason, OH 45040
Estados Unidos

Nacionalidad o Domicilio:
Mason, Ohio, Estados Unidos

Lugar de Constitución: Ohio,
Estados Unidos

Teléfono:
E. Mail:

Fax:

IDENTIFICACIÓN

C.C. ☐ NIT: ☐

C.E. ☐ OTRO ☐

NÚMERO _____

**3) REPRESENTANTE
O APODERADO**

Nombre: DILIA MARÍA
RODRÍGUEZ D'ALEMAN

Dirección: Carrera 11 N°. 86-
53 Piso 6 Bogotá D.C.

Teléfono: 6181088 Fax:
6350824

E. Mail:
info@clarkemodet.com.co

IDENTIFICACIÓN

C.C. ☒ NIT: ☐

C.E. ☐ OTRO ☐

NÚMERO: 41.654.882
TP: 20824 CSJ

4) NUMERO DE EXPEDIENTE: 04022977

5) DESCRIPCIÓN DE LA CORRECCIÓN O MODIFICACIÓN SOLICITADA:

Se presenta nuevo capítulo reivindicatorio y dibujos

6) Comprobante de pago No. 08-5,799 de 22 de enero de 2008

7) Anexos:

☒ Comprobante de la tasa

☐ Poderes, si fuere el caso

☐ Certificado de Existencia y Representación legal, cuando el solicitante sea persona Jurídica

8)

Nombre: DILIA RODRÍGUEZ D'ALEMAN

Firma

C.C.: 41.654.882 TP: 20824 CSJ

REIVINDICACIONES

1. Una película multicapa microporosa, respirable, que comprende una primera capa externa de película, una segunda capa interna de película y una tercera capa externa de película, donde la primera, segunda y tercera capas de película son coextruidas, donde cada capa de película comprende al menos un relleno formador de poro, volviendo cada capa de película microporosa y respirable por medio del estiramiento de la capa de película que tiene el relleno formador de poro, donde la primera y tercera capas externas de película tienen un primero y tercer tamaños de poro máximos, respectivamente, y la segunda capa interna de película tiene un segundo tamaño de poro máximo más pequeño que el primero y tercer tamaños de poro máximos y está formado de una composición de polímero que comprende homopolímero o copolímero de polipropileno, y donde la película multicapa microporosa es impermeable al líquido a presión atmosférica.
2. La película multicapa microporosa de acuerdo a la reivindicación 1, donde la primera y tercera capas de película están formadas de una primera y tercera composiciones de polímero, respectivamente, que consiste esencialmente de uno o más polímeros seleccionados del grupo que consiste de homopolímeros de polietileno, homopolímeros de polipropileno, copolímeros de etileno y propileno, poli(etileno-butenos), poli(etileno-hexeno), poli(etileno-octeno), y mezclas de dos o más de dichos polímeros.

3. La película multicapa microporosa de acuerdo a la reivindicación 1, donde la primera y tercera capas de película están formadas de primera y tercera composiciones de polímero, respectivamente, y la composición de polímero de es una segunda composición de polímero diferente de la primera y tercera composiciones de polímero.
4. La película multicapa microporosa de acuerdo a la reivindicación 3, donde cada capa de película comprende relleno formador de poro de carbonato de calcio.
5. La película multicapa microporosa de acuerdo a la reivindicación 3, donde la primera y tercera composiciones de polímero comprende uno o más de polietileno de densidad ultra baja, baja, lineal baja, media o alta.
6. La película multicapa microporosa de acuerdo a la reivindicación 1, donde la primera, segunda y tercera capas de película comprende un primero, segundo y tercer relleno, respectivamente, y el primero, segundo y tercer relleno son el mismo.
7. La película multicapa microporosa de acuerdo a la reivindicación 6, donde la primero, segundo y tercer relleno comprende carbonato de calcio.
8. La película multicapa microporosa de acuerdo a la reivindicación 1, donde la primera, segunda y tercera capas de película comprenden primero, segundo y tercer rellenos, respectivamente, y el segundo relleno es diferente del primero y tercer rellenos.

9. La película multicapa microporosa de acuerdo a la reivindicación 8, donde el primero y tercer rellenos tienen primero y tercer tamaños promedio de partícula, respectivamente, y el segundo relleno tiene un segundo tamaño promedio de partícula más pequeño que el primero y tercer tamaños promedio de partícula.
10. La película multicapa microporosa de acuerdo a la reivindicación 9, donde la primera capa de película, la segunda capa de película y la tercera capa de película comprenden la misma composición de polímero.
11. La película multicapa microporosa de acuerdo a la reivindicación 10, donde el primero relleno, el segundo relleno y el tercer relleno tienen la misma composición química.
12. La película multicapa microporosa de acuerdo a la reivindicación 8, donde el primero y tercer rellenos tienen composiciones químicas las cuales difieren de la composición química del segundo relleno.
13. La película multicapa microporosa de acuerdo a la reivindicación 8, donde la primera capa de película, la segunda capa de película y la tercera capa de película están formadas de la misma composición de polímero.
14. La película multicapa microporosa de acuerdo a la reivindicación 1, donde la primera y tercera capas de película comprenden primera y tercera cantidad de relleno, respectivamente, y la segunda capa de película

comprende una segunda cantidad de relleno diferente de la primera y tercera cantidades.

15. La película multicapa microporosa de acuerdo a la reivindicación 1, donde una de las primera y tercera capas de película es laminada a una capa no tejida.

16. La película multicapa microporosa de acuerdo a la reivindicación 1, donde la película multicapa es estirada por intermallado de dirección cruzada (DC) y/o de dirección de máquina (DM).

17. La película multicapa microporosa de acuerdo a la reivindicación 1, donde la película multicapa es estirada por intermallado de dirección cruzada (DC) y de dirección de máquina (DM) únicamente.

18. La película multicapa microporosa de acuerdo a la reivindicación 1, donde la película multicapa es estirada por intermallado de dirección cruzada (DC) y por orientación de dirección de máquina (ODM).

19. La película multicapa microporosa de acuerdo a la reivindicación 1, donde la película multicapa es estirada por intermallado de dirección cruzada (DC) y de dirección de máquina (DM) y por orientación de dirección de máquina (ODM).

20. La película multicapa microporosa de acuerdo a la reivindicación 1, donde la película multicapa es estirada por orientación de dirección de máquina (ODM).

255

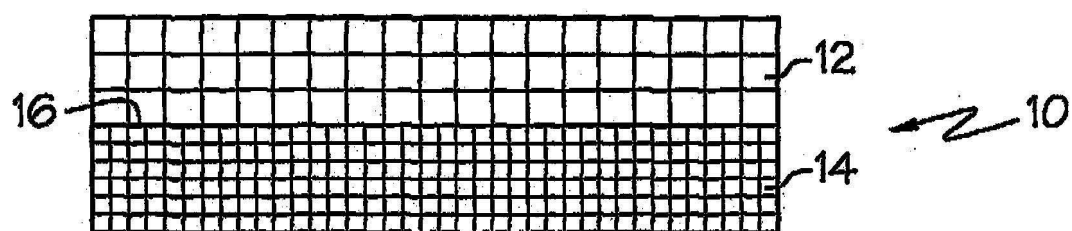


FIG. 1

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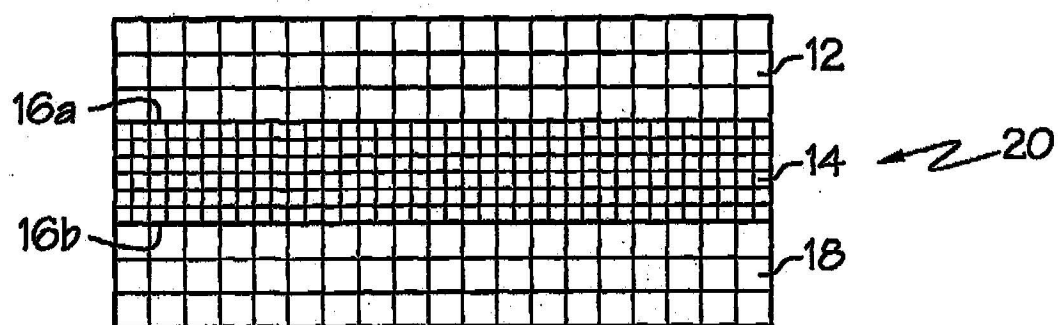


FIG. 2

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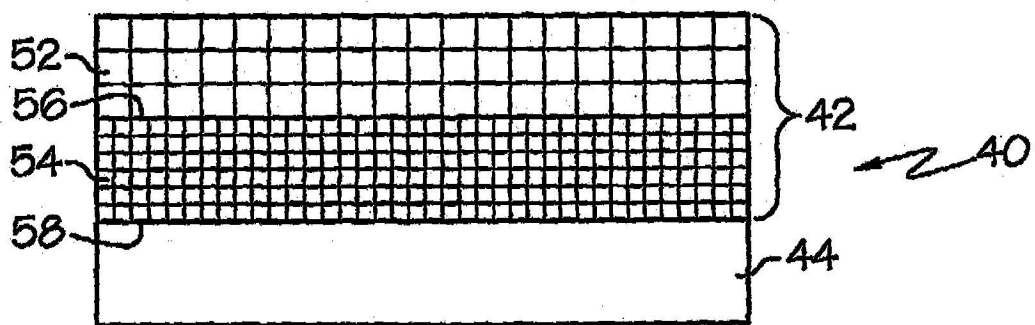


FIG. 3

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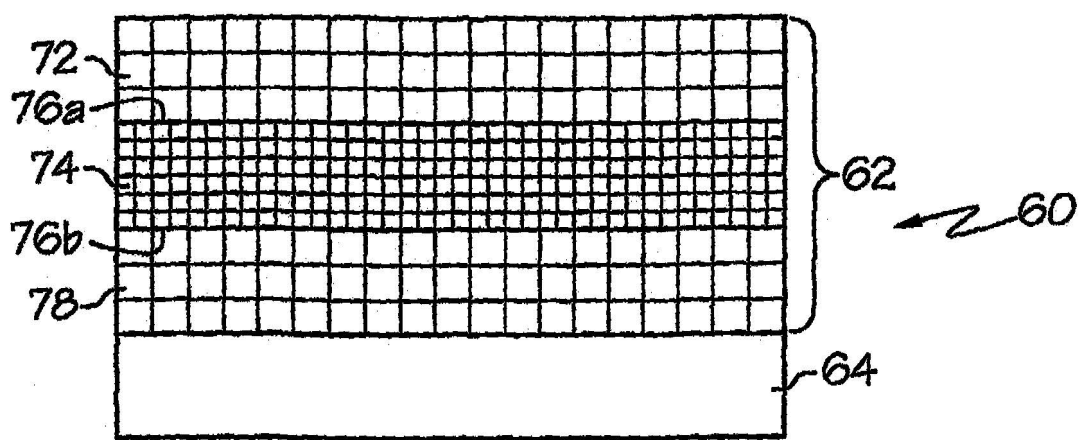


FIG. 4

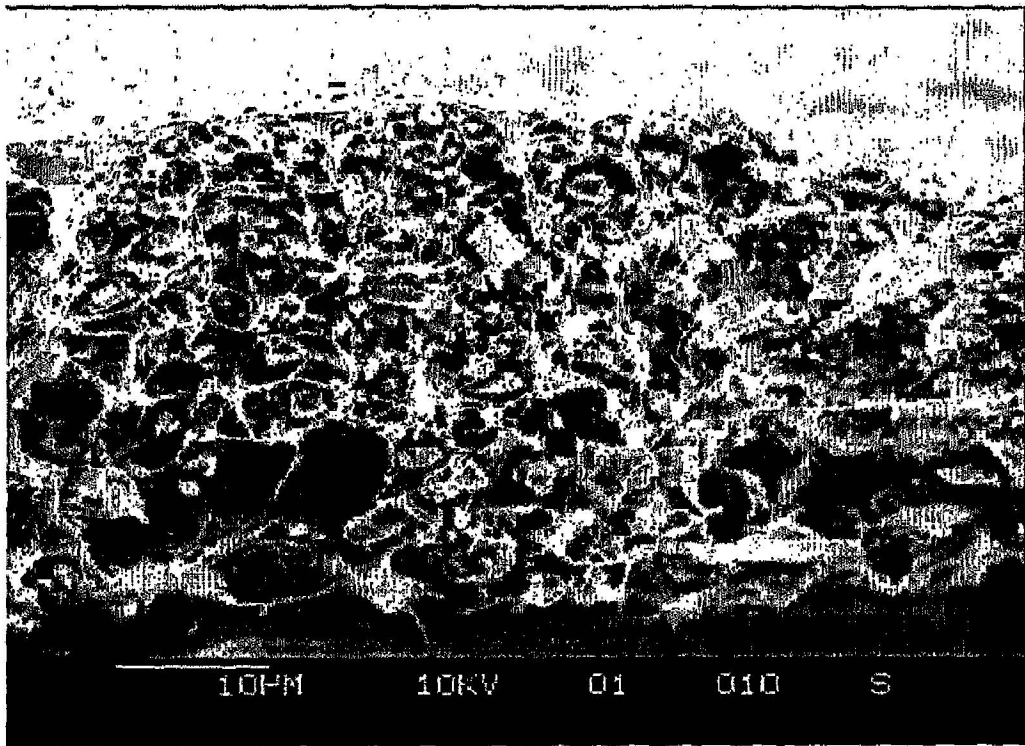


FIG. 5

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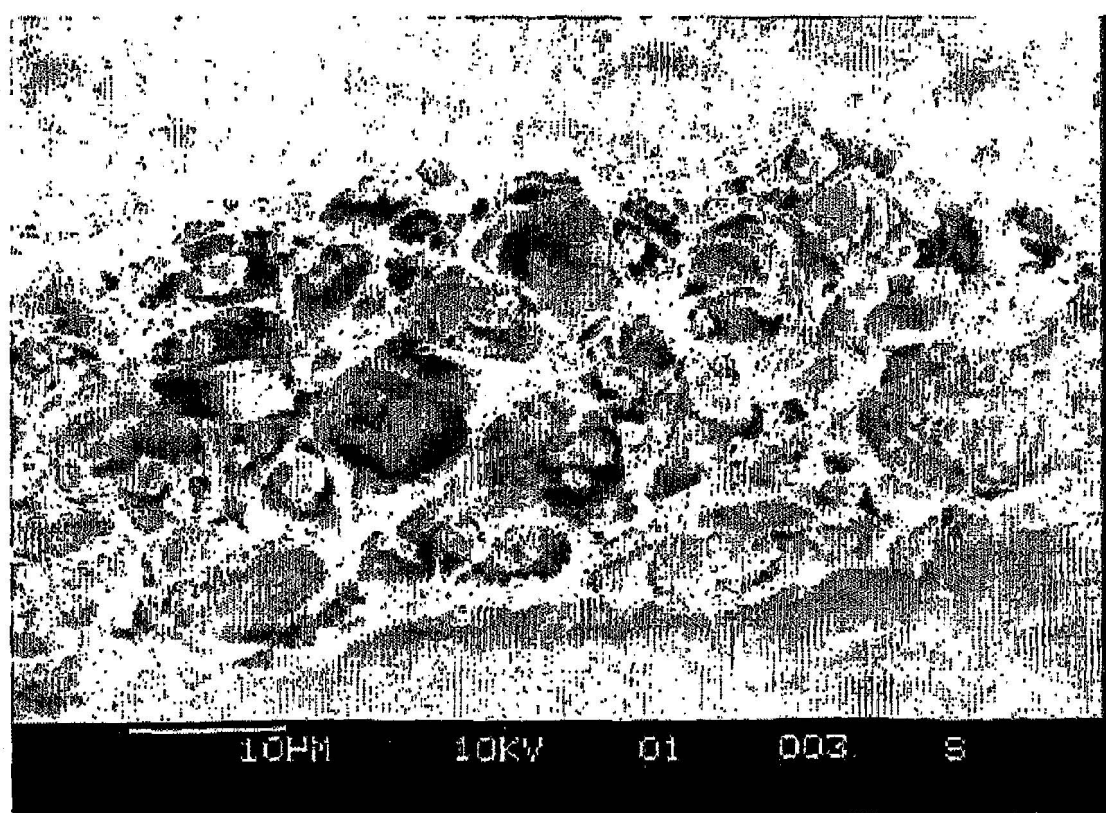


FIG. 6

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO
DIVISIÓN DE NUEVAS CREACIONES

2020
Bogotá, D. C., 11 de mayo de 2009

Doctora
Dilia Rodríguez D'Aleman
Representante **Cloplay Plastic Products Company**

ASUNTO	Radicación	04-022977
	Trámite	002
	Evento	001
	Actuación	430
	Oficio	5 9 3 8
	Folios	045

Patente de Invención ☒ Patente de Modelo de Utilidad ☐

Vía Nacional ☐
Vía PCT (fase nacional) ☒ Cap. I ☐ Cap. II ☒

No. Sol. Internacional **PCT/US02/25706**
Fecha de Presentación Internal. **13 de agosto de 2002**

Como resultado del examen de fondo, realizado con fundamento en el artículo 45 de la Decisión 486 de la Comisión de la Comunidad Andina, se le comunica:

1. Documentos estudiados

- | | | | |
|------|--------------------------|--|--|
| 1.1. | <u>Descripción:</u> | Folios: <u>32 a 74</u>
Folios <u>189 a 227</u> | tal como se radicó inicialmente
tal como se modificó el 29 de agosto de 2007 |
| 1.2. | <u>Reivindicaciones:</u> | Folios <u>75 a 84</u>
Folios <u>237 a 240</u>
Folios <u>228 a 232</u>

Folios <u>251 a 255</u> | tal como se radicó inicialmente
modificación fase Internacional
tal como se modificó el 29 de agosto de 2007
tal como se modificó el 7 de febrero de 2008 |
| 1.3. | <u>Dibujos:</u> | Folios <u>85 a 88</u>
Folios <u>256 a 262</u> | tal como se radicó inicialmente
tal como se modificó el 7 de febrero de 2008 |
| 1.4. | <u>Prioridad:</u> | Fecha 13 de agosto de 2001
País Estados Unidos
Número 60/312006 | |

2. Modificaciones (Artículo 34 D. 486 y Art. 22 Tratado PCT)

Se aceptan las modificaciones realizadas por el solicitante toda vez que no amplían el objeto inicial de la solicitud.

3. Objeto de la invención

- Título de la solicitud *debería ser:* **Películas Multicapa Microporosas**
- Las reivindicaciones 1 a 22 de la solicitud en estudio se refieren a una película multicapa microporosa, respirable **que comprende** una primera capa externa de película, una segunda capa interna de película y una tercera capa externa de película, donde capa de película comprende al menos un relleno formador de poro, volviendo cada capa de película microporosa y respirable por medio del estiramiento de la capa de película que tiene el relleno formador de poro, donde la primera y tercera capas externas de películas tienen un primero y un tercer tamaño de poros máximos, respectivamente, y la segunda capa interna de película tiene un segundo tamaño de poro máximo más pequeño que el primero y tercer tamaños de poro máximo y está formado de una composición de polímero que comprende homopolímero o copolímero de polipropileno y donde la película multicapa microporosa es impermeable al líquido a presión atmosférica.
- El anterior producto busca mejorar las películas microporosa conocidas en la técnica.
- La Clasificación Internacional de Patentes (IPC) para esta solicitud es B32B5/18.

4. Determinación del Estado de la Técnica

- La fecha que se ha tenido en cuenta para determinar el estado de la técnica es 13 de agosto de 2001
- Teniendo en cuenta la fecha indicada se realizó la búsqueda en el estado de la técnica de documentos relacionados con la solicitud encontrándose los siguientes documentos más relevantes:

Nº	Documento	Título	Fecha de publicación
D1	FR 2802849	Multilayered microporous film and procedure for its manufacture	29.06.2001
D2	WO 9960050	High speed method of making microporous film products	25.11.1999
D3	US 6235377	Microporous membrane with a stratified pore structure created in situ and process	2.05.2001
D4	US 6090441	Process for making reinforced three zone microporous membrane	18.07.2000
D5	US 6261674	Breathable microlayer polymer film and articles including same	17.07.2001
D6	US 4863792	Multilayer laminates of microporous films	5.09.1989
D7	US 5536413	Method for treating a parenteral emulsion containing medicament fluid	16.07.1996
D8	US 6264044	Reinforced three zone microporous membrane	24.07.2001
D9	US 5955187	Microporous film with liquid triggered barrier feature	21.09.1999

Nº	Documento	Título	Fecha de publicación
D10	US 6045900	Breathable filled film laminate	4.04.2000
D11	US 6114024	Multilayer breathable film	5.09.2000
n.	Varios documentos más		

5. Análisis de patentabilidad (Artículo 14 D. 486)

El solicitante pretende que se le proteja una película multicapa microporosa, respirable que comprende:

- una primera capa externa de película,
- una segunda capa interna de película y
- una tercera capa externa de película,
- donde capa de película comprende al menos un relleno formador de poro, volviendo cada capa de película microporosa y respirable por medio del estiramiento de la capa de película que tiene el relleno formador de poro,
- donde la primera y tercera capas externas de películas tienen un primero y un tercer tamaño de poros máximos, respectivamente, y la segunda capa interna de película tiene un segundo tamaño de poro máximo más pequeño que el primero y tercer tamaños de poro máximo y
- está formado de una composición de polímero que comprende homopolímero o copolímero de polipropileno y donde la película multicapa microporosa es impermeable al líquido a presión atmosférica.

El documento francés, D1, relaciona una película multicapa microporosa con al menos tres capas poliolefinicas (dos externas y al menos una interna) que son impermeables a los líquidos, cada capa es fabricada con homopolímeros o copolímeros que pueden ser de polipropileno. La capa intermedia (llamada B en dicho documento) contiene rellenos formadores de poro (ver página 11); las capas exteriores (A y C en dicho documento) también pueden ser polímeros poliolefinicos y en algunos casos pueden ser de polipropileno (ver páginas 13 y 14) e incorporan también rellenos que en el procedimiento de formación de película forman microporosidades. Como se desprende de lo anterior, el documento D1 posee en esencia todos los elementos enumerados en la reivindicación principal de la solicitud colombiana.

El documento D2 relaciona un procedimiento de fabricación de una película microporosa que incorpora poliolefinas con rellenos. Si bien no relaciona todos los elementos de la solicitud colombiana, si es evidente para una persona versada en la materia considerar partir de dicho conocimiento para llegar a la mencionada solicitud colombiana.

De la misma forma, cada uno de los documento D3 a D11 por aparte relaciona películas multicapa microporosas en las que in situ se fabrican dichos microporos.

De lo anterior se tiene que la presente solicitud carecería de los requisitos de patentabilidad para que se le conceda el privilegio solicitado.

6. Conclusión:

Los requisitos de patentabilidad de la presente solicitud se encuentran afectados así:

Nº	Documento Nº	Reivindicaciones afectadas	Requisito que afecta
D1	FR 2802849	1 - 22	Novedad
			Nivel inventivo
D2	WO 9960050	1 - 22	Nivel inventivo
D3	US 6235377	1 - 22	Novedad
			Nivel inventivo
D4	US 6090441	1 - 22	Novedad
			Nivel inventivo
D5	US 6261674	1 - 22	Novedad
			Nivel inventivo
D6	US 4863792	1 - 22	Novedad
			Nivel inventivo
D7	US 5536413	1 - 22	Novedad
			Nivel inventivo
D8	US 6264044	1 - 22	Novedad
			Nivel inventivo
D9	US 5955187	1 - 22	Novedad
			Nivel inventivo
D10	US 6045900	1 - 22	Novedad
			Nivel inventivo
D11	US 6114024	1 - 22	Novedad
			Nivel inventivo

En cumplimiento del artículo 45 de la Decisión 486 de la Comisión de la Comunidad Andina, se le indica que debe dar respuesta dentro del término de SESENTA días contados a partir de la fecha de notificación de la presente comunicación. En caso de no dar respuesta al presente requerimiento, o si a pesar de la respuesta subsistieran los impedimentos para la concesión, se denegará la patente.

Notifíquese el presente oficio conforme a lo dispuesto en el numeral 5.2, literal e), del capítulo quinto del título primero de la Circular Única Nº 10 de 2001.


Alix Carmentza Céspedes De Vergel
 Jefe de División de Nuevas Creaciones

Concepto Técnico No. **1504**

Examinador Técnico **202003**

El anterior requerimiento fue notificado por fijación en lista, de fecha

12 2 MAYO 2009

2802849

19: REPUBLIC OF FRANCE
NATIONAL INSTITUTE OF
INTELLECTUAL PROPERTY
PARIS

11 Publication No.: 2 802 849
(use only for reproduction requests)
21: National Registration No.:
89 16588
51: Int Cl.: B 28 C 47/06, B 32 B 27/32,
31/30, A 61 F 13/514, A 61 L 15/22

12 PATENT APPLICATION

A1

22 Filing Date: 28 December 1999
30 Priority:

43: Date of publication of the
application: 29 June 2001, Bulletin
01/26

56: List of documents cited in the
preliminary search report:
Appended at the end of this
application

60: References to other related
national documents:

71: Applicant(s): **TRIOPLANEX
FRANCE, Société Anonyme - FR.**

72: Inventor(s): **GUSTAFSON BO.**

73: Owner(s):

74: Counsel: **IXAS CONSEIL**

FR2 802 849 - A1

54: MULTILAYERED MICROPOROUS FILM AND PROCEDURE FOR ITS
MANUFACTURE

57:

The invention concerns a method of manufacture of a multilayered polyolefinic film that is impermeable to liquid but permeable to gas by coextrusion and drawing of at least three polyolefinic layers, according to at least one structure "A", "B", "C", or "A", "B", "A" or "C", "B", "C", whereby "A" is a skin layer, "B" is a central layer, and "C" is a skin/adhesion layer, in which:
-Skin layer "A" contains at least one thermoplastic polyolefinic copolymer and/or one grafted polyolefinic polymer, with a module E below 50 mPa (ASTM no. 882), fluidity between 1.5 and 10 g/10 min (ASTM D 1238 at 190°C and 230°C) and a water vapor transmission speed of at least 100 g/m²/24h at 38°C and 90% relative humidity;
-The central layer "B" has at least one homopolymer and/or one thermoplastic polyolefinic, at least one particle filler, and, in some cases, on or more elastomers;
-The skin/adhesion layer "C" contains at least one adhesion bonding agent and/or one thermoplastic polyolefinic homopolymer and/or copolymer, and at least one particle filler.

2802849

Multilayered Microporous Film and Procedure for its
Manufacture

Scope of the Invention

The invention concerns a procedure for the manufacture of a multilayered, microporous film, impermeable to liquids but permeable to air, specifically to water vapor.

More specifically, the invention concerns a procedure for the manufacture of a multilayered, microporous film that is impermeable to liquids, but permeable to water vapor, by coextrusion of thermoplastic compounds, consisting of mixtures of olefinic polymers and/or copolymers, and, in some cases, particle fillers, with every layer of said film having a specific composition.

The invention additionally concerns a blow-over film with a multilayered, microporous structure, that is impermeable to liquids and permeable to water vapor, as well as the rolled products that associate said film to at least one unwoven fabric, and disposable hygienic products, such as diapers for infants, for incontinent adults, or feminine hygiene products, making use of said microporous film and/or the rolled product.

State of the Art

The films obtained using polymers are naturally impermeable to liquids and to water vapor. They constitute a veritable barrier to these materials. When these barrier films are used as components of disposable sanitary products, such as diapers for infants or incontinent adults, or feminine hygiene products, they can cause skin irritation, a certain degree of discomfort, as the moisture cannot escape from the product when it is in use. Thus, there have been particular research efforts in the area of films to be used in diapers for infants and for incontinent adults, as well as in feminine hygiene products, focusing on the breathability of the film, its tactile feel, particularly for the external film (backsheet).

Several procedures have been developed for the manufacture of polymer films that are impermeable to

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water but permeable to water vapor (gas permeability) with a heightened transmission speed.

These procedures, for the most part, have succeeded in producing films that are breathable (due to their gas permeability), making use one or the other means that allows the physical creation of microporosity in said films, or using specific polymers, such as hydrophilic polymers, the chain structures of which facilitate both the absorption of water vapor and gas transfer.

The microporosity of films produced by known art methods may be obtained in numerous ways, including, e.g., mechanical microperforation.

However, the most frequently used method for manufacturing microporous films consists of first making use of a mixture of polymers and mineral fillers that is extruded (or blow extruded) in the form of a precursor film, then, in the second step, subjecting the film to longitudinal and/or drawing at a lower temperature than the fusion point of the polymer mixture, in order to create multiple pores or micro-holes.

Some such pores (or micro-holes) have diameters sufficiently small to prevent the passage of liquids, while permitting the transfer of gas (water vapor) at transmission speeds ranging from the most moderate to very high.

The scope of properties set by the polyolefin-based systems indicates that procedures and raw materials play a critical role in the determination of the profile of final properties. Electron microscopic micrography allows for the illustration, for example, of the differences in the shape of the pores in uniaxially or biaxially drawn films.

The test, which consists of determining the transmission speed of water vapor, is a means of measuring the breathability of the film, i.e. the mass or volume of gas transferred through the thickness, per unit of surface and unit of time, in well-defined environmental conditions.

In addition, gas-permeable (breathable) films that are impermeable to liquids can have a unilayer structure, or, more recently, a multilayered structure. The multilayered films are well known in the area of airtight food packaging. These multilayered films have the purpose of combining different families of mutually incompatible polymers, which, for this reason, require the presence of polar functional polymers in order to be assembled into a film. These multilayered films can be obtained both by a procedure consisting of coextrusion (direct or simultaneous) of all layers, followed by drawing them, and by a procedure of assembly by rolling of multiple layers (previously extruded or drawn), or by a procedure of extrusion coating on an existing layer, such as an unwoven fabric, followed by drawing.

Examples of such multilayered films that are breathable but impermeable to liquids have been described in numerous documents.

Patent US 5,164,258 describes a multilayered film that is permeable to water vapor, which features external layers produced in a microporous hydrophobic polymer material and a core layer made of hygroscopic polymer material, which, when dry, shows a very substantial oxygen-barrier capacity, but which loses this property when moist. This multilayered film also features adhesive layers placed between the external layers and the core layer. This patent provides that the water vapor transmission speed for the external layers must be approximately 500 g/m²/24h, in order to be able to evacuate the moisture resulting from sterilization treatment. Thus, the multilayered film is specifically adapted for application to packaging (requiring an oxygen barrier), and cannot be used in the area of sanitary applications or hygiene.

Patent US 4,828,556 describes a multilayered structure consisting of a breathable film made of polymer materials, forming a barrier to liquids, placed between two layers of microporous unwoven fabrics. This structure includes a porous sheet, coated by a polyvinyl alcohol film or rolled with a previously manufactured polyvinyl alcohol film.

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No supplementary adhesivity is necessary, as the polyvinyl alcohol film acts simultaneously as both an adhesive layer and as a water vapor-permeable layer.

Patent US 4,758,239 also describes a breathable multilayered structure that forms a barrier to liquids, which features a first layer made of porous unwoven fabric and a second layer connected to one of the surfaces of the first layer. This second layer is formed by a continuous film, obtained by coating with a water-soluble polymer material: this film is not microporous in the sense that it does not feature a substantial number of pores, but it can be traversed, through its thickness, by water molecules because such water molecules are removed in the polymer material.

Instead of a film obtained by coating, the continuous film may be a previously formed film, obtained by means of a water-soluble polymer material, rolled with the first layer of said structure, made of a porous unwoven fabric. In a preferred form, the water-soluble polymer material is a polyvinyl alcohol.

These various multilayered structures are obtained by means of families of different polymers in the various layers. The polyvinyl alcohols are known to be difficult to more transform than polyolefins.

The international patent application n W097/04955 describes a method of obtaining a breathable film with a symmetrical multilayered structure. The structure of this breathable film features, specifically, five layers. The first is the central layer. Two others are skin layers, and the two last layers are adhesion layers between the skin layers and the central layer. These different layers are obtained by means of two different families of polymers

- The central layer is made of a mixture of polyolefins and mineral fillers,
- The skin layers are made of hydrophilic polymer materials that are substantially free of mineral fillers,
- The intermediate adhesion layers are composed of a mixture of (recycled) polymers originating in the layers that constitute the skin and the core of the

breathable film, in order to allow for these three layers to adhere to each other.

All these methods for the manufacture of multilayered films present substantial problems (of manufacture), certain of which are mentioned below.

- First of all, hydrophilic, or water-soluble, polymers, used as raw material for the manufacture of an impermeable but breathable film, have a very high economic cost, compared to polyolefins, which are simultaneously used in the structure of said film;
- Secondly, these symmetrical multilayered structures are not specifically designed to allow for different assembly, as their design is essentially oriented on the search for maximum breathability;
- Moreover, it is also known that coextrusion procedures for the manufacture of a multilayered film are technically critical, and difficult to adjust, due to the deviations in viscosity that exist among the different families of polymers of which the various layers are made;
- Finally, the coextrusion procedures for the manufacture of a multilayered film are difficult to carry out when, for productivity reasons, they must be carried out rapidly.

Objectives of the Invention

Thus, the invention pursues a number of objectives with a view to eliminating the aforementioned problems. Throughout the description of the object of the invention, the gas permeability of the film shall be expressed in terms of the permeability of said film to water vapor.

A first object of the invention is the creation of a method of manufacture of a multilayered film that is impermeable to liquids and permeable to water vapor, which operates at high production speeds, and which uses polyolefins as components of the various layers.

Another object of the invention is the creation of said method of manufacture of a multilayered film that is impermeable to liquids but permeable to water vapor

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through multilayered coextrusion, in such a manner as to allow for great ease of adaptation of the architecture of the various layers. More specifically, the creation of an asymmetric architecture of the layers of the structure is an objective of the invention, in order to incorporate in the multilayered means of adhesion for different assembly of said film with other structures, including, e.g., unwoven fabric.

Another object of the invention is

- The optimization of the method of coextrusion manufacture of the multilayered film that is impermeable to liquids but permeable to water vapor, due to specific compositions of skin layers, viscosities of component materials of layers that are well adapted for said layers (for higher speeds and given temperatures), excellent compatibility among the layers, and
- Reduction of the risks of build-up of the polymer materials at the nozzle, thus reducing the frequency of user intervention for cleaning.

Another object of the invention is the elimination of all volatile materials present (humidity, air, or others) in the mixtures of raw materials, which could be released by heating, during extrusion, and which could disturb the controlled formation of the pores of the various layers of the microporous film.

Another object of the invention is the optimization of the breathability of the multilayered film, i.e. the speed of transmission of water vapor for the final structure, while keeping the film impermeable to liquids.

Another object of the invention is the creation, by said method, of a multilayered blow-over film that is impermeable to liquids and permeable to water vapor, which, however, is sufficiently tear-resistant to allow it to be used as the backsheet in diapers for infants and incontinent adults, and feminine hygiene products, assembled by rolling with an unwoven fabric, with the resultant rolled product used in the aforementioned products.

Summary of the Invention

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The invention concerns a method of manufacture of a multilayered polyolefinic film that simultaneously has the properties of permeability to water vapor and impermeability to liquids, which method includes the steps of:

- Simultaneous extrusion, through a nozzle, of at least three layers composed of thermoplastic polymer materials, forming a precursor film with at least the following structure: "A", "B", "C", or "A", "B", "A", or "C", "B", "C", whereby "A" is a skin layer, "B" is a central layer, and "C" is a skin/adhesion layer;
- The drawing of the coextruded multilayered precursor film to form the multilayered film permeable to water vapor but impermeable to liquids.

in which:

- The skin layer "A" contains at least one thermoplastic polyolefinic copolymer and/or a grafted polyolefinic polymer, which has an E module lower than 50 MPa (ASTM standard no. 882 - 15 micron cast film) a fluidity measure by the Melt Flow Index (MFI, ASTM standard D1238 2.16 kg, 190 C for polyethylenes and 230 C for polypropylenes) between 1.5 and 10 g/10 min, and a water vapor transmission speed of at least 100 g/m²/24h at 38 C and 90 % relative humidity;
- The central layer "B" contains at least one homopolymer and/or a thermoplastic polyolefinic copolymer, at least one specific filler, and, in some cases, one or more elastomers;
- The skin/adhesion layer "C" contains at least one adhesive binding agent and/or one homopolymer and/or thermoplastic polyolefinic copolymer, and at least one particle filler.

The invention also concerns a multilayered blow-over film that is permeable to water vapor and impermeable to liquids, used both alone and assembled by rolling together with an unwoven fabric, as a backsheet for disposable sanitary products, for infants, incontinent adults, and for feminine hygiene products.

Detailed Description of the Invention

According to the invention, the extrusion step, in the course of which the precursor film is formed, includes the simultaneous coextrusion of at least three layers, "A," "B," and "C," the thickness of each of which, expressed in terms of the percentage of the total thickness of the breathable multilayered film, are the following:

- from approximately 5% to approximately 30% of thickness for layer "A,"
- from approximately 40% to approximately 90% of thickness for layer "B," and
- from approximately 5% to approximately 30% of thickness for layer "C."

Said layers "A," "B," and "C" are entirely composed of polyolefinic materials.

Central layer "B"

According to the invention, central layer "B," which is made microporous by drawing, is formed by at least one homopolymer and/or one polyolefinic copolymer and at least one particle filler, and, in some cases, one or more polyolefin-based elastomers. These homopolymers or copolymers are chosen from the group made up of homo- and/or copolymeric polyethylenes, preferably low-density linear polyethylenes and/or homo- and/or copolymeric polypropylenes.

When homo- or copolymeric ethylene polymers are used, they are chosen from among those which have a density between 0.915 (kg/m³) and 0.965 (kg/m³) (ASTM standard 1505, density expressed in kg/m³), and preferably in the lower-density range of 0.915 (kg/m³) to 0.935 (kg/m³).

Low-density linear polyethylenes have a density between 0.890 (kg/m³) and 0.940 (kg/m³), and can be chosen from the group of ethylene copolymers and alpha-olefinic comonomers such as those from C₄ to C₁₀, which can be obtained, e.g., via catalytic polymerization in the presence of a catalyst, such as a metallocene, or by other methods. These comonomers from C₄ to C₁₀ are chosen, preferably, from the group consisting of butene-

1, pentene-1, hexene-1, 4-methylpentene-1, heptene-1, and octane-1.

The homo- or copolymeric propylene polymers include propylene homopolymers, propylene copolymers with ethylene, and propylene copolymers with alpha-olefinic comonomers from C₄ to C₁₀. For the propylene copolymers, one or more alpha-olefinic comonomers can be used. The alpha-olefinic propylene copolymers must have an alpha-olefin content of between 0.1 and 40% by weight. When using polypropylene copolymers, they are preferably to be chosen from the group of ethylene-propylene copolymers.

The polymers and/or copolymers of central layer "B" are chosen in such a way as to maintain a fluidity index based on the Melt Flow Index (MFI) between 0.2 and 15 g/10 min, measured based on a reference load of 2.16 kg, a reference temperature of 190 C for polyethylenes and 230 C for polypropylenes, with a standard orifice (ASTM standard D 1238).

For the cast process, the fluidity index can vary from 0.8 to 15 g/10 min, and for the blown process, from 0.2 to 10.0 g/10 min.

However, the central layer "B" is preferably manufactured from a linear polyethylene with weak density.

All these polymers or copolymers can be formulated with slip agents and anti-blocking agents, as well as with antioxidants and stabilizers.

According to the invention, the central layer "B" contains at least one particle filler of 30 to 80% weight, and preferably from 45 to 55% of the total weight of said particle filler and the polymer material.

These particle fillers known in the state of the art can come from all organic or non-organic materials with a weak affinity for water by nature or obtained by appropriate treatment, and a rigidity by opposition to the elasticity of the polymer material.

The organic particle fillers can include, for example, polymers with a high fusion point and/or a high viscosity, and particles with a size compatible with the drawing step of the procedure. Such polymers include, by

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way of example, polyethylenes, polypropylenes, polyamides, polyesters, and polyurethanes with high density and an extremely high molecular weight.

Non-organic particle fillers can include metal salts, such as barium carbonate, calcium carbonate, magnesium carbonate, magnesium sulfate, barium sulfate, calcium sulfate; metal hydroxides, such as aluminum hydroxide, magnesium hydroxide; metal oxides, such as calcium oxide, magnesium oxide, titanium oxide, titanium dioxide, and zinc oxide, or other particulate materials, such as clay, kaolin, talc, silica, diatomic earth, glass powder, mica, aluminum, and zeolites.

The non-organic particle fillers are preferably chosen from the group made up of calcium carbonate, barium sulfate, silica, alumina, kaolin, and talc.

Calcium carbonate is especially preferable due to its economic cost, its whiteness, its inertia, and its availability.

Non-organic particle fillers (such as calcium carbonate) can be surface treated in order to make them hydrophobic, and to improve the bond between the filler and the polymer. Calcium stearate, which is used in food, is a preferred coating. However, other coatings are possible.

Although the quantity of particle fillers inserted in central layer "B" has already been mentioned above, it is desirable to state more precisely the reasons for the weight percentage limitations mentioned above.

The quantity of particle fillers added to the polyolefins depends on the desired properties of the breathable film, which must have, *inter alia*, good tear resistance, sufficient water vapor transmission speed, as well as sufficient elasticity. However, it appears that a film cannot be sufficiently breathable when it is manufactured with a quantity of fillers below approximately 30% by weight of the polyolefin-filler compound. Thus, the minimum quantity of 30% by weight is necessary to ensure the creation of useful microporosity in the film during drawing. Furthermore, it appears that films cannot be used with a quantity of fillers greater than approximately 80% by weight of the polyolefin-filler

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compound, because larger quantities of fillers can cause problems during mixing, and cause significant losses in breathability for the film.

This is why the quantity of particle fillers in the composition of the layers according to the invention must be between approximately 30% and 80% by weight, based on the total weight of the polymer material and the filler. The mean diameters of the particle fillers used in the invention are chosen between 0.5 and 5 microns, preferably between 0.8 and 2.2 microns for the central layer "B," for films with a thickness between 20 and 100 microns before drawing.

The polymer materials and fillers used in this invention can be mixed by various known art methods.

According to the invention, the elastomers used in central layer "B" are chosen from the group made up of ethylene-propylene rubbers (EPR); modified ethylene-propylene-diene (EPDM), styrene-butadiene-styrene (SBS), styrene-ethylene-butadiene-styrene (SEBS) rubbers; styrene-butadiene (SBR), styrene-isoprene-styrene (SIS) rubbers; butyl rubbers (BR); nitrile rubbers (NBR), hydrogen-nitrile-butyl rubbers, and polyvinyl acetate; or used accordingly with a mixture (either in a reactor or by extrusion) of polyethylene and/or semi-crystalline propylene with at least one other elastomer, such as, e.g., polyethylene/ethylene-propylene rubber (PE/EPR), modified polyethylene/rubber modified ethylene-propylene-diene (PE/EPDM). It is also possible for the elastomeric fraction to be partially or completely reticulated, or for it to belong to the polypropylene (homopolymer) group with amorphous, semi-crystalline blocks and copolymers of propylene/ethylene or alpha-olefin with amorphous, semi-crystalline blocks.

All these polymers or copolymers can be formulated by introduction of various agents, such as slip agents, anti-blocking agents, antioxidants, and stabilizers.

According to the invention, as the central layer "B" is the thickest, and as it is not in contact with the lips of the nozzle, it can be used to recycle the waste material from multilayered material recovered during the procedure, before drawing or after drawing, or

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potentially after the assembly stages. The quantity of multilayered materials recycled in the central layer "B" can vary from 0 to 30% by weight, and is preferably between 0 and 15% by weight.

Skin Layer "A"

According to the invention, the microporous skin layer "A" consists of at least one polyolefinic copolymer with a module E of less than 50 mPa (ASTM 882). This copolymer is chosen from the group consisting of ethylene- and/or grafted polyolefinic polymer-based polar copolymers.

Some such polar copolymers and grafted polyolefinic polymers show differing levels of crystallinity from those of the homopolymer versions: they present greater water vapor transfer properties and improved tactile softness for the layer referred to as "A."

The gas and water vapor permeability of said layer "A" is measured by the water vapor transmission speed (expressed in g/m²/24 hours at a given temperature and a given relative humidity, e.g. at 38 C and 90% for a given thickness).

The tactile softness properties are measured (according to the tactile test ASTM D882) by a module E, which must be below 50 mPa.

The polar ethylene copolymer used in the manufacture of layer "A" is a copolymer composed of ethylene and at least one polar comonomer chosen from the group made up of the family of vinyl esters, and the family made up of the acrylic and methacrylic acids and esters. In a preferred method, the polar comonomer can be chosen from the group made up of vinyl acetate, vinyl propionate, acrylic acid, methacrylic acid, and their esters, as well as acrylates with 4 to 8 carbon atoms, such as methyl acrylate, ethyl acrylate, n-propyl acrylate, isopropyl acrylate, n-butyl acrylate, t-butyl acrylate, isobutyl acrylate, and methacrylates with 4 to 8 carbon atoms, such as n-propyl methacrylate, isopropyl methacrylate, n-butyl methacrylate, t-butyl methacrylate, and isobutyl methacrylate. One or more of these comonomers can be used simultaneously.

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The ethylene copolymers and at least one polar comonomer consist of at most 30% by weight of comonomer. A comonomer content of more than 30% by weight, copolymerized with ethylene, causes odor and adhesion problems.

The ethylene copolymers and at least one polar comonomer must have a fluidity index between 1 and 10 g/10 min in standard conditions (MFI standard ASTM D 1238 - 2.16 kg - 190°C).

The grafted polyolefinic polymers used in the manufacture of layer "A" can be manufactured by chemical grafting by means of acrylic acid, methacrylic acid, maleic anhydride, and alkyl acrylates and methacrylates in which the alkyl is a hydrocarbon chain from C1 to C8.

The fluidity index of such grafted polymers is within the same range of the aforementioned polar copolymers.

All these polymers or copolymers can contain slip agents and anti-blocking agents, as well as antioxidants and stabilizers.

Skin/Adhesion Layer "C"

According to the invention, the skin/adhesion layer "C," which will become microporous by drawing, includes at least one adhesive binding agent and/or a homopolymer and/or a thermoplastic polyolefinic copolymer, and at least one particle filler.

These polyolefinic polymers are chosen from the group made up of polyethylenes, and preferably low-density linear polyethylenes and/or polypropylenes and/or ethylene-propylene and ethylene and alpha olefin copolymers.

The polyolefinic homopolymer and/or copolymer components of the microporous skin layer "C" are low-density linear polyethylenes, with densities between 0.880 (kg/m³) and 0.940 (kg/m³), ethylene copolymers and alpha-olefinic comonomers, such as those in C4 to C10 and/or a polyethylene with density between 0.915 (kg/m³) and 0.965 (kg/m³), preferably between 0.915 (kg/m³) and 0.935 (kg/m³), and/or a polypropylene, and a propylene or

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ethylene copolymer, preferably chosen from a group of aleatory-block copolymers.

The current market evolution leads to more functional requirements for such breathable films that are impermeable to liquid, and include a coating that is soft to the touch and the ability to be assembled on unwoven fabrics. As in the majority of cases, the microporous films have a modest capacity for extension and too weak a resistance to tearing. They are frequently combined with a substrate that can be, for example, an unwoven fabric.

According to the invention, the adhesive/bonding agent present in the skin/adhesion layer "C" is chosen from the group of ethylene copolymers polar or nonpolar comonomers, propylene copolymers, and polar or nonpolar comonomers, and/or grafted (ethylene- or propylene-based) homopolymers or copolymers.

The nonpolar copolymers can be chosen from the group of elastomers, described above for central layer "B." the adhesive/bonding agent is introduced into the composition of said layer at a ratio of 2 to 20%, preferably 5 to 15% by weight.

The polar copolymers can be chosen from the group described above for the skin layer "A."

According to the invention, the skin/adhesion layer "C" includes 30 to 80% by weight, and preferably 45 to 55% by weight in particle fillers.

These various fillers, mentioned above for layer "B," include organic and mineral fillers, but are preferably selected from the group of mineral fillers that includes calcium carbonate, barium sulfate, silica, alumina, kaolin, talc, with particular preference for calcium carbonate. The average diameters of the particle fillers are between 0.2 and 3 microns, and preferably 0.8 and 1.5 microns for the skin/adhesion layer "C," in order to give the narrow gauge to the extremity of said layer "C."

The addition of white TiO_2 (or other pigments) is possible in any layer "A," "B," or "C."

All these polymers can be formulated by known art methods for better thermal stabilization.

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Coextrusion Procedure and Method of Manufacture of A Breathable Multilayered Film

The multilayered precursor film is extruded in a nozzle and affixed onto the cooling wheel by means of a vacuum box and/or an air-knife. The multilayered precursor is then reheated and drawn between at least two systems of drawing wheels (primary and secondary). A thermal stabilization stage is integrated into the manufacturing line, in order to release the tensions created in the film during the drawing stage.

Another stamping stage and a stage of embossing of the film can also be included in the invention.

Coextrusion Procedure / Cast Film

As stated above, the procedure consists

- of the simultaneous coextrusion of at least one precursor film with three layers from a nozzle, said precursor film having, at a minimum, the following structure: "A", "B", "C", or "A" "B", "A", or "C" "B" "C," with "A" being a skin layer, "B" a central layer, and "C" another binding skin layer, and of subsequently drawing said coextruded multilayered precursor film, in order to form the breathable multilayered film, creating micropores in the central layer and the skin layers, the various layers being formulated to allow for the creation of microporosity that allows for the passage of water vapor, but substantially impedes the passage of liquids.

Conventional methods of manufacture of multilayered or sheet films can be easily modified in order to allow for the use of the invention. Thus, the multilayered film can be obtained using a coextrusion line for a cast film, or a coextrusion line for a blown cast film.

For the cast film coextrusion procedure, the fusion temperature of the polymer material can be adjusted between approximately 200 C and 250 C, in accordance with the adjustment of the nozzle temperature.

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According to the present invention, the multilayered precursor film can be coextruded and affixed to a cooling wheel by an air-knife and/or a vacuum box, as described above. The multilayered precursor film is rapidly cooled. The temperature of the multilayered precursor film, when the cooling wheel is removed, is between 15 C and 60 C.

Coextrusion Procedure for Blown Cast Film

The breathable multilayered film can also be manufactured on a blown-cast coextrusion line. The fused polymer is extruded through a multilayered annular nozzle, then blown into a bubble, which is cooled by air via an air ring.

The fusion temperature of the polymer material can be between 150 C and 240 C.

The height of the cooling line (the cooling line corresponds to the change in dry foam resulting from the solidification of the fused polymer) is an important parameter to control. The height of the cooling line is normally between 10 and 80 cm from the nozzle surface.

Another parameter in the procedure that must be controlled is the blow proportions corresponding to the relationship between the diameter of the bubbles and the diameter of the nozzle: these blow proportions control the orientation of the direction traversed. These blow proportions vary normally from approximately 1.5 to 4.0.

The bubble is subsequently folded in order to form a flat film, layered and wound on a wheel or split and wound on two separate wheels.

The line speed is between 20 and 150 m/min for a 100 to 20-micron precursor film.

The precursor film is then drawn, in a similar manner to the stage described in the technology for the extrusion of a multilayered cast film.

Build-up in the Nozzle

When a single-layer film with particle fillers is extruded, the filler material moves on the lips of the extruder nozzle, blocking the extrusion procedure.

Depending on the temperature, the shape of the nozzle, the opening of the nozzle, the nozzle, the length of the lip of the nozzle, and the composition of polymers and particle fillers to be extruded, the nozzle-level movement will affect the aspects of the film and create grooves that reduce the strength of the film. For polymer compositions that include a very high quantity of fillers, after a few hours of use, the movement on the extruder nozzle is such that the extruder must be stopped, and the build-up residue must be mechanically removed from the lips of the extruder. Such a stop for this type of procedure is very expensive and time-consuming. Thus, the multilayered films that, when extruded, cause less build-up on the lips of the nozzle, are particularly in demand. In order to minimize or eliminate this phenomenon, it appears desirable for the skin layer not to have any particle filler, and for the humidity levels and amounts of volatile materials in the materials used to be closely controlled; if a high humidity and volatile materials in the fused polymer are simultaneously present, the phenomenon of build-up on the nozzle will accelerate and become a significant disturbance.

Thus, as mentioned above, one of the objects of the invention is to control the amount of material build-up on the nozzle, while deaerating the fused polymer that enters into the formation of every layer, in order to eliminate any humidity or volatile materials present in it in the course of extrusion.

Another object of the invention is the elimination by deaeration during extrusion of any volatile materials and humidity present, which could be released by heat and interfere with the ability to control the formation of holes, thereby giving the film its microporosity.

The deaeration stage must be carried out under vacuum conditions below 200 millibars in all extruders.

Use of Recycled Materials

The cut-off edges resulting from the production of the breathable film can be recycled in the central layer. Thus, it is desirable to deaerate the recycled material, which may contain enclosed air. This deaeration operation

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is carried out in an extruder dedicated to recycling and equipped with a means of deaeration.

The polymer raw materials and particle fillers can be dried as desired prior to extrusion, as can the raw materials that contain hygroscopic fillers.

Drawing

The highly loaded precursor film, when drawn in a controlled manner, produces a microporous film with a much narrower gauge, which has the desired breathability and liquid-impermeability properties.

According to the invention, the extrusion and the said drawing stages are carried out in such a way that the microporous multilayered film obtained has a thickness of no more than 40 microns, and, preferably, no more than 25 microns. Before being drawn, the multilayered precursor film that exits to the cooling wheel, is reheated to an adequate temperature for drawing, and then drawn to form a breathable multilayered film.

The coextruded multilayered precursor film can be drawn by any conventional art method, e.g. monoaxial or biaxial drawing. The preferred method is to draw the multilayered precursor film in one direction, i.e. that of the machine (longitudinal).

Drawing is carried out between at least two systems of wheels operating at different rotation speeds, in a standard drawing unit. The multilayered precursor film is drawn at a temperature between 20 C and 95 C, and the drawing ratio is between 1:1.5 and 1:6.

The drawing of the multilayered precursor film can be carried out in one or more stages, followed, in some cases, by a thermal stabilization stage.

As already mentioned above, the drawing wheel systems operate at different rotation speeds, in order to obtain e.g. starting with an 80-micron precursor film, a narrower, 20-micron film, corresponding to a monoaxial drawing ratio of 4:1, depending on relaxation; the speed ratio is known as the "drawing speed ratio;" this speed ratio among the entry and exit wheel systems is measured between the wheel systems at the entrance and exit of the

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drawing zone. In addition, the greater the distance between the wheel systems, the more significant the reduction of the width of the film.

Finally, after it has been drawn, the breathable film is thermically stabilized by the release of the tensions while passing through the heated wheel systems. The thermal stabilization temperatures (adjusted by the temperatures of the stabilization wheel systems) are between 30 C and 90 C for polyethylene and 30 C and 120 C for polypropylene.

The multilayered breathable film according to the invention can also be subjected to an embossing stage after drawing. This embossing gives makes the film softer to the touch and reduces shine. This embossing takes place between two adjusted wheels at a temperature of between 35 C and 100C.

Use of the Film

The breathable multilayered film according to the invention has a water vapor transmission speed of at least 500 g/m²/24 hours (at 38 C, 90% relative humidity), preferably between 2000 and 5000 g/m²/24 hours (at 38 C, 90% relative humidity), without losing its impermeability to liquids.

The breathable multilayered film according to the invention can be used in the manufacture of the backsheet of diapers for infants or incontinent adults, and disposable hygiene products, or assembled by rolling with an unwoven fabric and used as a rolled product for the backsheet of diapers for infants or incontinent adults, and disposable hygiene products. According to the invention, the multilayered breathable film has a thickness of less than 40 microns and preferably less than 25 microns.

Example 1

According to the invention, this example concerns the manufacture of a microporous, multilayered film with an asymmetrical "A," "B" structure. The film can be utilized as a backsheet in disposable hygienic products. Layer "A," which consists of an ethylene copolymer and methyl

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methacrylate, is soft to the touch, while the polypropylene layer "C" permits soldering/heat lamination.

The central (intermediate) layer "B" contributes to the transmission of water vapor.

Three different polymer compounds were prepared as dry mixtures of commercially available granules and composite granules, feeding three extruders, with "A," "B," and "C" corresponding, in this case, to the three different layers, "A," "B," and "C," the polymer compound, present in every extruder, and therefore in every layer, is described in Table I below.

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Table I

Distribution of Thickness	10%	80%	10%
Formulation of the polymer in every layer	Layer "A"	Layer "B"	Layer "C"
Polymer 1	100% "Lotryl 2D0MB08"	49% "Dowlex 2635"	40% "K-2033" (RAHECO-PP)
Polymer 2			10% HMS 100 F (fortified PP with high fusion point)
Filler		49% CaCO ₃ "Filmlink 520"	50% CaCO ₃ "Filmlink 400" (from ECC with D:50 = 2.0 microns)
Recycled material		2% debris, layer "A," 10% layer "B," 80% layer "C," 10%	
Additive			1800 ppm of antioxidant ("Irganox HP 2215", consisting of "Irganox 1010," "Irganox 1010," and lactone).

The adjustment of the thickness of each layer is measured using a microscope. In order to do this, each layer was lightly colored, and the film obtained was cut after extrusion-drawing: the thickness of each layer was checked and adjusted by means of microscopic measurement.

The various materials used in the manufacture of the film and mentioned in Table I are described below:

- The Borealis "Daplen K-2033" is an aleatory heterophasic copolymer (RAHECO). In general, the copolymers of heterophasic polypropylenes have a biphasic structure, including a matrix

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and an elastomeric phase. The fluidity index was 8.0 g/10 min (MFI ASTM standard D 1238 - 2.16 kg - 230 C) and the fusion point was approximately 140 C measured by differential scanning calorimetry;

- The Borealis "Daploy HMS 110F" is a reinforced polypropylene with a high fusion point. It is a homopolymer polypropylene with very long branching. In mixtures with this type of polypropylene, its presence significantly augments the fusion capacity of the mixture, the recycling capacity, and compatibility among the various polymer materials. The fluidity index is 5.0 g/10 min (MFI ASTM standard D 1238 - 2.16 kg - 230 C) and the fusion point is approximately 163 C;
- The English China Clay (ECC) "Filmlink 400" is a ground, moist calcium carbonate (CaCO_3) filler with an average diameter D50 of the particles of 1.2 microns. This filler possesses a hydrophobic coating of 1% and an Elrepho (brightness ISO) of 90;
- The Dow "Dowlex 2035" is an octene-based linear polyethylene with a fluidity index of 6.0 g/10 min (MFI ASTM standard D 1238 - 2.160 kg - 190 C) and a density of 0.919 (kg/m^3);
- The Atochem "Lotryl 20 MB08" is an ethyl (methacrylate) copolymer with a fluidity index of 8.0 g/10 min (MFI ASTM standard D 1238 - 2.16 kg - 190°C) with a methyl methacrylate content of 20%, formulated with slip agents and anti-blocking agents, in order to facilitate the procedure;

10% recycled material from the coextruded film is added to central layer "B," in the form of cut-off edges and/or pieces cut off on the final wheels.

The recycled material was previously processed on a regranulation line, where the film was cut and re-extruded via a recycling extruder.

The raw materials were formulated in order to be stable to heat according to known art formulations.

The CaCO_3 was pre-mixed in the "Dowlex 2035" LLDPE formulation and in the "Daplen K20333" and "Daploy HM 110F" PP mixture, on a double-screw extruder equipped with orifices. The compound was dried at 80°C for approximately 4 hours before the production of the film.

The three-layer precursor film was cast by coextrusion on a cooling wheel, and affixed by an air-knife and a vacuum box. The latter was also used to evacuate the exhaust of the nozzle lips using a suction device.

The temperatures of the extruder were set between 180°C and 230°C; the adapter and nozzle temperature are slightly above 235°C. An automatic nozzle was used to test the gauge precisely. This achieves a tolerance below $\pm 4\%$. The fusion temperature was measured at approximately 230°C.

All the fused polymers coming from the three extruders were thoroughly deaerated by setting the deaeration device, on each extruder, to a vacuum level below 200 millibars.

The multilayered precursor film with a thickness of 80 microns was produced at a line speed of approximately 25 m/min. After being drawn at a ratio of 4:1, the film reached a thickness of 20 microns and a breathability of approximately 2500 $\text{g/m}^2/24$ hours (at 38°C with a relative humidity of 90%).

All the compounds were easily processed on the extrusion line. No moisture problem was noted in the procedure or in the film. The good deaeration conditions on the extruders made it possible to avoid the build-up usually noted on the nozzle, even after 8 hours of continuous operation.

Additionally, the skin layer that contains the "Lotryl" raw material was placed in such a way as to be in contact with the cooling wheel, preventing the formation of CaCO_3 deposits on the wheel.

The cut-off edges were extracted from the procedure and regranulated in a deaeration extruder, operating at a vacuum level below 200 millibars. The recycled granules

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were incorporated in the central layer "B" at a proportion of 10% by weight.

After thermal stabilization, the film was embossed by heat and compression of the film under high pressure in a suitable embossing device. The embossing wheels were engraved according to the desired model.

An impression was made on the line after the embossing stage.

The film was cooled on line and stocked as a finished product in wheel form.

Example 2

This example concerns the manufacture of a microporous multilayered film with a symmetric "C," "B," "C" structure according to the invention.

The polymer compound present in each extruder is described in Table II below

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Table II

Distribution of thickness	15%	70%	15%
Polymer formulation in each layer	Layer "C"	Layer "B"	Layer "C"
Polymer 1	50% RAHECO PE "Daplen K2033"	38% LDPE "Dow Elite 5200"	50% RAHECO PE "Daplen K2033"
Polymer 2		10% LDPE "Dow SC 7641"	
Filler	50% CaCO ₃ "Filmlink 400"	52% CaCO ₃ "Filmlink 520"	50% CaCO ₃ "Filmlink 400"

The output conditions of the extruder, which represent distribution of the thickness of the layers in percent, were set to 15:70:15.

The various materials used in the manufacture of the layers and presented in Table II are described below:

- The Dow "Elite 5200" is a low-density, octene-based linear polyethylene with a fluidity index of 4.0 g/10 min (MFI ASTM standard D 1238 - 2.16 kg - 190 C) and with a density of 0.917 (kg/m³).
- The Dow "Dowlex SC 7641" is an LDPE (low-density branched polyethylene) with a fluidity index of 2.0 g/10 min (MFI ASTM standard D 1238 - 2.16 kg - 190 C) and a density of 0.924 (kg/m³).
- The English China Clay (ECC) "Filmlink 400" is a ground, moist calcium carbonate (CaCO₃) filler with an average D50 particle diameter of 1.2 microns. It has a 1% hydrophobic coating and an Elrepho (brightness ISO) of 90.
- The English China Clay (ECC) "Filmlink 520" is a "Filmlink 520" de English China Clay (ECC) ground, moist calcium carbonate (CaCO₃) filler with an average D50 particle diameter of 2.0 microns. It has a hydrophobic coating of 1% and an Elrepho (brightness ISO) of 90.

In "C" layers, the materials were introduced in the form of ready-to-use compounds, manufactured in a double-screw

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deaerating extruder, with a view to reducing the moisture content. The compounds were produced in the same conditions as in example I.

In the central layer "B," the polymer material used was composed of a dry mixture containing 70% of a compound including 74% CaCO_3 and 26% Dow "Elite 5200," 20% "Dow Elite 5200" and 10% Dow "SC 7641." The precursor film was cast on a cooling wheel, as in example I. The fusion temperature was approximately 235 C; the nozzle temperature was set at 230 C. The line speed was approximately 30 m/min for the production of the 60 micron-thick multilayered precursor film. All fused polymer materials were thoroughly deaerated on every extruder, with the deaerating device set to a vacuum level below 200 millibars. All compounds were easily processed on the casting line. No humidity problem was reported. These good deaeration conditions on the extruders are demonstrated by the lack of deposits on the nozzle; no build-up was observed on the nozzle, even after 6 hours of continuous operation.

After drawing at a ratio of approximately 3:1, the 60 micron, three-layer precursor film attained a thickness of 20 microns at a winding speed of 90 m/min. The water vapor transmission speed was 3000 $\text{g/m}^2/24$ hours (at 38°C with a relative humidity of 90%).

The microporous film was cut along the line before winding, then it was heat rolled on one of its surfaces on an unwoven polypropylene fabric, and hot bonded to a disposable product on its other surface. The heat bond strength between the two components - the multilayered breathable film and the unwoven fabric - was excellent, as demonstrated by tearing the threads during peeling.

Example 3

This example concerns the manufacture of a microporous multilayered film with a symmetrical "A," "B," "A" structure according to the invention.

Table 3

Distribution of thickness	10%	80%	10%
Polymer:	Layer "A"	Layer "B"	Layer "A"

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formulation in each layer			
Polymer 1	100% EMA "Lotryl 20 MB08"	50% LLDPE "Dowlex 2035"	100% EMA "Lotryl 20 MB082"
Polymer 2			
Filler		48% CaCO_3 "Filmlink 520"	
Additive		2% TiO_2	

The output conditions of the extruder, representing the distribution of thickness of the layers in percent, were set to 10:80:10.

These various materials, used in the manufacture of the various layers and shown in Table III, are described in detail below:

The line speed was approximately 20 m/min for the production of a 100 micron precursor film. The drawing ratio was approximately 4:1, producing a 25 micron film at a winding speed of 80 m/min.

The temperatures of the extruders that feed layer "A" were set to approximately 220 C in the final zone, while the temperature in the final zone of the extruder feeding layer "B" has been set to 240 C. The temperature of the nozzle was below 230 C.

The film produced had a surface that was very soft to the touch and a water vapor transmission speed of approximately 1500 $\text{g/m}^2/24$ hours (at 38 C, with a relative humidity of 90%).

The build-up on the nozzle was substantially reduced, as no sign of build-up was noted on the nozzle even after 12 hours of operation. No CaCO_3 was noted on the cooling wheel or on any other wheel of the machine. The addition of TiO_2 in the central layer improved the opacity of the film.

Example 4

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This example concerns the manufacture of a microporous multilayered film with a symmetric "A," "C," "B," "C," "A" according to the invention.

Distribution of thickness	10%	15%	50%	15%	10%
Polymer formulation in each layer	Layer "A"	Layer "C"	Layer "B"	Layer "C"	Layer "A"
Polymer 1	100% EMA "Lotryl 20 MB08"	30% RAHECO PP "Daplen K2033"	48% RAHECO PP "Daplen K2033"		100% EMA "Lotryl 20MB08"
Polymer 2		20% PP copolymer "Adflex X102S"		20% PP copolymer "Adflex X102S"	
Filler		50% CaCO ₃ "Filmlink 400"	52% CaCO ₃ "Filmlink 520"	50% CaCO ₃ "Filmlink 400"	

The various materials used in the manufacture of the various layers and shown in Table IV are described in detail below:

Montell "Adflex X102S" is an elastomeric polypropylene copolymer with a fluidity index of 8.0 g/10 min (MFI ASTM standard D 1238 - 2.16 kg - 230 C) and a density of 0.890 (kg/m³). It allows for compatibility among polymer materials, thus improving adhesion between layer "A" and layer "B." In addition, it provides a greater degree of softness to the touch.

The extruder feeding layer "A" was set to a temperature of 220 C. For the extruder feeding layers "B" and "C," the fusion temperature was set to 240 C.

An 80 micron precursor film was produced at a speed of 25 m/min. the film was drawn at a ratio of approximately 4:1, with a view to obtaining a breathable film of approximately 20 microns thickness.

12% of material recycled on line was added to the central layer "B." The recycled material was previously regranulated on a deaerating extruder with a vacuum level of less than 200 millibars.

No build-up was observed on the nozzle, even after 12 hours of continuous operation. No CaCO₃ was noted on the wheels.

The film had a water vapor transmission speed of 3200 g/m²/24 hours (at 38 C with a relative humidity of 90%).

Claims

1. Method of manufacture of a polyolefinic film with a multilayered structure, which simultaneously has the properties of being permeable to water vapor and impermeable to liquids, including the steps of:
 - The simultaneous extrusion, from a nozzle, of at least three layers composed of thermoplastic polymer materials, forming a precursor film with, at a minimum, the following structure: "A," "B," "C," or "A," "B," "A," or "C," "B," "C," whereby "A" is a skin layer, "B" is a central layer, and "C" is a skin/adhesion layer;
 - The drawing of the precursor film with multiple coextruded layers, forming the multilayered film that is permeable to water vapor but impermeable to liquids,

in which:

- The skin layer "A" contains at least one thermoplastic polyolefinic copolymer and/or one grafted polyolefinic polymer, which has a module E below 50 mPA (ASTM standard no. 882, 15 micron cast film), a fluidity measure by "Melt Flow Index" (MFI, ASTM standard D 1238 - 2.16 kg, 190 C for polyethylenes and 230 C for polypropylenes), between 1.5 and 10 g/10 min, and a water vapor transmission speed of at least 100 g/m²/24 h at 38 C and 90% relative humidity;

- The central layer "B" has at least one homopolymer and/or one thermoplastic polyolefinic copolymer, at least one particle filler, and, in some cases, one or more elastomers;
 - The skin/adhesion layer "C" contains at least one adhesion bonding agent and/or one homopolymer and/or thermoplastic polyolefinic copolymer, and at least one particle filler.
2. Method according to Claim 1, characterized by the fact that the extrusion stage includes the simultaneous coextrusion of at least three layers "A," "B," and "C," the thickness of each of which, expressed in percentage of the total thickness of the breathable multilayered film, are:
 - between approximately 5% and approximately 30% of the thickness for layer "A,"
 - between approximately 40% and approximately 90% of thickness for layer "B,"
 - and between approximately 5% and approximately 30% of thickness for layer "C."
 3. Method according to Claims 1 or 2, characterized by the fact that the homopolymers or copolymers entering into the composition of the central layer "B" are chosen from the group including homo- and/or copolymer polyethylenes, preferably low-density linear polypropylenes and/or homo- and/or copolymer polypropylenes.
 4. Method according to at least one of Claims 1 - 3, characterized by the fact that the homo- or copolymeric ethylene polymers entering into the composition of the central layer "B" are chosen from amongst those with a density between 0.915 (kg/m³) and 0.965 (kg/m³) (ASTM standard 15105, density expressed in kg/m³), and preferably in the lower-density range of 0.915 (kg/m³) to 0.935 (kg/m³).

5. Method according to Claims 3 or 4, characterized by the fact that the low-density linear polyethylenes are chosen from those with a density between 0.890 (kg/m³) and 0.940 (kg/m³), and preferably chosen from the group of ethylene copolymers and C4 to C8 alpha-olefinic comonomers.
6. Method according to Claim 5, characterized by the fact that the C4 to C10 alpha-olefinic comonomers are chosen from the group including butene-1, pentene-1, hexane-1, 4-methylpentene-1, heptene-1, and octene-1.
7. Method according to Claims 3 or 4, characterized by the fact that the homo- or copolymeric propylene polymers are chosen from the group made up of propylene homopolymers, propylene copolymers with ethylene, and propylene copolymers with C4 to C10 alpha-olefinic comonomers.
8. Method according to Claim 7, characterized by the fact that the propylene and C4 to C10 alpha-olefin copolymers have an alpha-olefin content of between 0.1 and 40% by weight, preferably between 1 and 10% by weight.
9. Method according to at least one of Claims 1 - 8, characterized by the fact that the polymers and/or copolymers of central layer "B" are chosen in such a way that their fluidity index, measured by the "Melt Flow Index" (MFI) method, is between 0.2 and 15 g/10 min, measured based on the reference value of a load of 2.16 kg, a temperature of 190 C for polyethylenes and 230 C for polypropylenes, with a standard orifice (ASTM standard D 1238).

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10. Method according to at least one of Claims 1 - 9, characterized by the fact that the central layer "B" contains at least one organic or mineral particle filler, at a proportion of 30 to 80% by weight, and preferably 45 to 55% by total weight of said particle filler and the polymeric material.

11. Method according to at least one of Claims 1 - 10, characterized by the fact that, according to the invention, the elastomers used in the central layer "B" are chosen from the group made up of the ethylene-propylene rubbers (EPR), modified ethylene-propylene-diene (EPDM) rubbers, styrene-ethylene-butadiene (SBS) rubbers, styrene-ethylene-butadiene-styrene (SEBS) rubbers, styrene-butadiene (SBR) rubbers, styrene-isoprene-styrene (SIS) rubbers, butyl rubbers (BR), nitrile rubbers (NB R), hydrogen-nitrile-butyl rubbers, and polyvinyl acetate used alone or in a mixture, with polypolyethylene and/or semi-crystalline propylene.

12. Method according to Claim 11, characterized by the fact that the elastomer fraction is chosen from the group of (homopolymeric) polypropylenes with amorphous and semi-crystalline blocks, propylene/ethylene or alpha-olefinic copolymers with amorphous and semi-crystalline blocks.

13. Method according to Claims 11 and 12, characterized by the fact that the elastomer fraction is partially or completely reticulated.

14. Method according to at least one of Claims 1 - 13, characterized by the fact that the central layer "B" is used to recycle the waste material of the multilayered materials recovered in the procedure, before drawing, after drawing, or after assembly of the film.

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15. Method according to Claim 14, characterized by the fact that the quantity of recycled multilayered waste material in central layer "B" varies from 0 to 30% by weight, preferably between 0 and 15% by weight, relative to said layer.

16. Method according to at least one of Claims 1 and 2, characterized by the fact that the microporous skin layer "A" is formed from at least one ethylene- and/or grafted polyolefinic polymer-based polar copolymer.

17. Method according to Claim 16, characterized by the fact that the polar ethylene copolymer used in the manufacture of layer "A" is composed of ethylene and at least one polar comonomer chosen from the group made up of the family of vinyl esters and the family of acrylic and methacrylic acids and esters.

18. Method according to one of Claims 16 and 17, characterized by the fact that the polar ethylene copolymer includes at least one comonomer, preferably chosen from the group made up of vinyl acetate, vinyl propionate, acrylic acid, methacrylic acid, methyl acrylate, ethyl acrylate, n-propyl acrylate, isopropyl acrylate, n-butyl acrylate, t-butyl acrylate, isobutyl acrylate, methyl methacrylate, ethyl methacrylate, n-propyl methacrylate, isopropyl methacrylate, n-butyl methacrylate, t-butyl methacrylate, and isobutyl methacrylate.

19. Method according to at least one of Claims 16 - 18, characterized by the fact that the ethylene copolymers and at least one polar comonomer consist of more than 30% comonomer by weight.

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20. Method according to one of Claims 16- 19, characterized by the fact that the polyolefinic polymers are grafted by means of acrylic acid, methacrylic acid, maleic anhydride, acrylates, and alkyl methacrylates, in which the alkyl is a hydrocarbon chain from C1 to C8.

21. Method according to at least one of Claims 1 - 20, characterized by the fact that the polyolefinic homopolymers and/or copolymers of the skin/adhesion layer "C" are chosen from the group consisting of polyethylenes, preferably low-density linear polyethylenes and/or polypropylenes and/or ethylene-propylene and ethylene and alpha-olefin copolymers.

22. Method according to Claim 21, characterized by the fact that the polyolefinic homopolymeric and/or copolymeric components of the skin/adhesion layer "C" are chosen from the group consisting of low-density linear polyethylenes, with densities between 0.880 (kg/m³) and 0.940 (kg/m³), ethylene copolymers, and C4 to C10 alpha-olefinic comonomers, polyethylenes with densities between 0.915 (kg/m³) and 0.965 (kg/m³), and polypropylenes and propylene and ethylene copolymers preferably chosen from among the block aleatory copolymers.

23. Method according to at least one of Claims 1 - 22, characterized by the fact that, according to the invention, the adhesive/bonding agent present in the skin/adhesion layer "C" is chosen from the group of ethylene copolymers and grafted ethylene- or propylene-based polar or non-polar comonomers and ethylene or propylene homopolymers or copolymers.

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24. Method according to Claim 23, characterized by the fact that the polar copolymers are chosen from those present in skin layer "A."

25. Method according to Claim 23, characterized by the fact that the non-polar copolymers are chosen from the group composed of the elastomers used in the composition of central layer "B."

26. Method according to at least one of Claims 1 - 25, characterized by the fact that the adhesive/bonding agent of the skin/adhesion layer "C" enters into the composition of said layer at a proportion of 2 to 20%, preferably 5 to 15% by weight.

27. Method according to at least one of Claims 1 - 26, characterized by the fact that the skin layer "C" includes 30 to 80% by weight, preferably 45 to 55% by weight, in particle fillers.

28. Method according to at least one of Claims 1 - 27, characterized by the fact that the particle fillers used in central layer "B" and skin/adhesion layer "C" are non-organic and organic, chosen from the group composed of high-density and high-molecular weight polyethylene, polyamide, polyester, polyurethane powders; barium carbonate and calcium carbonate; magnesium carbonate; magnesium sulfate; barium sulfate; calcium sulfate; aluminum hydroxide; magnesium hydroxide; calcium oxide; magnesium oxide; titanium oxide; titanium dioxide and zinc oxide, clay, kaolin, talc, silica, diatomic earth; glass, mica, aluminum, and zeolites powders; preferably calcium carbonate, barium sulfate, silica, alumina, kaolin, and talc.

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29. Method according to at least one of Claims 1 - 28, characterized by the fact that the particle fillers used in central layer "B" and skin/adhesion layer "C" have an average diameter of between 0.5 and 5 microns for the central layer "B," preferably between 0.8 and 2.2 microns, and of between 0.2 and 3 microns, preferably between 0.8 and 1.5 microns, for skin/adhesion layer "C."

30. Method according to at least one of Claims 1 - 29, characterized by the fact that the multilayered precursor film is obtained by coextrusion via a flat nozzle of a cast film at a temperature of between 200 C and 250 C, followed by cooling, by means of an appropriate wheel, to a temperature of between 15 C and 60 C.

31. Method according to at least one of Claims 1 - 29, characterized by the fact that the multilayered precursor film is obtained by coextrusion via an annular nozzle of a blown cast film at a temperature of between 150 C and 240 C, followed by cooling on a line set at between 10 and 80 cm from the surface of the nozzle and a blow ratio between 1.5 and 4.0.

32. Method according to at least one of Claims 1 - 31, characterized by the fact that the polymeric materials, fillers, and compounds involved in the manufacture of the various layers of the multilayered precursor film are dried prior to extrusion.

33. Method according to at least one of Claims 1 - 32, characterized by the fact that volatile materials, moisture, and air enclosed during manufacture of the various layers of the multilayered precursor film are eliminated by deaeration during extrusion.

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34. Method according to at least one of claims 1 - 33, characterized by the fact that the multilayered precursor film is drawn in the direction of the machine, in one or more steps, at a temperature of between 20 C and 95 C and a draw ratio (measured between the entrance and exit of the drawing area) between 1:1.5 and 1:6 so that the multilayered film has a thickness of no more than 40 microns and preferably no more than 25 microns.

35. Method according to at least one of Claims 1 - 34, characterized by the fact that the microporous multilayered film exiting the drawing area is subjected to embossing at a temperature of between 35 C and 100C.

36. Method according to at least one of Claims 1 - 35, characterized by the fact that the microporous multilayered film exiting the drawing area is subjected to a thermal stabilization at a temperature of between 30 C and 120 C.

37. Breathable microporous multilayered film obtained by the use of the method according to at least Claims 1 - 36, characterized by the fact that its thickness is less than 40 microns, and preferably less than 25 microns.

38. Breathable microporous multilayered film according to Claim 37, characterized by the fact that it has a water vapor transmission speed of at least 500 g/m²/24 hours (at 38 C, 90% relative humidity), preferably between 2000 and 5000 g/m²/24 hours (at 38 C, 90% relative humidity), without losing its impermeability to liquids.

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39. Breathable microporous multilayered film according to Claim 37, characterized by the fact that it is assembled by rolling with an unwoven fabric.

40. Use of the breathable microporous multilayered film according to one of Claims 37 - 39 as the backsheet of diapers for infants or incontinent adults and disposable hygienic products, or, after assembly by rolling with an unwoven fabric, as a rolled product for diapers for infants or incontinent adults, as well as disposable hygienic products.

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(54) Title: HIGH SPEED METHOD OF MAKING MICROPOROUS FILM PRODUCTS			
(57) Abstract			
Microporous film products permeable to moisture vapor and which act as barriers to liquid are made by a high speed method. Such microporous products are made at speeds in the order of above 500 fpm to about 1200 fpm. Thermoplastic polymers are melt blended to contain about 35 % to about 45 % by weight of a linear low density polyethylene, about 3 % to about 10 % by weight of a low density polyethylene; about 40 % to about 55 % by weight calcium carbonate filler particles, and about 2 % to about 6 % by weight of a triblock polymer of styrene.			

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HIGH SPEED METHOD OF MAKING MICROPOROUS FILM PRODUCTSBACKGROUND OF THE INVENTION

Methods of making microporous film products have been known for some time. For example, U. S. Patent No. 3,832,267, to Liu, teaches the melt-embossing of a polyolefin film containing a dispersed

5 amorphous polymer phase prior to stretching or orientation to improve gas and moisture vapor transmission of the film. According to the Liu '267 patent, a film of crystalline polypropylene having a dispersed amorphous polypropylene phase is first embossed prior to biaxially drawing (stretching) to produce an oriented impermeate film having greater

10 permeability. The dispersed amorphous phase serves to provide microvoids to enhance the permeability of the otherwise impermeate film to improve moisture vapor transmission (MVT). The embossed film is preferably embossed and drawn sequentially.

In 1976, Schwarz published a paper which described polymer

15 blends and compositions to produce microporous substrates (Eckhard C.A. Schwarz (Biax-Fiberfilm), "New Fibrillated Film Structures, Manufacture

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and films. More specifically, the '840 patent discloses conventional embossing techniques to form densified and undensified areas in nonwoven base plies prior to extrusion lamination to improve bonding between nonwoven fibrous webs and films by means of the densified fiber areas. The '941 patent also teaches that unstretched nonwoven webs that are extrusion laminated to single ply polymeric films are susceptible to pinholes caused by fibers extending generally vertically from the plane of the fiber substrate and, accordingly, this patent discloses using multiple co-extruded film plies to prevent pinhole problems. Furthermore, methods for bonding loose nonwoven fibers to polymeric film are disclosed in U. S. Patents Nos. 3,622,422; 4,379,197 and 4,725,473.

It has also been known to stretch nonwoven fibrous webs using intermeshing rollers to reduce basis weight and examples of patents in this area are U. S. Patents Nos. 4,153,664 and 4,517,714. The '664 patent discloses a method of incremental cross direction (CD) or machine direction (MD) stretching nonwoven fibrous webs using a pair of interdigitating rollers to strengthen and soften nonwoven webs. The '664 patent also discloses an alternative embodiment wherein the nonwoven fibrous web is laminated to the thermoplastic film prior to intermesh stretching.

Efforts have also been made to make breathable non-woven composite barrier fabrics which are impervious to liquids, but which are permeable to water vapor. United States Patent No. 5,409,761 is an

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example of a fabrication process from the patent art. According to this '761 patent, a nonwoven composite fabric is made by ultrasonically bonding a microporous thermoplastic film to a layer of nonwoven fibrous thermoplastic material. These methods and other methods of making breathable laminates of nonwoven and thermoplastic materials tend to involve expensive manufacturing techniques and/or expensive raw materials.

Notwithstanding the extensive development of the art for making breathable microporous films and laminates to provide air and moisture vapor permeabilities with liquid-barrier properties, further improvements are needed. In particular, improvements are desired for producing microporous film products and laminates on high-speed production machinery. It would be very desirable to produce microporous film products without undesirable pin holes and without draw resonance. In the past, attempts to increase production speeds have resulted in film breakage or film products with inconsistent properties.

SUMMARY OF THE INVENTION

This invention is directed to a high speed method of making a microporous thermoplastic film. The microporous film is permeable to air and water vapor, but is a barrier to liquid. Breathable laminates of microporous film with nonwoven substrates are also produced at high speeds according to the method of this invention.

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The high speed method of this invention involves melt-blending a composition comprising

- (a) about 35% to about 45% by weight of a linear low density polyethylene,
- (b) about 3% to about 10% by weight of a low density polyethylene,
- (c) about 40% to about 55% by weight calcium carbonate filler particles, and
- (d) about 2% to about 6% by weight of a triblock copolymer of styrene selected from the group consisting of styrene-butadiene-styrene, styrene-isoprene-styrene, and styrene-ethylene-butylene-styrene, and blends thereof.

The melt-blended composition is extruded, preferably through a slot die, into a nip of rollers with an air knife to form a film at a speed on the order of at least about 550 fpm to about 1200 fpm without draw resonance. Speeds of at least about 750 fpm to about 1200 fpm, or greater, have been achieved without draw resonance. The use of the air knife to assist in the elimination of draw resonance is known, for example, by reference to U. S. Patent No. 4,626,574. Thereafter, an incremental stretching force is applied to the film at the high speeds along lines substantially uniformly across the film and throughout its depth to provide a microporous film. Thus, this invention provides a high speed method of

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making microporous films and laminates with nonwoven substrates of uniform gauge. The problem of draw resonance which has heretofore resulted in irregular gauge or thickness in the film products is avoided, even though line speeds of about 750-1200 fpm are achieved.

The blend of LLDPE and LDPE within the approximate ranges of components enables the production of film without breakage and pin holes when balanced with the prescribed amount of calcium carbonate. In particular, the LLDPE is present in an amount of about 35% to about 45% by weight in order to provide a sufficient amount of matrix to carry the calcium carbonate filler particles thereby enabling the film to be handled and stretched without pin holing and breakage. The LDPE in an amount of about 3% to about 10% by weight also contributes to the production of film without pin holing and enables the high speed production without draw resonance. The polymeric matrix is balanced with an amount of about 40% to about 55% by weight of calcium carbonate particles having an average particle diameter of preferably about 1 micron to achieve sufficient MVT in the range of about 1000 gms/m²/day to 4000 gms/m²/day. Furthermore, the melt-blended composition requires a triblock polymer in an amount of about 2% to about 6% by weight to facilitate stretching in high-speed production without breakage. An incremental stretching force is applied inline to the formed film under ambient conditions or at an elevated temperature at speeds of at least about 550 fpm to about 1200 fpm, or more, along lines

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substantially uniformly across the film and throughout its depth to provide a microporous film.

The method of this invention also involves lamination of the microporous-formable thermoplastic film to a nonwoven fibrous web during extrusion. The extrusion lamination is conducted at the same high speeds where a nonwoven fibrous web is introduced into the nip of rollers along with the microporous-formable thermoplastic extrudate. The compressive force between the fibrous web and the extrudate is controlled to bond one surface of the web to the film and form a laminate.

The laminate is then incrementally stretched along lines substantially uniformly across the laminate and throughout its depth in one direction to render the film microporous. The laminate may be stretched in both the cross direction and the machine direction to provide breathable cloth-like liquid barriers capable of transmitting moisture vapor and air.

Other benefits, advantages and objectives of this invention will be further understood with reference to the following detailed description.

DETAILED DESCRIPTION OF THE INVENTION

It is the primary objective of this invention to produce a microporous film and laminated products thereof with nonwoven fibrous webs on high-speed production machinery. It is the further objective of the method to produce such microporous film products of regular gauge, uniform porosity and without breakage.

A. Materials for the Method

As developed above, these and other objectives are achieved in a preferred form of the invention by first melt blending a composition of

- (a) about 35% to about 45% by weight of a linear low density polyethylene,
- (b) about 3% to about 10% by weight of a low density polyethylene,
- (c) about 40% to about 55% by weight calcium carbonate filler particles, and
- (d) about 2% to about 6% by weight of a triblock copolymer of styrene selected from the group consisting of styrene-butadiene-styrene, styrene-isoprene-styrene, and styrene-ethylene-butylene-styrene, and blends thereof,

extruding said melt blended composition into a nip of rollers to form a film at a speed on the order of at least about 550 fpm to about 1200 fpm without draw resonance, and

applying an incremental stretching force to said film at said speed along lines substantially uniformly across said film and throughout its depth to provide a microporous film.

More particularly, in a preferred form, the melt-blended composition consists essentially of about 42% by weight LLDPE, about

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4% by weight LDPE, about 44% by weight calcium carbonate filler particles having an average particle size of about 1 micron, and about 3% by weight triblock polymer, especially styrene-butadiene-styrene. If desired, the stiffness properties of the microporous film products may be controlled by including high density polyethylene on the order of about 0-5% by weight and including 0-4% by weight titanium dioxide. Typically, processing aid such as a fluoro carbon polymer in an amount of about 0.1% to about 0.2% by weight is added, as exemplified by 1-propene, 1,1,2,3,3,3-hexafluoro copolymer with 1,1-difluoroethylene.

10 The triblock polymer may also be blended with oil, hydrocarbon, antioxidant and stabilizer. Antioxidants include tetrakis [methylene(3,5-di-tert-butyl-4-hydroxyhydrocinnamate)]methane (trade name is Irganox 1010), and tris(2,4-di-tert-butylphenyl)phosphite (trade name is Irgafos 168) at a total of 500-4000 ppm (parts per million).

15 Both embossed and flat films may be produced according to the principles of this invention. In the case of an embossed film, the nip of rollers comprises a metal embossing roller and a rubber roller. The compressive force between the rollers forms an embossed film of desired thickness on the order of about 0.5 to about 10 mils. It has also been

20 found that rollers which provide a polished chrome surface form a flat film. Whether the film is an embossed film or a flat film, upon incremental stretching, at high speeds, microporous film products are produced having high moisture vapor transmission rate (MVTR) within the acceptable range

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of about 1000 to 4000 gms/m²/day. It has been found that flat film can be incrementally stretched more uniformly than embossed film. The process may be conducted at ambient or room temperature or at elevated temperatures. As described above, laminates of the microporous film may

5 be obtained with nonwoven fibrous webs.

The nonwoven fibrous web may comprise fibers of polyethylene, polypropylene, polyesters, rayon, cellulose, nylon, and blends of such fibers. A number of definitions have been proposed for nonwoven fibrous webs. The fibers are usually staple fibers or continuous filaments. The nonwovens are usually referred to as spunbond, carded, meltblown, and the like. The fibers or filaments may be bicomponent to facilitate bonding. For example, a fiber having a sheath and core of different polymers such as polyethylene (PE) and polypropylene (PP) may be used; or mixtures of PE and PP fibers may be used. As used herein

15 "nonwoven fibrous web" is used in its generic sense to define a generally planar structure that is relatively flat, flexible and porous, and is composed of staple fibers or continuous filaments. For a detailed description of nonwovens, see "Nonwoven Fabric Primer and Reference Sampler" by E. A. Vaughn, Association of the Nonwoven Fabrics Industry, 3d Edition

20 (1992).

In a preferred form, the microporous laminate employs a film having a gauge or a thickness between about 0.25 and 10 mils and, depending upon use, the film thickness will vary and, most preferably, in

disposable applications is the order of about 0.25 to 2 mils in thickness. The nonwoven fibrous webs of the laminated sheet normally have a weight of about 5 gms/yd² to 75 gms/yd², preferably about 20 to about 40 gms/yd². The composite or laminate can be incrementally stretched in the cross direction (CD) to form a CD stretched composite. Furthermore, CD stretching may be followed by stretching in the machine direction (MD) to form a composite which is stretched in both CD and MD directions. As indicated above, the microporous film or laminate may be used in many different applications such as baby diapers, baby training pants, catamenial pads and garments, and the like where moisture vapor and air transmission properties, as well as fluid barrier properties, are needed.

B. Stretchers for the Microporous Film and Laminates

A number of different stretchers and techniques may be employed to stretch the film or laminate of a nonwoven fibrous web and microporous-formable film. These laminates of nonwoven carded fibrous webs of staple fibers or nonwoven spun-bonded fibrous webs may be stretched with the stretchers and techniques described as follows:

1. Diagonal Intermeshing Stretcher

The diagonal intermeshing stretcher consists of a pair of left hand and right hand helical gear-like elements on parallel shafts. The shafts are disposed between two machine side plates, the lower shaft being located in fixed bearings and the upper shaft being located in

bearings in vertically slidable members. The slidable members are adjustable in the vertical direction by wedge shaped elements operable by adjusting screws. Screwing the wedges out or in will move the vertically slidable member respectively down or up to further engage or disengage the gear-like teeth of the upper intermeshing roll with the lower intermeshing roll. Micrometers mounted to the side frames are operable to indicate the depth of engagement of the teeth of the intermeshing roll.

Air cylinders are employed to hold the slidable members in their lower engaged position firmly against the adjusting wedges to oppose the upward force exerted by the material being stretched. These cylinders may also be retracted to disengage the upper and lower intermeshing rolls from each other for purposes of threading material through the intermeshing equipment or in conjunction with a safety circuit which would open all the machine nip points when activated.

A drive means is typically utilized to drive the stationary intermeshing roll. If the upper intermeshing roll is to be disengageable for purposes of machine threading or safety, it is preferable to use an antibacklash gearing arrangement between the upper and lower intermeshing rolls to assure that upon reengagement the teeth of one intermeshing roll always fall between the teeth of the other intermeshing roll and potentially damaging physical contact between addenda of intermeshing teeth is avoided. If the intermeshing rolls are to remain in constant engagement, the upper intermeshing roll typically need not be

driven. Drive may be accomplished by the driven intermeshing roll through the material being stretched.

The intermeshing rolls closely resemble fine pitch helical gears. In the preferred embodiment, the rolls have 5.935" diameter, 45° helix angle, a 0.100" normal pitch, 30 diametral pitch, 14½° pressure angle, and are basically a long addendum topped gear. This produces a narrow, deep tooth profile which allows up to about 0.090" of intermeshing engagement and about 0.005" clearance on the sides of the tooth for material thickness. The teeth are not designed to transmit rotational torque and do not contact metal-to-metal in normal intermeshing stretching operation.

2. Cross Direction Intermeshing Stretcher

The CD intermeshing stretching equipment is identical to the diagonal intermeshing stretcher with differences in the design of the intermeshing rolls and other minor areas noted below. Since the CD intermeshing elements are capable of large engagement depths, it is important that the equipment incorporate a means of causing the shafts of the two intermeshing rolls to remain parallel when the top shaft is raising or lowering. This is necessary to assure that the teeth of one intermeshing roll always fall between the teeth of the other intermeshing roll and potentially damaging physical contact between intermeshing teeth is avoided. This parallel motion is assured by a rack and gear arrangement wherein a stationary gear rack is attached to each side frame in

juxtaposition to the vertically slidable members. A shaft traverses the side frames and operates in a bearing in each of the vertically slidable members. A gear resides on each end of this shaft and operates in engagement with the racks to produce the desired parallel motion.

The drive for the CD intermeshing stretcher must operate both upper and lower intermeshing rolls except in the case of intermeshing stretching of materials with a relatively high coefficient of friction. The drive need not be antibacklash, however, because a small amount of machine direction misalignment or drive slippage will cause no problem. The reason for this will become evident with a description of the CD intermeshing elements.

The CD intermeshing elements are machined from solid material but can best be described as an alternating stack of two different diameter disks. In the preferred embodiment, the intermeshing disks would be 6" in diameter, 0.031" thick, and have a full radius on their edge. The spacer disks separating the intermeshing disks would be 5 1/2" in diameter and 0.069" in thickness. Two rolls of this configuration would be able to be intermeshed up to 0.231" leaving 0.019" clearance for material on all sides. As with the diagonal intermeshing stretcher, this CD intermeshing element configuration would have a 0.100" pitch.

3. Machine Direction Intermeshing Stretcher

The MD intermeshing stretching equipment is identical to the diagonal intermeshing stretch except for the design of the intermeshing

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rolls. The MD intermeshing rolls closely resemble fine pitch spur gears. In the preferred embodiment, the rolls have a 5.933" diameter, 0.100" pitch, 30 Diametral pitch, 14 1/2° pressure angle, and are basically a long addendum, topped gear. A second pass was taken on these rolls with the gear hob offset 0.010" to provide a narrowed tooth with more clearance. With about 0.090" of engagement, this configuration will have about 0.010" clearance on the sides for material thickness.

4. Incremental Stretching Technique

The above described diagonal, CD or MD intermeshing stretchers may be employed to produce the incrementally stretched film or laminate of nonwoven fibrous web and microporous-formable film to form the microporous film products of this invention. For example, The stretching operation may be employed on an extrusion laminate of a nonwoven fibrous web of staple fibers or spun-bonded filaments and microporous-formable thermoplastic film. In one of the unique aspects of this invention a laminate of a nonwoven fibrous web of spun-bonded filaments may be incrementally stretched to provide a very soft fibrous finish to the laminate that looks like cloth. The laminate of nonwoven fibrous web and microporous-formable film is incrementally stretched using, for instance, the CD and/or MD intermeshing stretcher with one pass through the stretcher with a depth of roller engagement at about 0.060 inch to 0.120 inch at speeds from about 550 fpm to 1200 fpm or faster. The results of such incremental or intermesh stretching produces

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laminates that have excellent breathability and liquid-barrier properties, yet provide superior bond strengths and soft cloth-like textures.

The following examples illustrate the method of making microporous film and laminates of this invention. In light of these examples and this further detailed description, it is apparent to a person of ordinary skill in the art that variations thereof may be made without departing from the scope of this invention.

BRIEF DESCRIPTION OF THE DRAWINGS

The invention is further understood with reference to the drawings in which:

FIG. 1 is a schematic of an inline extrusion lamination and incremental stretching apparatus for making the microporous laminate of this invention.

FIG. 2 is a cross sectional view taken along the line 2-2 of Fig. 1 illustrating the intermeshing rollers in diagrammatic form.

FIG. 3 is a graph demonstrating the line speeds for Examples 1-5.

FIG. 4 is a graph demonstrating the moisture vapor transmission properties of both embossed and flat microporous films.

FIG. 5 is a graph demonstrating the moisture vapor transmission rate can be adjusted by heating the precursor film.

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EXAMPLES 1-5

Blends of LLDPE and LDPE having the compositions reported in the following TABLE 1 were extruded to form films and the films were then incrementally stretched to provide microporous films.

TABLE 1

Formulation (by wt.)	1	2	3	4	5
CaCO ₃	44.2	44.2	44.2	44.2	44.2
LLDPE	44.1	44.9	41.9	41.9	41.9
LDPE	1.5	3.7	3.7	3.7	3.7
Others*	10.2	10.2	10.2	10.2	10.2
Screw RPM	A 33	45	57	64	75
	B 33	45	57	64	75
Basis wt. (gms/m ²)	45	45	45	45	45
Gauge (mils)	2	2	2	2	2
Line Speed (fpm)	550	700	900	1000	1200
Air Knife (cfm/inch)	5-25	5-25	5-25	5-25	5-25
Web Stability	Poor gauge control with draw resonance	Good web stability without draw resonance			

*Other components include 2.5% by weight of a styrene-butadiene-styrene (SBS) triblock polymer, Shell Kraton 2122X, which is an SBS <50% by wt. + mineral oil <30% by wt., EVA copolymer <15% by wt., polystyrene <10% by wt., hydrocarbon resin <10% by wt., antioxidant/stabilizer <1% by wt., and hydrated amorphous silica <1% by wt.

Each of the formulations of 1-5 were extruded into films employing an extrusion apparatus as shown diagrammatically in FIG. 1. As shown, the apparatus may be employed for film extrusion with and without lamination. In the case of film extrusion, the formulations of Examples 1-5 were fed from an extruder 1 through slot die 2 to form the

extrudate 6 into the nip of a rubber roll 5 and a metal roll 4 with an air knife 3. Where extrusion lamination is practiced, there is an incoming web of fibrous material 9 from roller 13 which is also introduced into the nip of the rubber roll 5 and metal roll 4. In Examples 1-5, the thermoplastic film was produced for subsequent incremental stretching to form the microporous film. As shown in TABLE 1, over speeds of about 550 fpm to 1200 fpm, a polyethylene film 6 on the order of about 2 mils in thickness was made which is taken off at roller 7. The air knife 3 has a length of about 120" and an opening of about 0.035"-0.060" and air is blown through the opening and against the extrudate 6 at about 5 cfm/inch to 25 cfm/inch. The compressive force at the nip and the air knife are controlled such that the film is made without pin holing and without draw resonance in the case of Examples 2-5. Where the LDPE was included in the composition at a level of 1.5% by weight, draw resonance was encountered at a line speed of 550 fpm. However, when the LDPE was included in the formulation at a level of 3.7% by weight with the LLDPE at a level of 44.1-44.9% by weight, film production was able to be achieved at high speeds greater than 550 fpm up to 1200 fpm without draw resonance. The melt temperatures from the feed zone to the screw tip of extruders A and B were maintained at about 400-430°F with die temperatures of approximately 450°F to extrude the precursor film around 2 mils (45 gms/m²).

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FIG. 3 is a graph demonstrating the line speeds for Examples 1-5. Example 1, which contained only 1.5% by weight of LDPE, resulted in a poor film gauge control with draw resonance even with the air knife 3. However, when the LDPE was increased to about 3.7% by weight, excellent web stability was achieved without draw resonance even when line speeds were increased to about 1200 fpm. This is shown diagrammatically in FIG. 3.

FIG. 4 is a graph demonstrating the moisture vapor transmission properties of both embossed and flat films resulting from incrementally stretching the precursor films of Examples 2-5 under different temperatures and stretch roller engagement conditions. As shown schematically in FIG. 1, where the incoming film 12 at ambient temperature was passed through temperature controlled rollers 20 and 21 before CD and MD incremental stretching rollers (10 and 11, and 10' and 11'), the temperatures and the depths of engagements can be controlled. Remarkably, the MVTR of the flat film exceeded the MVTR of the embossed film as shown in FIG. 4. In brief, MVTRs for the embossed film on the order of about 1200-2400 gms/m²/day were achieved, whereas MVTRs for the flat film on the order of about 1900-3200 gms/m²/day were achieved. Unexpectedly, as also shown in FIG. 5, the MVTR of the microporous film can also be controlled by the web temperature during the stretching. Fig. 5 shows the film when heated to different temperatures before CD stretching can result in different MVTRs. The data reported in

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FIG. 5 was for a CD rollers engagement dept of 0.065" and MD rollers engagement depth of 0.040" where the temperature of roller 21 was maintained at ambient. The embossed film was made with a metal embossing roller having a rectangular engraving of CD and MD lines with about 165-300 lines per inch. This pattern is disclosed, for example, in U. S. Patent No. 4,376,147 which is incorporated herein by reference. This micro pattern provides a matte finish to the film but is undetectable to the naked eye.

In view of the above detailed description, it will be understood that variations will occur in employing the principles of this invention depending upon materials and conditions, as will be understood to those of ordinary skill in the art.

WHAT IS CLAIMED IS:

1. A high speed method of making a microporous thermoplastic film comprising

melt blending a composition comprising

(a) about 35% to about 45% by weight of a linear low density polyethylene,

(b) about 3% to about 10% by weight of a low density polyethylene,

(c) about 40% to about 55% by weight calcium carbonate filler particles, and

(d) about 2% to about 8% by weight of a triblock copolymer of styrene selected from the group consisting of styrene-butadiene-styrene, styrene-isoprene-styrene, and styrene-ethylene-butylene-styrene, and blends thereof,

extruding said melt blended composition into a nip of rollers with an air knife to form a film at a speed on the order of at least about 550 fpm to about 1200 fpm without draw resonance, and

applying an incremental stretching force to said film at said speed along lines substantially uniformly across said film and throughout its depth to provide a microporous film.

2. The high speed method of claim 1 wherein said melt blended composition consists essentially of about 42% by weight linear low density polyethylene, about 4% by weight low density polyethylene, about 44% calcium carbonate filler particles, and about 3% by weight triblock polymer.

3. The high speed method of claim 1 wherein said melt blended composition further comprises about 0-5% by weight high density polyethylene, about 0-4% by weight titanium dioxide, and about 0.1% to about 0.2% by weight processing aid.

4. The high speed method of claim 3 wherein said melt blended composition comprises about 4% by weight high density polyethylene, about 3% by weight titanium dioxide, and about 0.1% by weight fluorocarbon polymer processing aid.

5. The high speed method of claim 4 wherein said fluorocarbon polymer processing aid is 1-propene, 1,1,2,3,3,3-hexafluoro copolymer with 1,1-difluoroethylene.

6. The high speed method of claim 1 wherein said triblock polymer is preblended with oil, hydrocarbon, antioxidant and stabilizer.

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7. The high speed method of claim 1 wherein said nip of
rollers comprises a metal embossing roller having an engraving of CD and
MD lines within 185-300 lines/inch and a rubber roller and the
compressive force between said rollers is controlled to form an embossed
5 film.

8. The high speed method of claim 1 wherein said rollers
provide a polished chrome surface to form a flat film.

9. The high speed method of claim 1 comprising
introducing a nonwoven fibrous web into said nip of rollers and controlling
10 the compressive force between the web and the film at the nip to bond
the surface of the web to the film to form a laminated microporous sheet.

10. The high speed method of claim 9 wherein said fibrous
web comprises polyolefin fibers.

11. The high speed method of claim 10 wherein said fibers
15 are selected from the group consisting of polypropylene, polyethylene,
polyesters, cellulose, rayon, nylon and blends or coextrusions of two or
more such fibers.

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12. The high speed method of claim 11 wherein the
fibrous web has a weight of from about 5 to about 70 gms/yd² and the
microporous film has a thickness on the order of about 0.25 to about
10 mils.

5 13. The high speed method of claim 12 wherein said web
is formed from staple fibers or filaments.

14. The high speed method of claim 1 wherein said
incremental stretching step is conducted at ambient temperature.

15 10 15. The high speed method of claim 1 wherein said
incremental stretching step is conducted at an elevated temperature.

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16. A high speed method of making a microporous thermoplastic film comprising

melt blending a composition comprising

(a) about 35% to about 45% by weight of a linear low density polyethylene,

(b) about 3% to about 10% by weight of a low density polyethylene,

(c) about 40% to about 55% by weight calcium carbonate filler particles, and

(d) about 2% to about 6% by weight of a triblock copolymer of styrene selected from the group consisting of styrene-butadiene-styrene, styrene-isoprene-styrene, and styrene-ethylene-butylene-styrene, and blends thereof,

slot die extruding said melt blended composition into a nip of rollers with an air knife to form a film of about 0.5 to about 10 mills in thickness at speeds on the order of at least about 750 fpm to about 1200 fpm without draw resonance,

cooling said film to ambient temperature, and

applying an incremental stretching force to said cooled film at said speed along lines substantially uniformly across said film and throughout its depth to provide a microporous film.

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17. The high speed method of claim 16 wherein said film is traveling in a machine direction and incremental stretching force is applied across the machine direction of the traveling film and by application of a stretching force in the machine direction of the traveling film to provide the microporous film.

18. The high speed method of claim 16 wherein said composition consists essentially of about 42% by weight linear low density polyethylene, about 4% by weight low density polyethylene, about 44% by weight calcium carbonate filler particles, about 3% by weight triblock polymer, about 0-5% by weight high density polyethylene, about 0-4% by weight titanium dioxide, and about 0.1% to about 0.2% by weight processing aid.

19. The high speed method of claim 16 wherein said melt blended composition comprises about 4% by weight high density polyethylene, about 3% by weight titanium dioxide, and about 0.1% by weight fluorocarbon polymer processing aid.

20. The high speed method of claim 19 wherein said fluorocarbon polymer processing aid is 1-propene, 1,1,2,3,3,3-hexafluoro copolymer with 1,1-difluoroethylene.

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21. The high speed method of claim 20 wherein said triblock polymer is preblended with oil, hydrocarbon, antioxidant and stabilizer.

22. The high speed method of claim 16 wherein said nip of rollers comprises a metal embossing roller having an engraving of CD and MD lines with about 165-300 lines/inch and a rubber roller and the compressive force between said rollers is controlled to form an embossed film.

23. The high speed method of claim 16 wherein said rollers provide a polished chrome surface to form a flat film.

24. The high speed method of claim 16 comprising introducing a nonwoven fibrous web into said nip of rollers and controlling the compressive force between the web and the film at the nip to bond the surface of the web to the film to form a laminated microporous sheet.

25. The method of claim 24 wherein said fibrous web is formed of fibers selected from the group consisting of polypropylene, polyethylene, polyesters, cellulose, rayon, nylon and blends or coextrusions of two or more such fibers.

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26. The method of claim 25 where in the fibrous web has a weight of from about 5 to about 70 gms/yd² and the microporous film has a thickness on the order of about 0.25 to about 10 mils.

27. The high speed method of claim 16 wherein said incremental stretching step is conducted at ambient temperature.

28. The high speed method of claim 16 wherein said incremental stretching step is conducted at an elevated temperature.

29. The product of the method of claim 16.

30. The product of the method of claim 17.

31. The product of the method of claim 18.

32. The product of the method of claim 19.

33. The product of the method of claim 25.

34. The product of the method of claim 26.

35. The product of the method of claim 1.

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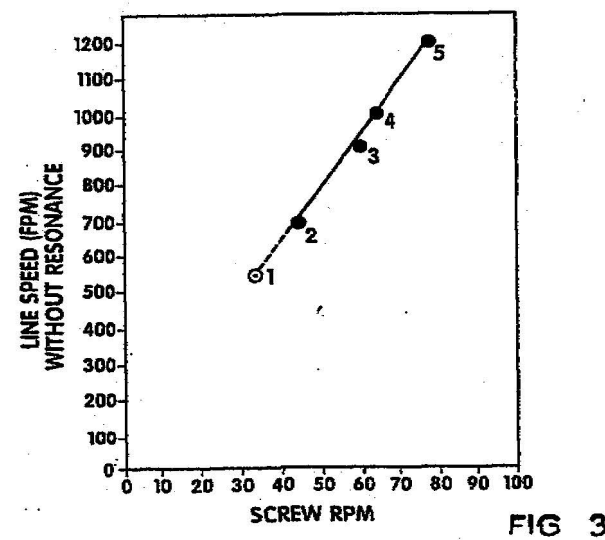
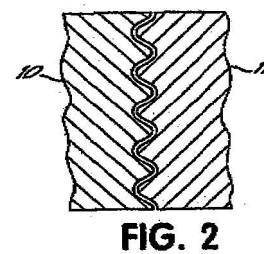
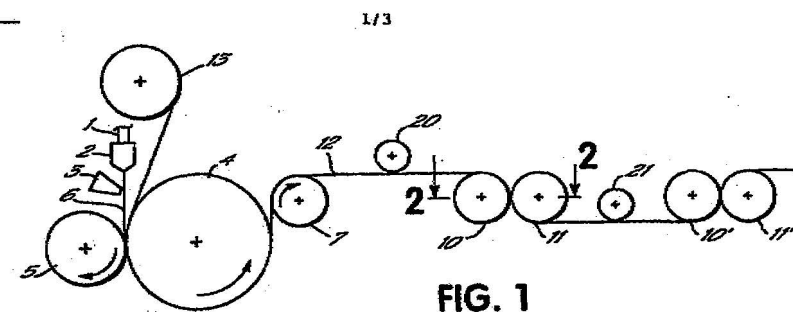
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36. The product of the method of claim 2.

37. The product of the method of claim 3.



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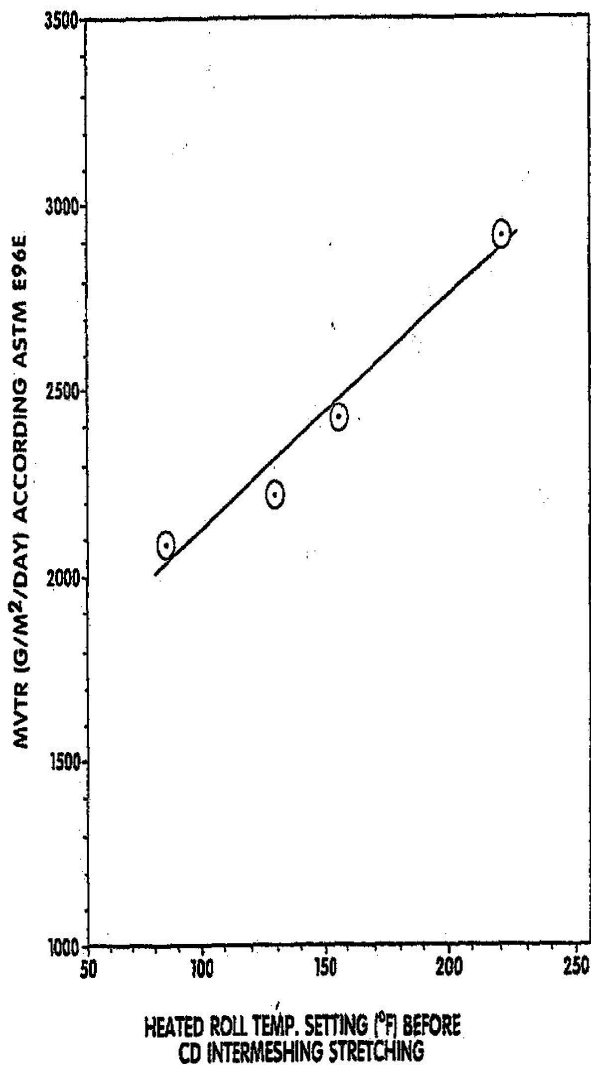


FIG. 5

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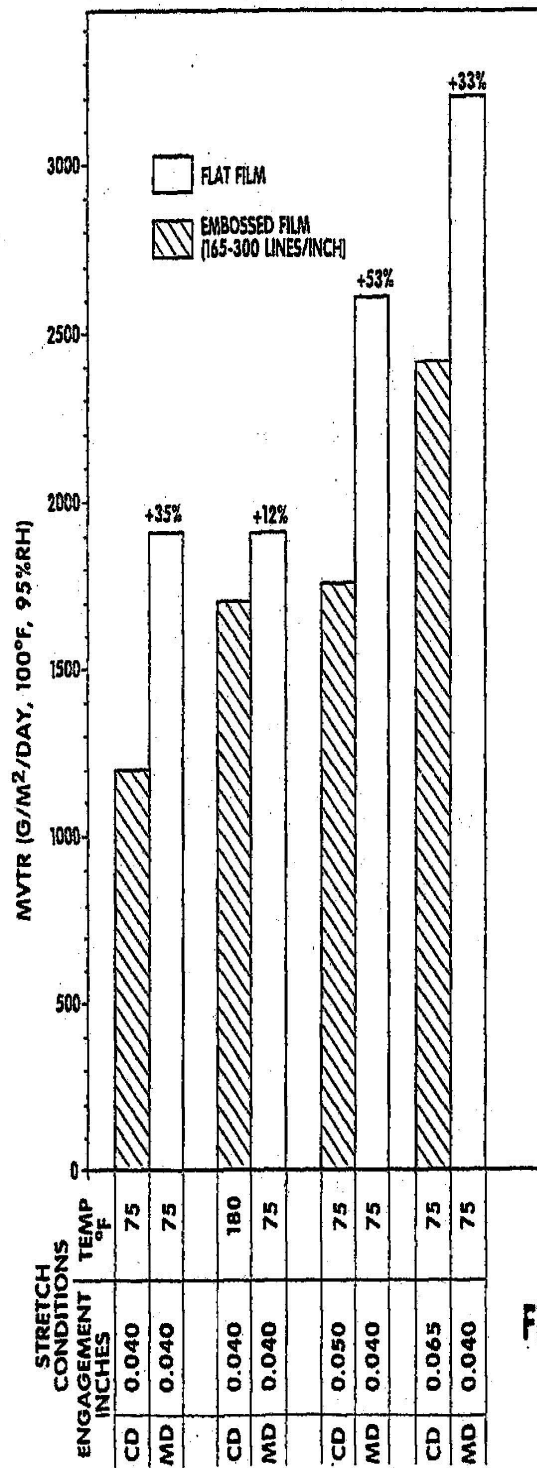


FIG. 4

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US06235377B1

(12) United States Patent
Dillon et al.

(10) Patent No.: US 6,235,377 B1
(45) Date of Patent: *May 22, 2001

(54) MICROPOROUS MEMBRANE WITH A STRATIFIED PORE STRUCTURE CREATED IN SITU AND PROCESS

(75) Inventors: Mark E. Dillon, Huntingdon Valley, PA; Richard Brandimarte, Bensalem, PA; Raymond E. Triglia, Levittown, all of PA (US)

(73) Assignee: Bio-Med Sciences, Inc., Allentown, PA (US)

(*) Notice: This patent issued on a continued prosecution application filed under 37 CFR 1.53(d), and is subject to the twenty year patent term provisions of 35 U.S.C. 154(e)(2).

Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

(21) Appl. No. 08/523,278
(22) Filed: Sep. 5, 1995

(51) Int. Cl.: B32B 7/02
(52) U.S. Cl.: 428/212, 428/218, 428/316.6, 428/421, 428/422, 428/447

(58) Field of Search: 428/310.5, 312.6, 428/315.5, 315.9, 421, 447, 316.6, 422, 212, 218

(56) References Cited

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Primary Examiner: Blaine Copenhafer
(74) Attorney, Agent, or Firm: John F. A. Earley, John F. A. Earley III, Harding, Earley, Follmer & Frailey

(57) ABSTRACT

A microporous membrane is described comprising at least two layers, wherein each layer is characterized by nodes interconnected by fibrils, the layers are bonded by means of plastic flow at temperatures below the melting point of either membrane material, and the pore architecture is formed in situ by an expansion process. A stratified microporous membrane is produced wherein the pore architecture of each layer may be discretely controlled. The article is useful for filtration and medical applications where a pore size gradient is required.

9 Claims, 1 Drawing Sheet



US06090441A

United States Patent
Vining, Jr. et al.

(10) Patent Number: 6,090,441
(45) Date of Patent: Jul. 18, 2000

(54) PROCESS OF MAKING REINFORCED, THREE ZONE MICROPOROUS MEMBRANE

(75) Inventors: Jack H. Vining, Jr., Coventry, Mark T. Meyering, Middlefield, C. Thomas Badenhop, Westport, all of Conn.

(73) Assignee: Cuno, Inc.

(21) Appl. No. 09/040,816

(22) Filed: Mar. 16, 1998

(51) Int. Cl.: B05D 1/26; B05D 1/34; B05D 1/36; B05D 3/03; B05D 7/04

(52) U.S. Cl.: 427/244; 427/245; 427/246; 427/412; 210/490

(58) Field of Search: 427/412, 152, 427/179, 210, 245, 246, 244, 420, 336, 210/490

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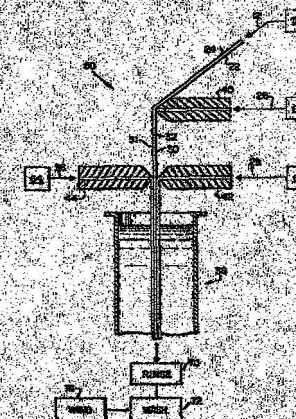
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Primary Examiner: Diana Dugan
Attorney, Agent, or Firm: Cummings & Lockwood

(57) ABSTRACT

A process for producing a three zone, reinforced, continuous, geometrically symmetrical microporous membrane including a porous support material encapsulated within a middle zone disposed between an upper zone and a lower zone wherein at least one of the three zones has a pore size at least about twenty (20%) percent greater than the pore size of the other two zones is disclosed. Apparatus for fabricating a three zone, reinforced, continuous, geometrically symmetrical microporous membrane and the fabricated membrane are also disclosed.

25 Claims, 10 Drawing Sheets





US006261674B1

(12) United States Patent

Branham et al.

(10) Patent No.: US 6,261,674 B1
(45) Date of Patent: Jul. 17, 2001

(54) BREATHABLE MICROLAYER POLYMER FILM AND ARTICLES INCLUDING SAME

(75) Inventors: Kelly Dean Branham, Lawrenceville, GA (US); Vasily Ippolitarov, Appleton; Dave A. Sorens, Neenah, both of WI (US)

(73) Assignee: Kimberly-Clark Worldwide, Inc., Neenah, WI (US)

(*) Notice: Subject to any disclaimer, the term of this patent, is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

(21) Appl. No.: 09/221,100

(22) Filed: Dec. 28, 1998

(51) Int. Cl.⁷ B32B 7/00

(52) U.S. Cl. 428/218; 428/315.5; 428/316.6; 442/370; 442/372; 442/374; 442/375

(58) Field of Search 442/370, 372, 442/374, 375; 428/315.5, 316.6, 218

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Primary Examiner—Blaine Coppenheaver

Assistant Examiner—Ula C. Ruddock

(74) Attorney, Agent, or Firm—Kilpatrick Stockton, LLP

(57) ABSTRACT

A breathable microlayer polymer film comprising a plurality of coextruded microlayers including a first layer comprising a first melt-extrudable polymer and a second layer comprising second melt-extrudable polymer, the first melt-extrudable polymer having a first water vapor transmission rate and the second melt-extrudable polymer having a second water vapor transmission rate less than the first water vapor transmission rate. A method for making such a breathable film is also disclosed. The microlayer polymer film is breathable, but can also be a barrier to liquid, microbial organisms, organic toxins, and body fluids, and is suitable as a covering material for disposable items such as diapers. While the first polymer is more breathable, the second polymer can impart other properties to the microlayer film such as enhanced tensile properties.

38 Claims, 3 Drawing Sheets

United States Patent

Mrozinski

(11) Patent Number: 4,863,792
(45) Date of Patent: Sep. 3, 1989

(54) MULTI-LAYER LAMINATES OF MICROPOROUS FILMS

(75) Inventor: James S. Mrozinski, Oakdale, Minn.

(73) Assignee: Minnesota Mining and Manufacturing Company, St. Paul, Minn.

(21) Appl. No.: 257,949

(22) Filed: Oct. 14, 1988

(51) Int. Cl.⁴ B32B 3/00; B32B 5/14; B32B 5/18

(52) U.S. Cl. 428/315.5; 156/308.2; 156/308.6; 428/315.7; 428/316.6

(58) Field of Search 156/308.2, 308.6; 428/315.5, 315.7, 315.9, 316.6

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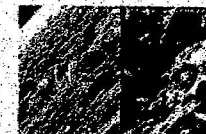
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Primary Examiner—William J. Van Buren
Attorney, Agent, or Firm—D. M. Sell; W. N. Kim; C. Truesdale

(57) ABSTRACT

Multi-layer, microporous polyolefin sheet materials are provided. The sheet materials comprise at least two microporous polyolefin layers, the layers being autogenously bonded and having substantially the same porosity as prior to bonding.

8 Claims, 2 Drawing Sheets





US05536413A

United States Patent [19]

Bormann et al.

[11] Patent Number: 5,536,413

[45] Date of Patent: Jul. 16, 1996

[54] METHOD FOR TREATING A PARENTERAL EMULSION-CONTAINING MEDICAMENT FLUID

[75] Inventors: Thomas J. Bormann, Molville; Thomas C. Gsell, Viado I. Matkovich, both of Glen Cove; Gerard R. Del Giaccio, Yonkers, all of N.Y.

[73] Assignee: Pall Corporation, East Hills, N.Y.

[21] Appl. No.: 875,774

[22] Filed: Apr. 29, 1992

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 620,775, Dec. 3, 1990, Pat. No. 5,252,222.

[51] Int. Cl.⁴ B01D 39/00; B01D 61/00

[52] U.S. Cl. 210/650; 210/436; 210/472; 210/651; 210/767; 422/1

[58] Field of Search 210/641, 650, 210/651, 653, 654, 188, 321.64, 767, 321.84, 435, 436, 472, 489, 492, 500.42, 500.38, 500.23; 604/405, 406; 422/1, 101; 436/177, 178; 55/421; 95/241; 96/155

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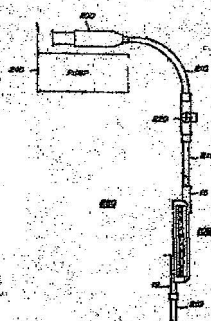
Primary Examiner—John Kim

Attorney Agent, or Firm—Leydig, Voit & Mayer

[57] ABSTRACT

Processes and systems are provided for treating parenteral emulsion-containing medicament fluids are provided.

23 Claims, 4 Drawing Sheets



US06264044B1

[12] United States Patent

Meyering et al.

(10) Patent No.: US 6,264,044 B1

(45) Date of Patent: Jul. 24, 2001

(54) REINFORCED, THREE ZONE MICROPOROUS MEMBRANE

(75) Inventors: Mark T. Meyering, Middlefield; Jack H. Vithig, Jr., Coventry; C. Thomas Badenhop, Westport, all of CT (US)

(73) Assignee: Cuno, Inc.

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

(21) Appl. No.: 09/040,979

(22) Filed: Mar. 18, 1998

Related U.S. Application Data

(60) Provisional application No. 60/043,184, filed on Apr. 11, 1997.

(51) Int. Cl.⁴ B01D 39/00

(52) U.S. Cl. 210/490; 210/507; 210/508; 210/645; 210/500.27

(58) Field of Search 210/488, 489, 210/490, 504, 506, 507, 508, 508.36, 500.38, 500.42, 645, 500.27; 55/524; 96/7, 9, 11, 12, 13

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Primary Examiner—Ana Fortune

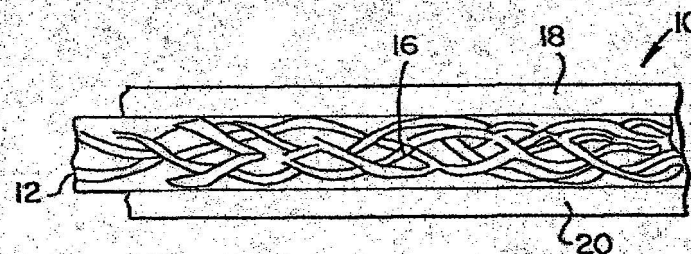
Assistant Examiner—Richard W. Ward

(74) Attorney Agent, or Firm—Cummings & Lockwood

(57) ABSTRACT

A three zone, reinforced, continuous, geometrically symmetrical microporous membrane including a porous support material encapsulated within a middle zone disposed between an upper zone and a lower zone wherein at least one of the three zones has a pore size at least about twenty (20%) percent greater than the pore size of the other two zones is disclosed. Apparatus and methods for fabricating three zone reinforced, continuous, geometrically symmetrical, microporous membrane are also disclosed.

75 Claims, 10 Drawing Sheets



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US005955187A

United States Patent [19] McCormack et al.

[11] Patent Number: 5,955,187
[45] Date of Patent: Sep. 21, 1999

[54] MICROPOROUS FILM WITH LIQUID TRIGGERED BARRIER FEATURE

[75] Inventors: Ann Louise McCormack, Cumming; David Craige Strack, Canton; Jay Sheldon Shultz, William F. Cartwright, both of Roswell; Carol A. Blazney, Roswell, all of Ga.

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Related U.S. Application Data

[63] Continuation-in-part of application No. 08/956,924, Oct. 23, 1997, which is a continuation of application No. 08/469,052, Jun. 6, 1995, abandoned.

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[58] Field of Search 428/213, 315.5, 428/315.7, 315.9, 316.6, 317.1, 317.9, 319.3, 326, 327, 330, 331, 913; 442/77, 370, 372, 374

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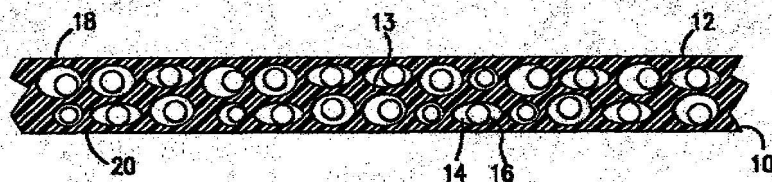
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[57] ABSTRACT

A self-regulating breathable microporous film layer transmits water vapor at normal use conditions, and reduces or eliminates the vapor transmission when the vapor in the environment becomes excessive. The film layer includes a voided polymer matrix and a plurality of fine, water-swelling filler particles disposed within the voids. When there is an excess of vapor, the filler particles swell to block or partially block transmission of vapor through the voids and the film layer.

59 Claims, 4 Drawing Sheets



United States Patent [19] Haffner et al.

[11] Patent Number: 6,045,900
[45] Date of Patent: Apr. 4, 2000

[54] BREATHABLE FILLED FILM LAMINATE

[75] Inventors: William Bela Haffner, Kenosaw, Ann Louise McCormack, Cumming, both of Ga.

[73] Assignee: Kimberly-Clark Worldwide, Inc., Neenah, Wis.

[21] Appl. No. 08/929,562

[22] Filed: Sep. 15, 1997

[51] Int. Cl.⁷ B32B 5/18

[52] U.S. Cl. 428/315.9; 428/315.9; 428/316.6; 428/317.9; 428/332; 442/370; 442/394; 442/398

[58] Field of Search 442/394, 398; 428/315.5, 315.9, 317.9, 316.6, 332

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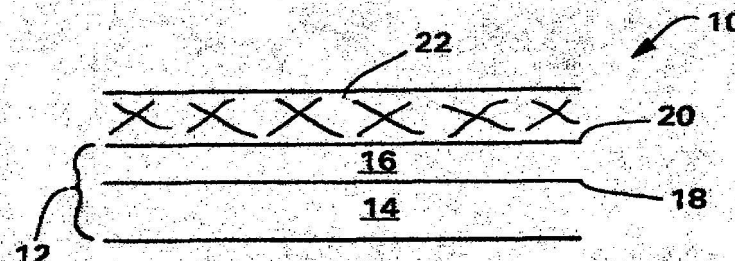
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Primary Examiner—Elizabeth M. Cole
Attorney, Agent, or Firm—Douglas H. Tulley, Jr.

[57] ABSTRACT

A breathable barrier laminate is disclosed having a first film layer comprising a microporous breathable barrier film; a second film layer comprising a breathable filled film which comprises about 50% to about 70% by weight filler and an amorphous polymer such as an elastomeric ethylene polymer having a density less than 0.89 g/cm³; and a third fibrous layer comprising a breathable outer layer, such as a non-woven web of spunbonded fibers. The multiple layers can be thermally laminated wherein laminate has a peel strength in excess of 200 grams and a WVTR in excess of 300 g/m²/day.

30 Claims, 2 Drawing Sheets





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United States Patent [19] Forte

[11] Patent Number: 6,114,024
[45] Date of Patent: Sep. 5, 2000

[54] MULTILAYER BREATHABLE FILM

1315427, 12/1989 Japan 428/316.6

[75] Inventor: Nicholas F. Forte, Newport News, Va.
[73] Assignee: Kimberly-Clark Worldwide, Inc.,
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[21] Appl. No.: 08/690,063
[22] Filed: Jul. 31, 1996

Primary Examiner—Allan R. Kuhn
Attorney, Agent, or Firm—Pillsbury Madison & Suto LLP

[57] ABSTRACT

Provided is a method of making a stretched, multilayer breathable film having the combination of properties of:
(i) providing a barrier to microorganisms; and
(ii) providing a barrier to blood and bodily fluids;
said method comprising the steps of:

(a) simultaneously extruding at least a five-layer film from a die, said five-layer film having as a minimum the following structure:
C-A-B-A-C;

where B comprises a microporous core layer containing at least one thermoplastic polymer and at least one particulate filler;

C comprises an outer monolithic layer containing a hydrophilic polymeric resin capable of absorbing and desorbing moisture and providing a barrier to aqueous fluids and microorganisms, said C layer being substantially free of particulate filler, and

A comprises a microporous adhesive layer for bonding said C layers to said core layer B, wherein said C layer substantially prevents the buildup of particulate filler material on said die during said extrusion step;

(b) stretching said extruded five-layer film to thereby form micropores in said microporous core layer and said microporous adhesive layer;

wherein said stretching step is conducted and said microporous core layer and said microporous adhesive layers have been formulated so as to provide micropores which allow the passage of gaseous water but substantially prevent the passage of liquid water. The invention also relates to a multilayer film.

Related U.S. Application Data
[60] Provisional application No. 69/001,818, Aug. 1, 1995.
[51] Int. Cl. B32B 7/12
[52] U.S. Cl. 428/315.9; 428/315.5;
428/315.7; 428/316.6; 428/317.1; 428/317.5;
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[58] Field of Search 428/315.5, 315.7,
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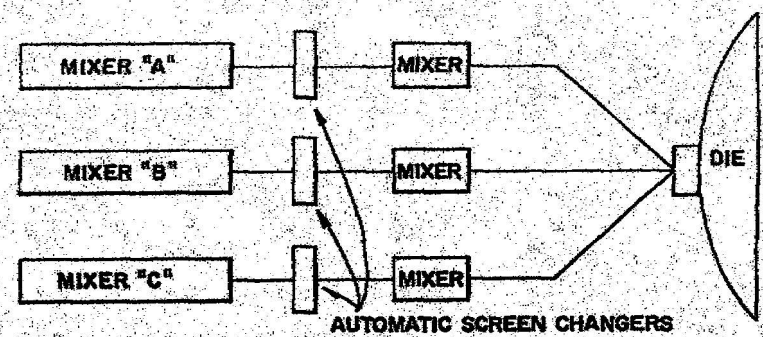
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12 Claims, 4 Drawing Sheets



United States Patent [19] Haffner et al.

[11] Patent Number: 6,045,900
[45] Date of Patent: Apr. 4, 2000

[54] BREATHABLE FILLED FILM LAMINATE

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[73] Assignee: Kimberly-Clark Worldwide, Inc.,
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[52] U.S. Cl. 428/315.9; 428/315.5;
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