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103

Superintendencia de Industria y Comercio
Radicación: 03096825 000/0002 Folios: 2
Fecha (AAA): 2005-10-24 16:03:21
Trámite: 002 PATENTES D 1 REGISTRO/ 538 PETICION
Dependencia: 2020 DIVISION DE NUEVAS CREACIONES

Trámite : 011
Evento : 379
Actuación : 538

Referencia : Expediente No. 03096825

Asunto : Solicitud de patente para **COMPOSICIÓN PARA MOLDEAR PARTES CON PAREDES DELGADAS, Y TUBO PARA APRETAR MOLDEADO POR INYECCIÓN HECHO DE ESTA**

Solicitante : SONOCO DEVELOPMENT, INC.

Fecha de solicitud : 30 de octubre de 2003

Publicada en : Gaceta 551 del 29 de abril de 2005

1. Yo, Emilio FERRERO, Identificado como aparece al pie de mi firma, actuando como apoderado en el asunto de la referencia, atentamente, solicito se efectúe el examen de patentabilidad de la solicitud en referencia según lo establecido en el artículo 44 de la Decisión 486 de la Comisión de la Comunidad Andina. Para tal efecto presento junto con este escrito el recibo por valor de \$371.000.00, que corresponde a la tasa fijada según lo dispuesto en la resolución No. 31980 del 24 de diciembre de 2004.

2. Ruego atentamente a la Señora Jefe se sirva ordenar que se anexe este recibo, para que se efectúe dicho examen y se continúe con el trámite de la solicitud.

Bogotá, 24 OCT. 2005
Señora Jefe,



EMILIO FERRERO
T.P.A. No. 31.929

COLO 12500-801-004-8
ZCA/ZCA/ID-000031/WPC12500

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SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO
Radicacion : 43036025 00000002 Folios: 2
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Tramite : 04 PATENTES D 1 REGISTRO/ S.M. PETICION
Dependencia: 2000 DIVISION DE NUEVAS CREACIONES

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO

NIT : 800176089-2

RECIBO OFICIAL DE CAJA : 05 - 46,067
FECHA : JUNIO 21 DE 2005

***** CONSIGNACION *****

DEPOSITANTE	TIPO PAGO	BANCO	CUENTA	No. PAGO	FECHA PGO	Vr. PAGO
CAVELIER ABOGADOS	CONSIGNACION	BANCO POPULAR	050-00110-6	40117916	21/06/2005	62,639,000.00

***** CONCEPTO *****

CANT.	RENTISTICO	CONCEPTO	TOTAL CONCEPTO
1	50005-01-01 SOLICITUDES	85 EXAMEN DE PATENTABILIDAD DE INVEN	371,000.
		TOTAL :	\$ 371,000.00

SON: TRESCIENTOS SETENTA Y UNO MIL PESOS

RESPONSABLE : 

RECIBO DE CAJA APLICADO AL EXPEDIENTE No. _____

Colo 12500-201-004-8

**SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO
DIVISIÓN DE NUEVAS CREACIONES**

2020

Bogotá, D. C., 5 de Mayo de 2006

Doctor

EMILIO FERRERO

Representante **SONOCO DEVELOPMENT, INC.**

ASUNTO

Radicación No. **03-96825**

Trámite **002**

Evento **001**

Actuación **486** **5612**

Oficio

Folios **031**

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:

- a) Para el presente estudio se tendrán en cuenta el capítulo descriptivo, comprendido en los folios 8 a 35 de la solicitud en estudio.
- b) Para el presente estudio se tendrán en cuenta los dibujos comprendidos en el folio 48 de la solicitud en estudio.
- c) Para el presente estudio se tendrá en cuenta el capítulo reivindicatorio que comprende 33 reivindicaciones en los folios 36 a 45 de la solicitud en estudio.
- d) Conforme lo establece los artículos 9, 10 y 11 de la decisión 486 de la Comisión de la Comunidad Andina, la presente solicitud en estudio fue presentada el 30 de octubre de 2003, y en el momento de la radicación SI se reclamo prioridad de la primera solicitud presentada en Estados Unidos US 10/285261

2) Objeto de la Invención

- a) Las reivindicaciones 1 a 33 de la solicitud en estudio se refieren a:
 - i) (1.)- Una composición para moldear partes flexibles con paredes delgadas, comprende una mezcla de: cerca de 65 a 95 por ciento en peso de polietileno de baja densidad que tiene una densidad menor de cerca de 0,925 g/cc y un índice de fusión de por lo menos cerca de 50 g/10 minutos; y cerca de 5 a 35 por ciento en peso de polipropileno que tiene un índice alto de fusión mayor de cerca de 800 g/10 minutos, dicho índice de fusión alto es logrado por degradación de peróxido del polipropileno durante el proceso de fusión.
 - ii) (8) Una composición para moldear partes flexibles de pared delgada...
 - iii) (14) Una composición para moldear partes flexibles de pared delgada...
 - iv) (20) Un tubo de apriete moldeado por inyección...
- b) Los anteriores productos buscan composiciones poliméricas mejoradas.

- c) Según la Clasificación Internacional de Patentes, la codificación para esta solicitud corresponde a C 08 L 23/00

3) Claridad de la Solicitud

- a) El artículo 28 de la Decisión 486 de la Comisión de la Comunidad Andina de Naciones establece

"La descripción deberá divulgar la invención de manera suficientemente clara y completa para su comprensión y para que una persona capacitada en la materia técnica correspondiente pueda ejecutarla"

La descripción no es clara toda vez que las unidades de medida no corresponden a las que exige la legislación, o sea, que pertenezcan al Sistema Internacional de Unidades. Debe anexarse nuevo capítulo completo con las unidades de forma correcta.

- b) El artículo 30 de la Decisión 486 de la Comisión de la Comunidad Andina establece que

"Las reivindicaciones definirán la materia que se desea proteger mediante la patente. Deben ser claras y concisas y estar enteramente sustentadas por la descripción. Las reivindicaciones podrán ser independientes o dependientes. Una reivindicación será independiente cuando defina la materia que se desea proteger sin referencia a otra reivindicación anterior. Una reivindicación será dependiente cuando defina la materia que se desea proteger refiriéndose a una reivindicación anterior. Una reivindicación será dependiente cuando defina la materia que se desea proteger refiriéndose a una reivindicación anterior.- Una reivindicación que se refiera a dos o más reivindicaciones anteriores se considerará reivindicación dependiente múltiple."

El capítulo reivindicatorio no es claro toda vez que:

- i) Frases tales como 'cerca de...' son inaceptables en un capítulo reivindicatorio toda vez que no precisan el alcance de la solicitud. Deben eliminarse. De la misma forma son inaceptables frases como "densidad menor", "Índice alto de fusión" y todas las frases similares.
- ii) No se precisa la materia sobre la cual se solicita protección. Cómo se explicará en el punto 4), la presente solicitud no posee unidad de invención, por lo que no está definida la materia sobre la cual se solicita protección.
- iii) No se pueden aceptar caracterizaciones hechas por el solicitante con pruebas que el mismo solicitante aplica y no son universalmente aceptadas. Esto no permite establecer una relación con el arte conocido, no pudiéndose entonces validar dichos parámetros. No se pueden aceptar dichas reivindicaciones

De acuerdo a lo anterior, el capítulo reivindicatorio no cumple con el requisito de claridad de acuerdo a lo establecido en el Art. 30 de la Decisión 486.

4) Evaluación de la Unidad de Invención

El artículo 25 de la Decisión 486 de la Comisión de la Comunidad Andina establece

"La solicitud de patente sólo podrá comprender una invención o un grupo de invenciones relacionadas entre sí, de manera que conformen un único concepto inventivo"

La presente solicitud carece de unidad de invención toda vez que configura cuatro diferentes objetos. Aunque se dirigen a composiciones poliméricas, la definición de la materia que caracteriza a cada una de las reivindicaciones independientes es muy diferente entre sí. Esto permite afirmar que no se trata del mismo producto. Todo el problema radica en configurar varias reivindicaciones independientes con materia diferente. El solicitante debe establecer una sola reivindicación independiente dirigida al producto en la forma más simple de la solicitud de invención. Partiendo de allí establecer reivindicaciones dependientes que amplíen esa forma más simple hasta su forma más compleja.

De acuerdo a lo anterior, la presente solicitud no cumple con el requisito de unidad de invención de acuerdo al Art. 25 de la Decisión 486. De continuar con el impedimento, esta oficina procederá a estudiar solo el primer grupo de invenciones que conformen un único concepto inventivo.

5) Reivindicaciones de uso

El artículo 14 de la Decisión 486 de la Comisión de la Comunidad Andina establece:

"Los Países Miembros otorgarán patentes para las invenciones sean de producto o procedimiento, en todos los campos de la tecnología, siempre que sean nuevas, tengan nivel inventivo y sean susceptibles de aplicación industrial".

Tal como esta contemplado en la legislación el uso no se protege. Se protegen los productos o procedimientos, donde el producto este correctamente definido por su conformación, y los procedimientos por la serie de etapas que busquen un fin. El uso no corresponde ni a un uso ni a un procedimiento. El uso es simplemente la aplicación industrial de esos productos o procedimientos. De acuerdo a lo observado en la presente solicitud, el solicitante quiere proteger un envase fabricado por la composición de las primeras reivindicaciones. Lo característico allí es simplemente el uso de la composición.

Por lo anterior, las reivindicaciones 20 a 33 no son patentables de acuerdo al Art. 14 de la Decisión 486.

6) Determinación del Estado de la Técnica

El artículo 16 de la Decisión 486 de la Comisión establece:

"El estado de la técnica comprenderá todo lo que haya sido accesible al público por una descripción escrita u oral, utilización, comercialización o cualquier otro medio antes de la fecha de presentación de la solicitud de patente o, en su caso, de la prioridad reconocida."

"Sólo para el efecto de la determinación de la novedad, también se considerará dentro del estado de la técnica, el contenido de una solicitud de patente en trámite ante la oficina nacional competente cuya fecha de presentación o de prioridad fuese anterior a la fecha de presentación o de prioridad de la solicitud de patente que se estuviese examinando, siempre que dicho contenido este incluido en la solicitud de fecha anterior cuando ella se publique o hubiese transcurrido el plazo previsto en el artículo 40."

Consultadas las bases de datos y los archivos con que cuenta la entidad, especialmente bajo las clasificaciones C 08 L 23/00 y las más cercanas a ellas, se encontró que antes del 31 de octubre de 2002 (fecha para determinar el estado de la técnica) habían sido publicados los documentos que se enumeran en la siguiente tabla los cuales se relacionan con composiciones poliméricas.

De acuerdo con lo establecido en el artículo 16 se determinó el estado de la técnica y se encontró el siguiente antecedente:

Nº	Documento	Título	Fecha de Publicación
D1	EP 0 530 782	Environmental stress crack resistant polyethylene blends	1993.03.10
D2	US 6 407 171	Blends of polyethylene and polypropylene	2002.06.18
D3	US 6 159 566	Flexible thermoplastic and compressible tube made of this material	2000.12.12
D4	US 6 124 008	Injected molded package of blended ethylene / olefin copolymers	2000.09.26

7) Evaluación de los requisitos de patentabilidad

El artículo 14 de la Decisión 486 de la Comisión de la Comunidad Andina establece:

"Los Países Miembros otorgarán patentes para las invenciones, sean de producto o procedimiento, en todos los campos de la tecnología, siempre que sean nuevas tengan nivel inventivo y sean susceptibles de aplicación industrial".

En cumplimiento con este artículo, se procedió a evaluar los requisitos de novedad, nivel inventivo y aplicación industrial con el fin de establecer la patentabilidad de la invención reivindicada en la solicitud en estudio.

a) Evaluación del Nivel Inventivo

El art. 18 de la Decisión 486 de la Comisión de la Comunidad Andina establece:

"Se considerará que una invención tiene nivel inventivo, si para una persona del oficio normalmente versada en el arte en la materia técnica correspondiente, esa invención no hubiese resultado obvia ni se hubiese derivado de manera evidente del estado de la técnica".

La solicitud colombiana se refiere a una composición que comprende una mezcla de: (a) 65 a 95 por ciento en peso de polietileno de baja densidad (densidad menor de 0,925 g/cm³) y un índice de fusión de por lo menos 50

g/10 minutos; y (b) 5 a 35 por ciento en peso de polipropileno que tiene un punto de fusión mayor de 800 g/10 minutos.

Todos los documentos enumerados, D1 (EP 530 782), D2 (US 6 407 171), D3 (US 6 159 566) y D4 (US 6 124 008) relacionan mezclas de poliolefinas con propiedades muy similares a las que esboza la presente solicitud. Un técnico medio podría considerar uno cualquiera de dichos documentos para desarrollar la propuesta hecha por el solicitante colombiano. Podría afirmarse que no existe altura inventiva, toda vez que mezclas de poliolefinas como la que se muestra en la presente solicitud se utilizan con frecuencia en la técnica usual.

b) Resumen

En conclusión los requisitos de patentabilidad de la presente solicitud se podrían ver afectados así:

Nº	Documento	Reivindicaciones afectadas	Requisito que afecta
D1	EP 0 530 782	1 - 19	Nivel inventivo
D2	US 6 407 171	1 - 19	Nivel inventivo
D3	US 6 159 566	1 - 19	Nivel inventivo
D4	US 6 124 008	1 - 19	Nivel inventivo

8) Notificación

En cumplimiento del artículo 45 de la Decisión 486 de la Comisión de la Comunidad Andina, se le indica que dentro del término de sesenta días contados a partir de la fecha de la notificación de la presente comunicación debe responder a la notificación. 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 por el numeral 5.2, literal e) del capítulo quinto del título primero de la Circular Única N° 10 de 2001



DORIS POLO C.

Jefe División de Nuevas Creaciones (E)

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

25 MAYO 2006

Concepto Técnico N°	EXAMINADOR TÉCNICO Código No.	EXAMINADOR JURÍDICO Código No.
726	202003	

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⑪ Publication number: **0 530 782 A1**

⑫ **EUROPEAN PATENT APPLICATION**

⑰ Application number: **92115010.8**

⑱ Int. Cl.⁸: **C08L 23/06, //(C08L23/06, 23:04)**

⑳ Date of filing: **02.09.92**

㉑ Priority: **03.09.91 US 754507**

㉒ Date of publication of application: **10.03.93 Bulletin 93/10**

㉓ Designated Contracting States: **AT BE CH DE DK FR GB IT LI NL SE**

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㉗ **Environmental stress crack resistant polyethylene blends.**

㉘ A resin blend for the production of articles having improved environmental stress crack resistance comprising:

(a) a linear low density copolymer of ethylene and a C₄ - C₈ higher olefin having from about 10 to about 15 long chain branches per 1000 carbons; and

(b) a low density polyethylene produced by high pressure free radical polymerization, the low density polyethylene having a density of from about 0.917 to about 0.925, a melt index of from about 0.1 to about 10 and an environmental stress crack resistance less than about 25 hours;

said resin blend having a swell ratio of from about 1.70 to about 2.20; and,

wherein said linear low density copolymer comprises an effective amount of from about 25% to about 35% of the blend to improve the environmental stress crack resistance of articles produced from the blend.

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This invention relates generally to polyolefin resin blends suitable for use in the production of plastic articles such as sheets, tubes and bottles where environmental stress crack properties are desirable and a method of producing such articles. In particular, the resin blends are suitable for producing articles by extrusion, blow molding, injection molding and similar processes, having improved environmental stress crack resistance.

Low density polyethylenes (LDPE) are known for their ease of processibility, which facilitates their conversion into finished articles such as bottles and tubes using a variety of processes including extrusion, blow molding and injection molding processes. The properties of low density polyethylenes are, however, not always totally satisfactory due to environmental stress cracking in applications in which the finished product is in contact with materials that contain detergents, surfactants and similar compounds.

Environmental stress cracking (ESC) is a term used to describe a mechanism of chemical attack in which an agent that does not appreciably attack or dissolve a polymer in an unstressed condition will cause failure through the initiation and propagation of cracks or crazes when the polymer is stressed while in contact with the agent. The mechanism and rate at which environmental stress cracking occurs in a given plastic depends upon the specific agent, its concentration, the plastic, the temperature, the amount of stress and other factors such as surface roughness and polymer morphology, the effect of which is not completely understood.

Certain low density polyethylenes are susceptible to environmental stress cracking. Consequently the use of these low density polyethylenes to manufacture products such as tubes and bottles that are ultimately placed in contact with materials containing detergents, surfactants and similar agents has been restricted. Thus, there is a need for a resin blend that combines the processibility of low density polyethylenes with improved resistance to environmental stress cracking.

In accordance with the present invention, resin blends are provided that substantially retain the processibility of low density polyethylene while providing improved environmental stress crack resistance (ESCR). The blends contain: (a) from about 25% to about 35% of a linear low density polyethylene (LLDPE) containing from about 8% to about 12% octene and having from about 10 to about 15 long chain branches per 1000 carbons; and (b) a LDPE having a melt index of less than about 10, a density of less than about 0.925 g/cm³ and an environmental stress crack resistance of less than about 25 hours as determined in accordance with ASTM 1683, Condition A. The blends provide dramatically improved environmental stress crack resistance while simultaneously providing the processibility of low density polyethylenes. The blends fit the swell ratio/melt index processing window imposed by existing equipment, processes and product specifications and are particularly useful in the production of plastic articles such as bottles, tubes and the like, produced by extrusion, blow molding, injection molding and similar processes.

Low density, highly branched polyethylenes produced by high pressure free radical polymerization of ethylene in an autoclave or tubular type reactor possess a unique combination of properties including toughness, high impact strength and flexibility. Certain low density polyethylenes are, however, susceptible to environmental stress cracking, a phenomena that occurs when the polyethylene is exposed to detergents, surfactants and similar materials while under stress. Consequently, the applicability of these low density polyethylenes to the production of plastic containers such as tubes and bottles for shampoos, soaps, detergents and the like has been limited.

The low density polyethylenes of interest in connection with the practice of the present invention have an environmental stress crack resistance that is typically less than about 25 as determined in accordance with ASTM 1683, ENVIRONMENTAL STRESS-CRACKING OF ETHYLENE PLASTICS, Condition A, which is incorporated herein by reference. Low density polyethylenes useful in the practice of the invention include low density branched polyethylenes having a density of from about 0.917 grams/cm³ to about 0.925 grams/cm³ and a melt index of less than about 10, e.g. from about 0.1 to about 10, and preferably from about 1.0 to 8.0.

Linear low density polyethylenes are copolymers of ethylene and a higher olefin, typically C₄ - C₈ alpha olefins. These copolymers exhibit improved strength and environmental stress crack resistance over low density polyethylenes. Linear low density polyethylene, however, because of its linearity and narrow molecular weight distribution, has poorer processing characteristics, requiring increased temperatures and pressures in forming processes such as extrusion, blow molding and injection molding. Thus, substantial substitution of linear low density polyethylene for low density polyethylene cannot normally be accomplished without expensive retooling. Discussions of various blow molding, extrusion and injection molding processes are presented in the 1989 Mid-October issue of Modern Plastics Encyclopedia, at pages 217-224, 242-244, and 264-276, respectively and are incorporated herein by reference.

A factor that must be considered in the selection of materials for blow molding and similar applications is the swell of the parison as it exits the die. This parameter is important in the production of articles that

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must meet size specifications. Therefore, in order to utilize existing equipment with a given polymer blend, the swell characteristic of the polymer must match the processing capability of the equipment. The swell characteristics of the blends of the present invention are such that the blends may be readily adapted to applications where improved ESCR is required or desired using existing equipment.

5 One measure of the swell characteristics of a resin blend is the swell ratio: the ratio of the diameter of an extrudate to the diameter of a die under specified conditions. The low density polyethylenes and the LDPE/LLDPE blends of interest typically have a swell ratio of from about 1.70 to about 2.20 as determined by measuring the diameter of the semimolten extrudate from a 0.0825 inch die using a standard melt indexer with a dead weight of 4.9 Kg. at 210° C. The diameter of the extrudate is measured at a point
10 approximately 5.0 cm. from the tip of the die using a Model No. 183-100 dual axis laser scanner manufactured by Laser Mike Inc., of Dayton, Ohio. Measurements are taken at a rate of 1 reading every 2 seconds for a period of 10 seconds and readings averaged. Preferably, the resin blends have a swell ratio of from about 1.70 to about 2.20. More preferably, the resin blends have a swell ratio of from about 1.8 to about 2.1.

15 An additional element of the processing window imposed by existing equipment and processes is the melt index of resin blends that may be used in a given process. Thus, a processing "window" imposed by existing equipment and process dictates a range on the swell ratio and melt index of resin blends that may be appropriate for a given product application using existing processes and equipment. For the purposes of the invention, resin blends of low density polyethylene and linear low density polyethylenes preferably have
20 a melt index of from about 0.5 to about 2.5 to fit the applicable processing windows. Most preferably, the resin blends have a melt index of from about 0.5 to about 2.0.

It was also discovered that the amount of improvement in environmental stress crack resistance obtained by blending low density polyethylenes with linear low density polyethylenes was not only a function of the percentage of linear low density polyethylene in the blend but also varied widely with the
25 specific linear low density polyethylene used in the blend. While not wishing to be bound or limited to any particular theory, it is believed that the improvement in environmental stress crack resistance provided by the resin blends of the invention is at least partially attributable to the degree of long chain branching in the linear low density polyethylene. A long chain branch, as used herein, refers to a branch having more than five carbon atoms, as determined by C-13 NMR analysis. A method of determining polyethylene branching is disclosed in H. N. Cheng, Determination of Polyethylene Branching Through Computerized ¹³C NMR Analysis, Polymer Bull., 16, 445 (1988).

It is believed that an optimal number of long chain branches in the linear low density polyethylene prevent or slow crack growth, thereby increasing the time to failure. When the degree of branching is above the optimum range, the branches are not as effective in preventing or retarding crack growth as crack
35 growth can take a number of paths. Thus, it was discovered that a blend of about 25% to about 35% linear low density polyethylene having 10 to 15 long chain side branches per 1000 carbons with 65% to 75% low density polyethylene provided dramatically improved environmental stress crack resistance as compared to LDPE alone or other LLDPE/LDPE blends.

Suitably the linear low density polyethylene has a density of less than about 0.93 g/cm³, preferably of
40 from about 0.915 g/cm³ to about 0.925 g/cm³, a melt index of less than 1.5, e.g. of from about 0.8 to about 1.2, preferably of from about 0.9 to about 1.1.

A linear low density polyethylene useful in the practice of the present invention has a density of about 0.92 grams/cm³, a melt index of about 0.8, an octene content of about 11% and approximately 13 long chain branches per 1000 carbon atoms and is manufactured and sold by Dow Chemical under the trade
45 designation Dowlex 2045.

It was also discovered that environmental stress crack resistance of samples produced from the LLDPE/LDPE blends was at least partially a function of the melt index of the particular low density polyethylene included in the blend. In order to produce a blend having a high degree of environmental stress crack resistance with a low density polyethylene having a relatively high melt index, for example
50 about 8, a proportionally greater amount of linear low density polyethylene is required. The relationship between the minimum amount of linear low density polyethylene having 10 to 15 long chain side branches per 1000 carbons required to produce a blend having high ESCR, for example greater than 100, and the melt index of the low density polyethylene in the blend is approximated by the following relationship:

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$$\%LLDPE = 16.33 + 21.01 \log (\text{melt index of LDPE})^*$$

* Relationship specific to LLDPE #3 of Examples.

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Preferably, the resin blends of the present invention have a density less than about 0.93 g/cm³, preferably less than 0.925 g/cm³, and contain an amount of linear low density polyethylene having approximately 10 to 15 long chain side branches per 1000 carbons to increase the environmental stress crack resistance of a low density polyethylene having a relatively low environmental stress crack resistance, for example less than 25 hours, e.g. from about 1 hour to about 25 hours, to a value of at least 100 hours as measured by ASTM 1683, Condition A. More preferably, the environmental stress crack resistance of the blends is improved to a value of at least 300 hours.

The effectiveness of a linear low density polyethylene with an optimum number of long chain branches in improving environmental stress crack resistance is evidenced in the following examples which illustrate the invention; however, the scope of the invention is not to be limited thereby.

EXAMPLES

The following low density polyethylenes of Table 1 below, commercially available from Flexene Products Company, Odessa, Texas were blended with various amounts of the different linear low density polyethylenes of Table 2.

TABLE 1

LOW DENSITY POLYETHYLENES		
Low Density Polyethylene	Melt Index	Density g/cm ³
XO849	0.5	0.924
PE8010	1.0	0.921
PE8014	1.3	0.919
PE1017	2.0	0.920
PE2030	5.0	0.919
PE5020	4.0	0.917
XO880	1.2	0.917
XO882	2.5	0.918
XO873	6.0	0.920

TABLE 2 - LINEAR LOW DENSITY POLYETHYLENES

	#1	#2	#3	#4
MI, g/10 min	1.0	3.9	0.9	0.9
Comonomer	butene	octene	octene	octene

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TABLE 2 (continued)

	#1	#2	#3	#4
Wt % Comonomer	7.7	2.7	10.7	12.7
Density (gm/cm ³)	0.919	0.940	0.921	0.912
Long Chain Branches per 1000 carbons	0.0	3.4	13.1	17.5
Molecular Weight Data*				
Mn X 10 ⁻³	26	24	30	24
Mw X 10 ⁻³	95	75	100	90
Mz X 10 ⁻³	215	155	230	215
PDI=Mw/Mn	3.7	3.1	3.3	3.8

* Reference standard used was NIST 1475 polyethylene standard

Environmental stress crack resistance of polyethylenes is determined in accordance with ASTM D1683 Condition A and reported in hours. Compression molded samples are longitudinally notched and bent into C shaped test specimens. The test specimens are immersed in 100% Igepal (a strong detergent) and the time to failure monitored. The ESCR value in hours is determined graphically as the time for 50% failure. ESCR values for various blends of the low density and linear low density polyethylenes identified in Tables 1 and Table 2 are tabulated below.

TABLE 3

BLEND	MELT INDEX	ESCR-ASTM D1683 CONDITION A (HRS)
100% PE8010	1.0	1
90% PE8010 - 10% LLDPE #1	1.0	3
80% PE8010 - 20% LLDPE #1	0.8	12
70% PE8010 - 30% LLDPE #1	-	24
60% PE8010 - 40% LLDPE #1	-	>240
90% PE8010 - 10% LLDPE #2	-	1
80% PE8010 - 20% LLDPE #2	-	10
70% PE8010 - 30% LLDPE #2	-	>216
60% PE8010 - 40% LLDPE #2	-	>216
90% PE8010 - 10% LLDPE #3	0.9	20, 11
85% PE8010 - 15% LLDPE #3	-	108, 80
80% PE8010 - 20% LLDPE #3	0.8	>216, 253, 841* >744
75% PE8010 - 25% LLDPE #3	0.7	>720, >720, >720, >720
70% PE8010 - 30% LLDPE #3	-	>216
60% PE8010 - 40% LLDPE #3	-	>216
85% PE8010 - 15% LLDPE #4	-	25, 48
80% PE8010 - 20% LLDPE #4	0.8	22, 228

(*) Sample conditioned for about 2-3 weeks after molding rather than 40-86 hours as specified in the test method

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TABLE 4

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BLEND	MELT INDEX	ESCR-ASTM D1693 CONDITION A (HRS)
100% X0849	0.5	3, 22
97.5% X0849 - 2.5% LLDPE #3	0.5	33
95% X0849 - 5.0% LLDPE #3	0.8	40
90% X0849 - 10% LLDPE #3	0.5	285, 188, 115
85% X0849 - 15% LLDPE #3	0.5	388, 180, >648
90% X0849 - 10% LLDPE #4	-	18,17
85% X0849 - 15% LLDPE #4	-	127, 188

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TABLE 5

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BLEND	MELT INDEX	ESCR-ASTM D1693 CONDITION A (HRS)
100% PE8014	1.3	2
90% PE8014 - 10% LLDPE #3	-	23
80% PE8014 - 20% LLDPE #3	-	188
70% PE8014 - 30% LLDPE #3	0.8	>720, >720, >720, >720

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TABLE 6

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BLEND	MELT INDEX	ESCR-ASTM D1693 CONDITION A (HRS)
100% PE1017	2.0	2
90% PE1017 - 10% LLDPE #3	-	17
80% PE1017 - 20% LLDPE #3	-	49
75% PE1017 - 25% LLDPE #3	1.2	185
72.5% PE1017 - 27.5% LLDPE #3	1.1	>720, 294, 288, 851
70% PE1017 - 30% LLDPE #3	1.1	>720

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TABLE 7

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BLEND	MELT INDEX	ESCR-ASTM D1693 CONDITION A (HRS)
100% PE2030	5.0	1
80% PE2030 - 20% LLDPE #3	-	10
70% PE2030 - 30% LLDPE #3	1.9	114
65% PE2030 - 35% LLDPE #3	1.7	>720, 645, 822
60% PE2030 - 40% LLDPE #3	1.8	>720

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TABLE 8

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BLEND	MELT INDEX	ESCR-ASTM D1693 CONDITION A (HRS)
100% PE5020	4.0	1
80% PE5020 - 20% LLDPE #3	-	18
75% PE5020 - 25% LLDPE #3	-	42
70% PE5020 - 30% LLDPE #3	1.5	270
60% PE5020 - 40% LLDPE #3	1.3	>720

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TABLE 9

	BLEND	MELT INDEX	ESCR-ASTM D1893 CONDITION A (HRS)
5	100% X0880	1.2	2
	70% X0880 - 30% LLDPE #3	0.8	>720, >720, >720
	100% X0882	2.5	8
	72.5% X0882 - 27.5% LLDPE #3	1.2	>720, >720, >720
	70% X0882 - 30% LLDPE #3	1.2	>720, >720, >720
10	100% X0873	8.0	1
	65% X0873 - 35% LLDPE #3	2.0	>720, >720, >720

15 The swell ratio of a number of the low density polyethylenes and the low density/linear low density blends identified above was determined as described above. Swell is reported in Table 10 as the ratio of the diameter of the extrudate to the diameter of the die.

TABLE 10

	BLEND	BLEND DENSITY	SWELL
20	100% PE8010	0.921	1.77
	80% PE8010 - 20% LLDPE #3	-	1.73
	75% PE8010 - 25% LLDPE #3	0.922	1.74
	100% PE8014	0.919	1.80
25	70% PE8014 - 30% LLDPE #3	0.921	1.84
	100% PE1017	0.920	1.88
	70% PE1017 - 30% LLDPE #3	-	1.84
	100% X0880	0.917	2.21
	70% X0880 - 30% LLDPE #3	0.919	2.03
30	100% X0882	0.918	2.14
	72.5% X0882 - 27.5% LLDPE #3	-	2.04
	70% X0882 - 30% LLDPE #3	0.919	1.98
	65% PE2030 - 35% LLDPE #3	0.919	1.75
	100% X0873	0.920	2.02
35	65% X0873 - 35% LLDPE #3	0.919	1.88

40 The foregoing examples illustrate that blends of from about 25% to about 35% of a linear low density polyethylene with about 10 to about 15 long chain branches per 1000 carbons with a low density polyethylene having a melt index of less than about 10 and a density of less than about 0.925 g/cm³ have improved environmental stress crack resistance as compared to low density polyethylene and other LLDPE/LLDPE blends. Additionally, these blends retain the desirable processing characteristics of low density polyethylene and may therefore be used without expensive retooling.

45 While particular embodiments of the present invention have been described, it will be apparent to those skilled in the art that various changes and modifications can be made without departing from the spirit and scope of the invention. The following claims are intended to cover all such modifications that are within the scope of the invention.

Claims

- 50 1. A resin blend for the production of environmental stress crack resistant articles comprising:
- 65 (a) a low density polyethylene having a density of from about 0.917 g/cm³ to about 0.925 g/cm³, a melt index of from about 0.1 to about 10 and an environmental stress crack resistance less than about 25 hours; and
- (b) a linear low density copolymer of ethylene and a C₄-C₈ higher olefin having from about 10 to about 15 long chain branches per 1000 carbon atoms wherein said linear low density copolymer comprises an effective amount of from about 25% to about 35% of the blend to improve the environmental stress crack resistance of articles produced from the blend;

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said resin blend having a density of less than about 0.930 g/cm³, a melt index of from about 0.5 to about 2.5 and a swell ratio of from about 1.70 to about 2.20.

2. The resin blend of claim 1 wherein the low density polyethylene is produced by high pressure free radical polymerization of ethylene.
3. The resin blend of anyone of claims 1 or 2 wherein the linear low density polyethylene has a density of less than 0.93 g/cm³, preferably of from about 0.915 g/cm³ to about 0.925 g/cm³.
4. The resin blend of anyone of claims 1 to 3 wherein the linear low density copolymer of ethylene and a C₄-C₈ olefin has a melt index of less than 1.5, e.g. of from about 0.8 to about 1.2 and preferably of from about 0.9 to about 1.1.
5. The resin blend of anyone of claims 1 to 4 wherein the linear low density polyethylene is a copolymer of ethylene and from about 8% to about 12% octene.
6. The resin blend of claim 5 wherein the linear low density copolymer of ethylene and octene has a density of about 0.92 g/cm³, a melt index of about 0.9, an octene content of about 11% and approximately 13 long chain branches per 1000 carbons.
7. The resin blend of anyone of claims 1 to 6 wherein the resin blend has a density of less than about 0.925 g/cm³.
8. The resin blend of anyone of claims 1 to 7 wherein the low density polyethylene has a melt index of from about 1.0 to about 6.0.
9. The resin blend of anyone of claims 1 to 7 wherein the resin blend has a melt index of from about 0.5 to about 2.0.
10. The resin blend of anyone of claims 1 to 9 wherein the linear low density polyethylene is present in an amount effective to increase the environmental stress crack resistance of articles produced from the blend to at least 100 hours, preferably to at least 300 hours.
11. An article produced from the resin blend of anyone of claims 1 to 10.
12. A method of producing a resin blend comprising:
blending a low density polyethylene resin produced by high pressure free radical polymerization of ethylene having a density from about 0.917 gm/cm³ to about 0.925 gm/cm³, a melt index of from about 0.1 to about 10.0 and an environmental stress crack resistance of less than about 25 hours with a linear low density copolymer of ethylene and a C₄ - C₈ higher olefin having from about 10 to about 15 long chain branches per 1000 carbon atoms, a density of less than about 0.93 and a melt index of less than 1.5, said linear low density copolymer being present in the blend in an amount effective to produce articles having an environmental stress crack resistance of at least 100 hours, preferably of at least 200 hours and most preferably of at least 300 hours, said resin blend having a density of less than about 0.930 g/cm³, a swell index of from about 1.7 to about 2.20 and a melt index of from about 0.5 to about 2.5.
13. The method of claim 12 wherein the resin blend comprises from about 25% to about 35% of a linear low density copolymer of ethylene and a C₄ - C₈ higher olefin having from about 10 to about 15 long chain branches per 1000 carbon atoms.
14. A method of increasing the environmental stress crack resistance of plastic containers comprising:
producing a tube or bottle suitable for use as a container for liquids containing surfactants or detergents from a blend of a low density polyethylene resin produced by high pressure free radical polymerization of ethylene having a density from about 0.917 gm/cm³ to about 0.925 gm/cm³, a melt index of from about 0.1 to about 10.0 and an environmental stress crack resistance of less than about 25 hours with a linear low density copolymer of ethylene and a C₄ - C₈ higher olefin having from about 10 to about 15 long chain branches per 1000 carbon atoms, a density of less than about 0.93 and a

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melt index of less than 1.5, said linear low density copolymer being present in the blend in an amount effective to increase the environmental stress crack resistance of articles produced from the blend to a value of at least 300 hours, said resin blend having a density of less than about 0.930 g/cm³, a swell index of from about 1.7 to about 2.20 and a melt index of from about 0.5 to about 2.5.

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15. The method of anyone of claims 12 to 14 wherein said articles are produced by blow molding, extrusion or injection molding.

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Agarwal et al.

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(54) **BLENDS OF POLYETHYLENE AND
POLYPROPYLENE**

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(58) **Field of Search** 525/191, 240

(56) **References Cited**

U.S. PATENT DOCUMENTS

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(57) **ABSTRACT**

Disclosed are compositions comprising: a) an ethylene poly-
mer component having a melting temperature greater than or
equal to about 75° C., an ethylene crystallinity level of 5
weight percent or more, and a narrow compositional distri-
bution; and b) a propylene polymer component having a
melt flow rate of 500 dg/min. or more at 230° C. and a
melting temperature greater than or equal to about 125° C.

11 Claims, No Drawings

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BLEND OF POLYETHYLENE AND POLYPROPYLENE

SUMMARY

This invention relates to blends of polyethylene with polypropylene and to films made herefrom having improved tear strength.

BACKGROUND

Plastic films have found utility in a wide variety of packaging applications such as bags, pouches, tubes, trays, and the like. In many film packaging applications it is desirable for the film to possess good physical and mechanical properties such as resistance to tearing, tensile strength, and processability in high speed equipment.

Linear low and medium density polyethylene copolymers (LLDPE) produced with conventional Ziegler-Natta catalysts are widely used commercially in films which are conventionally prepared by blown film extrusion. Such films have generally good properties, but often exhibit undesirably low stiffness for many uses. Some such films are also difficult to process and consume a great deal of power to extrude and draw down the film. To address such shortcomings, many have developed blends with other polymers to tailor the balance of properties.

For example, U.S. Pat. No. 4,565,847 describes films formed from blends of LLDPE, polypropylene and ethylene-propylene rubbers having improved stiffness and good tear strength. U.S. Pat. No. 4,929,681 discloses films containing LLDPE having high modulus and good tear strength. The high modulus and improved processing conditions are achieved by blending minor amounts of polystyrene (or other aromatic polymer) and polypropylene with the LLDPE. In both of these inventions, the addition of a minor amount of polypropylene to LLDPE produced with conventional Ziegler-Natta catalysts showed an improvement in the modulus of the film but a decrease in the MD tear strength. The further addition of EPDM or polystyrene was required to achieve a desired balance of properties.

Some of the deficiencies of polymers produced with Ziegler-Natta catalysts are improved in polymers produced with metallocene catalysts. Some of these improvement result from the ability of metallocene catalyst to control certain structural variables in polyolefins which affect the ultimate properties of the polymer. Some of the most important structural variables are composition distribution (CD), molecular weight, and MWD. CD refers to the distribution of comonomer between copolymer molecules. This feature relates directly to polymer crystallizability, optical properties, toughness and many other important use characteristics. MWD plays a significant role in melt processability as well as in physical properties. Broadly speaking, weight average molecular weight (M_w) is strongly related to melt viscosity and the ultimately desired physical properties of the polymer. All of these structural features are readily controllable through the use of metallocene catalysts as exemplified in U.S. Pat. No. 4,937,299, which is fully incorporated by reference herein for purposes of U.S. patent practice.

Three distinctive features of films produced from copolymers produced with metallocene catalysts relative to conventional Ziegler-Natta copolymers are their low extractables (and associated low reblock), their good clarity, and their unusual tensile properties at low elongation. It would be desirable to produce a film having improved balance of stiffness, tear strength, clarity, and low extractables.

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Although polymers produced with metallocene catalysts provide many property enhancements over those produced with Ziegler-Natta catalysts, a film property where metallocene-produced copolymers do not compare as favorably to those made with conventional Ziegler-Natta catalysts is tear strength in the machine direction.

In view of the ongoing need for films of optimum quality for growing market needs, it would be desirable to provide compositions that utilize the ability of metallocene catalysts to tailor polymer structure for an improved balance of properties while using as few blend components and processing steps as possible.

Accordingly, the present invention relates to blends of polyethylene having those desirable qualities resulting from production with a metallocene catalyst system and a polypropylene component having a high melt flow rate (MFR). The blends of the present invention are particularly useful in film applications requiring tear strengths and stiffness as high or higher than those produced with Ziegler-Natta catalysts without compromising clarity, low extractables content, and other attractive attributes of films formed from polyethylene polymers produced using metallocenes or other single-site catalyst systems.

SUMMARY OF THE INVENTION

According to one embodiment of this invention there are provided polymer blend compositions comprising: (a) an ethylene polymer component, having a melting temperature greater than or equal to 75° C. and crystallinity as measured by differential scanning calorimetry (DSC) of 10% or more, and (b) a propylene polymer component, having a melting temperature greater than or equal to 125° C. and a MFR of 500 dg/min. or more at 230° C. Preferably, both polymer components are produced with a metallocene catalyst system. In the polymer blend, component (a) is preferably about 90 to about 99.9 weight percent of the blend based on the total weight of (a) and (b). The polymer blend is formed by mixing blend components (a) and (b) under high shear mixing conditions. A unit such as a twin-screw extruder would be an example of a suitable piece of mixing equipment. Other means to achieve a well mixed blend will be apparent to those skilled in the art.

Another embodiment of this invention comprises film or sheet articles formed from a polymer blend as described above. According to yet another embodiment of this invention there are provided multiple layer films comprising at least one layer formed from the polymer blend as described above.

DESCRIPTION OF THE INVENTION

The polymer blends of this invention include, and preferably consist essentially of (a) an ethylene polymer component produced with a metallocene catalyst; and (b) a propylene polymer component having a high melt flow rate and preferably produced using a metallocene catalyst. All references to metallocene catalyst shall include other catalysts (e.g. single-sited catalyst) capable of producing polymers having properties the same as or similar to metallocene-produced polymers (e.g. narrow MWD, narrow CD, low extractables content, good optical properties). Such blends can optionally include additives well known to those skilled in the art.

The ethylene polymer component can be a single polyethylene polymer or a blend of two or more polyethylenes. The ethylene polymer component has a melting temperature greater than or equal to 75° C. and crystallinity of 10% or

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more DSC. If the ethylene polymer component is a blend of more than one ethylene-based polymer, preferably each ethylene polymer so blended will also have a melting temperature greater than or equal to 75° C. and crystallinity of 10% or more as measured by DSC.

Polyethylene, as used herein, can be a homopolymer or a copolymer and includes plastomers, VLDPE, LLDPE, LDPE, and HDPE. Plastomers, as used herein, refers generally to a class of ethylene based copolymers with density of less than about 0.900 g/cc (down to about 0.865 g/cc) and having a weight average molecular weight (M_w) greater than about 20,000 (about 200 MI and lower). Plastomers have an ethylene crystallinity between plastics (i.e. linear low density and very low density polyethylenes) and ethylene/alpha-olefin elastomers. VLDPE is very low density polyethylene, typically having a density in the range of from 0.90 to 0.915 g/cc. LLDPE is linear low density polyethylene, typically having a density in the range of from 0.915 to 0.930 g/cc. LDPE is low density polyethylene, typically having a density in the range of from 0.915 to 0.930 g/cc. HDPE is high density polyethylene, typically having a density in the range of from 0.930 to 0.960 g/cc. Densities above about 0.90 g/cc were measured using standard accepted procedures. At densities below about 0.90 g/cc, the samples are preferably conditioned by holding them for 48 hours at ambient temperature (23° C.), prior to density measurement.

The melt index (MI) of the ethylene polymer component of the present invention is in the range of about 0.2 dg/min to about 10 dg/min. Preferably the MI is in the range of about 0.4 dg/min. to about 8 dg/min. For blown film applications, the most preferred range is 0.5 dg/min to about 2 dg/min. For cast film applications, the most preferred range is 1 dg/min to about 7 dg/min.

The ethylene polymer component of the present invention preferably has melting point characteristics with a major melting point (T_m) as determined by Differential Scanning Colorimetry (DSC) in the range of about 50° C. to about 140° C. Preferably, the DSC peak, or T_m , is in the range of about 60° C. to about 125° C. "Melting point" as used herein means that at least about 80% by weight of the material corresponds to a single T_m peak in the range of about 60° C. to about 125° C. Preferably, substantially all the ethylene polymer component melts prior to reaching a temperature of about 140° C., as determined by DSC analysis.

The polyethylene polymers utilized in the polyethylene component of the blends of the present invention, comprise ethylene and one or more alpha-olefins. Such α -olefins include linear, branched, or ring-containing C_3 to C_{30} α -olefins or combinations thereof capable of being copolymerized with ethylene by a selected metallocene or other single-site catalyst. Preferred linear α -olefins include C_3 to C_8 α -olefins, more preferably propylene, 1-butene, 1-hexene, and 1-octene, even more preferably propylene or 1-butene. Preferred branched α -olefins include 4-methyl-1-pentene, 3-methyl-1-pentene, and 3,5,5-trimethyl-1-hexene as well as geminally di-substituted such as isobutylene. Preferred ring-containing olefins include norbornene and alkyl-substituted norbornene such as methyl-norbornene. Generally, such polyethylenes will comprise in the range of about 85 to about 96 mole percent ethylene.

Preferred polyethylene copolymers are produced with metallocene catalysis and display narrow molecular weight distribution, meaning that the ratio of the weight average molecular weight to the number average molecular weight will be equal to or below 4, most typically in the range of from 1.7 to 4.0, preferably from 1.8 to 2.8.

Preferably, polyethylene copolymers produced with metallocene catalysts will also display narrow composition distribution, meaning that the fractional comonomer content from molecule to molecule will be similar. This can be measured using Fourier Transform Infrared Spectroscopy coupled to a Gel Permeation Chromatograph (GPC-FTIR) to determine comonomer content in discrete ranges of number or weight average molecular weights (M_n or M_w), or by using a Temperature Rise Elution Fractionation analysis to determine the composition distribution breadth index (CDBI) or solubility distribution breadth index (SDBI). A preferred polyethylene copolymer has a comonomer distribution when measured by GPC-FTIR such that the comonomer content of any discrete molecular weight range comprising 10 weight % or more of the total eluted copolymer is within $\pm 30\%$ of the weight average comonomer content of the polyethylene copolymer where this average equates to 100%, more preferably within $\pm 20\%$, even more preferably within $\pm 10\%$. Where measurement by SDBI is applicable, the SDBI of the polyethylene copolymer is preferably less than about 35° C., generally in the range of about 10° to about 25° C., preferably in the range of about 15° to about 20° C., and most preferably in the range of about 15° to about 18° C. Where CDBI is applicable, the CDBI of the polyethylene copolymer is preferably greater than 40%, more preferably greater than 50%, even more preferably greater than 60%. The polyethylene copolymer has a narrow compositional distribution if it meets the GPC-FTIR, CDBI, or SDBI criteria as outlined above.

In a particularly preferred embodiment, the copolymer is a single-site catalyzed "polyethylene," preferably produced using metallocene catalysis. "Polyethylene," as used herein, means a copolymer in which ethylene is the major monomer. Such polyethylene materials are commercially available from Exxon Chemical Company of Houston, Tex. under the trade name "Exact™". These materials may be made in a variety of processes (including slurry, solution, high pressure and gas phase) employing metallocene catalysts. Processes for making a variety of polyethylene materials with metallocene catalyst systems are well known. See, for example, U.S. Pat. Nos. 5,017,714, 5,026,798, 5,055,438, 5,057,475, 5,096,867, 5,153,157, 5,198,401, 5,240,894, 5,264,405, 5,278,119, 5,281,679, 5,324,800, 5,391,629, 5,420,217, 5,504,169, 5,547,675, 5,621,126, 5,643,847, 5,801,113, 5,408,017, 5,621,054, 5,635,573, 5,767,208, 5,851,945, 5,866,665, 5,942,587, and 5,972,823, U.S. patent application Ser. Nos., 08/877,390, 08/473,693, and 60/048,965, and international patent application nos. EPA 277,004, WO 92/03333, and WO 94/03506, each fully incorporated herein by reference for purposes of U.S. patent practice. Production of copolymers of ethylene and cyclic olefins are described in U.S. Pat. Nos. 5,635,573 and 5,837,787, and of copolymers of ethylene and geminally di-substituted monomers, such as isobutylene, are described in U.S. Pat. No. 5,763,556, all of which are fully incorporated herein for purposes of U.S. patent practice.

Utilizing a metallocene catalyst, the polyethylene polymers useful in the ethylene polymer component of the present invention can be produced in accordance with any suitable polymerization process, including a slurry polymerization, gas phase polymerization, and high pressure polymerization process.

The polypropylenes useful in this invention are homopolymers or copolymers of propylene and one or more olefins selected from ethylene or linear or branched C_4 to C_{30} α -olefins, preferably ethylene or C_4 to C_8 α -olefins, more preferably ethylene, 1-butene, 1-hexene, 4-methyl-1-

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pentene, 3-methyl-1-pentene, 3,5,5-trimethyl-1-hexene, and 1-octene, even more preferably propylene or 1-butene, and optionally, minor amounts of non-conjugated diolefins, preferably C_6 - C_{20} diolefins. In one embodiment, the α -olefin can contain cyclic structures that are fully saturated such that the α -olefin monomer does not contain a cyclic moiety with any olefinic unsaturation or any aromatic structures. Preferred α -olefins are mono-olefins. These propylene copolymers with prescribed range of comonomer levels can be prepared by polymerization of the suitable olefins in the presence of supported or unsupported metallocene catalyst systems.

Isotactic polypropylene homopolymer is preferred over random copolymers having a high propylene content since both crystallinity and melting temperatures decrease as comonomer content increases. The concept of blending a small amount of polypropylene with the polyethylene component would however also apply to polypropylene copolymers having small amounts of α -olefins such as ethylene-1, butene-1, hexene-1, and octene-1.

The propylene-based polymer component of the present invention is a polypropylene homopolymer, a random copolymer of polypropylene, or a mixture thereof, wherein the propylene-based polymer component has an MFR of 500 dg/min. or more at 230° C. as measured by ASTM D-1238, preferably 1000 dg/min. or more, more preferably 1500 dg/min. or more. Even more preferably, the propylene-based polymer component copolymer is isotactic polypropylene homopolymer having a MFR as specified above. Even more preferably, the propylene based polymer will also have a MWD of from 1.8 to 4.0. Such polymers are conveniently produced using a stereospecific metallocene catalyst system.

When the propylene-based polymer component either consists of or contains one or more copolymers, such copolymers are preferably composed of propylene as a main monomer and an α -olefin other than propylene. The content of the propylene is generally 88 mole percent or more, more preferably 99 mole percent or more. The content of the α -olefin (e.g. ethylene) other than propylene is generally 12 mole percent or less, more preferably 1 mole percent or less.

The crystallinity in the polypropylene copolymer are derived from isotactic or syndiotactic polypropylene sequences, preferably isotactic polypropylene sequences, obtained by use of a stereospecific metallocene catalyst and limiting the amount of comonomer. Preferred polypropylene polymers have an average propylene content on a molar basis of about 95% or more, preferably 98% or more, more preferably 100%. The balance of the copolymer is one or more linear or branched α -olefins as specified above and optionally minor amounts of one or more diene monomers.

The semi-crystalline propylene-based polymer component preferably has a heat of fusion from about 10 J/g to about 160 J/g, more preferably from about 1.9 J/g to about 151 J/g, more preferably from about 28 J/g to about 142 J/g, even more preferably from about 38 J/g to about 113 J/g. The crystallinity of the polypropylene copolymer arises from crystallizable stereoregular propylene sequences.

In another embodiment, the crystallinity of the propylene-based polymer component is expressed in terms of percent crystallinity. The thermal energy for the highest order of polypropylene is estimated at 189 J/g. That is, 100% crystallinity is equal to 189 J/g. Therefore, according to the aforementioned energy levels, the present invention preferably has a polypropylene crystallinity of about 5% to about 85%, more preferably from about 10 % to about 80%, even

more preferably from about 15% to about 75%, even more preferably from about 20% to about 60%.

The propylene-based polymer component preferably has a single melting point (T_m) in the range of from about 25° C. to about 110° C., preferably in the range of from about 30° C. to about 105° C., more preferably in the range of from about 35° C. to about 90° C.

The polypropylene copolymer of the present invention preferably comprises a random crystallizable copolymer having a narrow compositional distribution. The intermolecular composition distribution of the polymer is determined by thermal fractionation in a solvent. A typical solvent is a saturated hydrocarbon such as hexane or heptane. This thermal fractionation procedure is described below. Typically, approximately 75% by weight and more preferably 85% by weight of the polymer is isolated as one or two adjacent, soluble fraction with the balance of the polymer in immediately preceding or succeeding fractions. Each of these fractions has a composition (wt. % ethylene, or other α -olefin, content) with a difference of no greater than 20% (relative) and more preferably 10% (relative) of the average weight % comonomer, such as ethylene or other α -olefin, content of the polypropylene copolymer. The polypropylene copolymer has a narrow compositional distribution if it meets the fractionation test outlined above.

Preferred propylene-based polymer components according to the invention are conveniently prepared by polymerizing propylene and optionally one or more C_3 or C_4 - C_{20} α -olefin comonomers in the presence of a chiral metallocene catalyst with an activator and optional scavenger, most preferably ethylene and propylene. Preferred stereospecific metallocenes are those known to favor incorporation of propylene in predominantly isotactic polypropylene pentads and statistically random incorporation of the α -olefin or other olefinic comonomer(s). Stereospecific catalysts for the production of the crystalline polymer segments (isotactic or syndiotactic α -olefin-diene copolymers) of this invention include any catalyst system capable of copolymerizing the select α -olefin monomer(s) and diolefin monomer(s). Such stereospecific catalysts should at the same time polymerize the α -olefin monomer(s) in a stereospecific structure such that the crystalline polymer segments contain isotactic or syndiotactic monomer sequences sufficient to produce a heat of fusion, as measured by DSC, of 10 J/g or more. For additional detail on such catalysts, reference can be made to U.S. Pat. No. 5,770,753 and to W. Spaleck, et al., "The Influence of Aromatic Substituents on the Polymerization Behavior of Bridged Zirconocene Catalysts," *Organometallics*, 13, 954-963 (1994), both of which are fully incorporated by reference herein for purposes of U.S. patent practice.

Such catalysts are known to those skilled in the art. For additional details on such catalysts, reference can be made to U.S. Pat. Nos. 5,324,800; 5,198,401; 5,278,119; 5,387,568; 5,120,867; 5,017,714; 4,871,705; 4,542,199; 4,752,597; 5,132,262; 5,391,629; 5,243,001; 5,278,264; 5,296,434; and 5,304,614, all of which are incorporated by reference for purposes of U.S. patent practice.

Illustrative, but not limiting examples of preferred stereospecific metallocene catalysts for the synthesis of propylene-based polymers, are the racemic isomers of: [dimethylsilanediybis(2-methyl-4-phenylindenyl)]metal dichloride; [dimethylsilanediybis(2-methyl)]metal dichloride; [dimethylsilanediybis(indenyl)]metal dichloride; [dimethylsilanediybis(indenyl)]metal dimethyl;

[dimethylsilanediy]bis(tetrahydroindenyl)metal dichloride; [dimethylsilanediy]bis(tetrahydroindenyl)metal dimethyl; [dimethylsilanediy]bis(indenyl)metal diethyl; and [dibenzylsilanediy]bis(indenyl)metal dimethyl; wherein the metal can be chosen from Zr, Hf, or Ti, preferably Zr. Wherein M is chosen from a group consisting of Zr, Hf, or Ti.

The polypropylene polymer component can be a single polypropylene or a blend of two or more polypropylenes. The propylene polymer component has a melting temperature greater than or equal to 125° C. and a melt flow rate (MFR) of 500 dg/min. or more at 230° C. If the propylene polymer component is a blend of more than one polypropylene, preferably each propylene polymer so blended will also have a melting temperature greater than or equal to 125° C. and a melt flow rate (MFR) of 500 dg/min. or more at 230° C.

The blend composition will generally comprise in the range of about 90 to about 99.9 weight percent, low melting ingredient and in the range of about 10 to about 0.1 weight percent of a propylene based polymer both based on the total weight of the low melting ingredient and propylene based polymer. These are preferred ranges. The particular polyethylene component, the particular polypropylene component, and the relative amounts of each used in the blend of this invention will depend on the requirements of the particular application in which the blend will be utilized, economics, and other process factors. Generally a beneficial contribution from the addition of the polypropylene component will be noted at a level of about 5 wt %. At a level above 10 wt % polypropylene component, the blend product may show deficiencies in properties such as rigidity, abrasion resistance, and elevated temperature resistance, among others.

With respect to the physical process of producing the blend, sufficient mixing should take place to assure that a uniform blend will be produced prior to conversion into a finished product. Thus, in the cases of injection molding of medical devices, casting and blowing of packaging films, extrusion of tubing and profiles, etc. simple solid state blends of the pellets serve equally as well as pelletized melt state blends of raw polymer granules, of granules with pellets, or of pellets of the two components since the forming process includes a remelting and mixing of the raw material. In the process of compression molding of medical devices, however, little mixing of the melt components occurs, and a pelletized melt blend would be preferred over simple solid state blends of the constituent pellets and/or granules. Those skilled in the art will be able to determine the appropriate procedure for blending of the polymers to balance the need for intimate mixing of the component ingredients with the desire for process economy.

The polymer blend compositions of the present invention can be cast extruded or coextruded into film using a flat die or blown extruded or coextruded into film using a tubular die. Such films may optionally be further oriented (either uniaxially or biaxially) using technologies well known to those skilled in the art. The films formed from the composition of the invention are useful as shrink films, cling film, stretch film, sealing films, oriented films, snack packaging, heavy duty bags, grocery sacks, baked and frozen food packaging, medical packaging, industrial liners, membranes, etc. in food-contact and non-food contact applications.

In some applications, for example in food and flexible packaging, it is important that the amount of haze in the final film be minimized so that the film can clearly display the

packaged contents and be aesthetically pleasing. In selecting the low melting polymer ingredient and the propylene based polymer, it is believed that a deterioration of haze can be mitigated by blending low melting polymer ingredient and propylene based polymer having similar densities to minimize refractive index differences, and having similar rheologies (i.e. shear viscosities under processing conditions) to obtain optimum dispersed phase domain size/morphology.

The polymer components used to fabricate the films of the present invention may also contain appropriate amounts of other additives normally included in such compositions. These include slip agents, such as talc, antioxidants, fillers, dyes, pigments, stabilizers, such as radiation stabilizers, and like additives known to those skilled in the art.

Some preferred properties of the final composition and film are, tensile strength, film rigidity, haze, gloss, and tear strength. The extractables content for the compositions of the invention and films therefrom is preferably less than or equal to 2.0 wt. %, more preferably less than or equal to 1.6 wt. %, most preferably less than or equal to 1.4 wt. % as measured by ASTM D-5227. Typically, however, the extractables content will be at least 0.5 wt. %.

Haze values for the compositions of the invention and films therefrom are preferably less than or equal to 25%, more preferably less than 20%, even more preferably less than 15%. Typically, however, haze values for the compositions and films of the invention can be 2% or more, and frequently 5% or more.

Films according to the invention are formed by any suitable method well known in the art, or once formed, the film can be subjected to a combination of post orienting and/or annealing to effect changes in its unload power. Such methods of making film are discussed by J. H. Briston and L. L. Katan in *Plastic Films*, (2nd ed. 1983) and U.S. Pat. Nos. 4,436,520 and 5,066,526, all of which are herein incorporated by reference for purposes of U.S. patent practice. Commonly known methods of producing film include casting (extrusion and solvent), calendering, and extrusion methods, such as blow, slit extrusion, or cast die extrusion.

Regardless of the method of first producing the film, once made, the film can be used as is, or it can be further processed to improve unload power of the film. This is accomplished by a combination of orienting and/or annealing the film. In one embodiment, the annealing is conducted at a temperature between the film softening point and melting point.

Orientation of non-elastic films to improve clarity, impact strength and, particularly in the case of polypropylene, its barrier properties, is well known in the art. The orienting and annealing of the film may be carried out monoaxially in the machine direction (MD) or the transverse direction (TD) or in both directions (biaxially) either simultaneously or sequentially using conventional equipment and processes following cooling of the film.

Blown films are preferentially stretched in machine direction or in both directions. Cast films are preferably stretched in the machine direction. Generally, for orientation in the machine direction, the film is passed around two rollers driven at different surface speeds and finally to a take up roller. The second driven roller which is closest to the take up roll is driven faster than the first driven roller. As a consequence the film is stretched between the driven rollers. Conventional "godet" stands as are well known in the art may also be utilized.

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Film orientation in another embodiment may also be carried out in a tentering device with or without machine direction orientation to impart transverse direction orientation in the film. The film is gripped by the edges for processing through the tentering device. For most final applications, the film is monoaxially oriented in the machine direction.

In one embodiment, the film of the invention is annealed at a temperature between the film softening point and melting point. The annealing step is necessary to anneal or perfect the crystallites that survived the orienting step and to relax out stresses. This annealing aids in maintaining the orientation or extension induced in the orienting step. The annealing temperature is preferably less than the orienting temperature. Generally once the film leaves the annealing step, ambient cooling is sufficient. In most cases, the film from the annealing step is then spooled in a winding unit.

In yet another embodiment, at least one layer formed from the composition of the invention and at least one additional layer are joined to form a multi-layer film. The layers can be joined by lamination, heat sealing, co-extrusion, or any method of joining film layers well known to those skilled in the art. The additional layer or layers can be the same or different polymers.

EXAMPLES

Tests and Standards

Density measurements were made according to ASTM D-792.

Molecular weight distribution (MWD) means M_w/M_n , where M_w is the weight average molecular weight and is M_n the number average molecular weight as determined by gel permeation chromatography using polyisobutylene standards on a Waters 150 gel permeation chromatograph detector and an on-line Chromatix KMX-6 light scattering photometer. The system is used at 135° C. with 1,2,4-trichlorobenzene as the mobile phase. Showdex (from Showa Denko America, Inc.) polystyrene gel columns 802, 803, 804 and 805 were used. This technique is discussed on "Liquid Chromatography of Polymers and Related Materials III" J. Cazes editor, Marcel Dekker, 1981, p. 207. No corrections for column spreading were employed. M_w/M_n was calculated from elution times. The numerical analyses were performed using the commercially available Beckman/CIS LALLS software in conjunction with the standard Gel Permeation package.

Haze was measured according to ASTM D-1003.

Gloss was measured according to ASTM D-2457.

Tensile stress at yield, elongation at yield, ultimate tensile strength, elongation at break, and secant modulus (1%) were measured according to ASTM D-882.

Elmendorf tear, machine direction (MD) and transverse direction (TD), Tensile Tear, Y Mod., and Notch Tensile Tear, were measured according to ASTM D-1922.

Differential Scanning Calorimetry (DSC), ASTM E-1356, at a heating rate of 10° C./minute). DSC measurements were made on a Perkin Elmer System 7 Thermal Analysis System. Melting information reported are second melting data i.e. sample heated at programmed rate of 10° C. min. to a temperature above its melting range. Sample then cooled in instrument at programmed rate of 10° C./min. to temperature below its crystallization range. Sample reheated (2nd melting) at programmed rate of 10° C./min.

Melting point (T_m), glass transition temperature (T_g), heat of fusion (Δh_f), multiple melting peak, and any measurements related to detection of crystalline melting or crystallization are measured using Differential Scanning Calorimetry (DSC) or obtained from commonly accepted publications such as typical transition temperatures shown in Principles of Polymer Systems, Rodriguez, 2d ed., McGraw Hill Chemical Engineering Series, p. 38, Table 3-1. DSC was performed by ASTM method E-1356a modified version of ASTM method D-3417. Preferably, about 6 mg to about 10 mg of a sheet of the preferred polymer pressed at approximately 200° C. to 230° C. is removed with a punch die and is aged at room temperature for at least 24 hours. At the end of this period, the sample is placed in a Differential Scanning Calorimeter and cooled to about -50° C. to -70° C. The sample is heated at about 10-20° C./minute to attain a final temperature of about 200° C. to about 220° C. The thermal output is recorded as the area under the melting peak, or peaks, of the sample which is typically at a maximum peak at about 30° C. to about 150° C. and occurs between the temperatures of about 0° C. and about 180° C. The thermal output is measured in Joules as a measure of the heat of melting. The melting point is recorded as the temperature of the greatest heat absorption within the range of melting temperature of the sample.

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Melt index (MI) was determined according to ASTM D-1238 (190/2.16). High load MI was determined according to ASTM D-1238 (190/21.6).

Melt Flow Rate (MFR) was measured by ASTM method D-1238(L).

Notched Tensile Test was determined according to ASTM D-1003.

Table 1 shows the properties of the polymers used in the examples prior to blending. PE-1, PE-3, PP-1, and PP-2 were all produced with metallocene catalysts. PE-2 was produced with a Zeigler-Natta catalyst.

TABLE 1

Properties of Polymer Blend Components					
Polymer Properties	PE-1	PE-2	PE-3	PP-1	PP-2
M_n	44,665	48,233	23,308	26,000	—
M_w	106,749	115,278	85,306	53,000	—
MWD	2.39	3.96	3.66	2.10	—
MI	1.02	1.01	1.10	NA	NA
MFR	NA	NA	NA	1896	2050
T_m , 1st (° C.)	118	125	116	148	—
Heat of Fusion (H_f) J/g	128	128	128	93	—
T_m , 2nd (° C.)	106	—	102	145	—
CDBI	66.7	19.0	81.8	NA	NA
Density	0.918	0.919	0.919	—	—

NA — not applicable

Table 2 compares the performance of polyethylenes produced by Zeigler-Natta and metallocene catalyst systems both before and after the addition of high MFR polypropylene.

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TABLE 2

PE/PP Blends and Properties										
Example Comparative/Invention	1 C	2 I	3 I	4 I	5 I	6 C	7 C	8 C	9 C	10 C
PE-1	100	100	100	100	100	—	—	—	—	—
PE-2	—	—	—	—	—	100	100	100	100	100
PP-1	—	0.5	1	2	5	—	0.5	1	2	5
Modulus[1], kpsi (MPa)	34.2 (235.6)	39.7 (273.5)	42.3 (291.4)	38.2 (263.2)	38.4 (264.6)	38.7 (266.6)	39.9 (274.9)	44.5 (306.6)	38.8 (267.3)	41.6 (286.6)
Elongation at Break[1], %	43.9	58.8	44.7	44.5	44.9	59.2	59.7	58.8	60.6	61.5
Yield Strength[1], kpsi (MPa)	1.44 (9.92)	1.46 (10.06)	1.61 (11.09)	1.57 (10.82)	1.50 (10.33)	1.46 (10.06)	1.51 (10.40)	1.53 (10.54)	1.50 (10.33)	1.56 (10.75)
Yield Elongation[1], %	14.3	11.9	12.9	13.9	13.3	12.4	12.7	11.5	13.2	12.9
Energy/Thickness[1]	177	223	196	193	182	227	234	233	239	252
Ib-ia/ia (N-m/m)	(788)	(992)	(872)	(899)	(810)	(1010)	(1041)	(1037)	(1064)	(1121)
T _m (1st), ° C. [2]	114.9	—	113.6	—	—	123.6	—	123.0	—	—
delta H _m , J/g [2]	102.8	—	106.5	—	—	106.8	—	81.9	—	—
T _m (2nd), ° C. [2]	116.9	—	116.7	—	—	124.1	—	124.1	—	—
delta H _m , J/g [2]	117.8	—	110.9	—	—	121.7	—	89.4	—	—
T _{cr} , ° C. [2]	103.1	—	103.0	—	—	109.7	—	109.3	—	—
delta H _{cr} , J/g [2]	125.3	—	116.7	—	—	128.6	—	93.9	—	—

1 Notched Tensile Test (A.T. @ 0.5"/min. (1.27 cm/min))
2 DSC 10° C/min

The notched tensile test results summarized in Table 2 show that the blends of this invention help achieve a new and unexpected balance of properties. Examples 2-5, as compared to comparative Example 1 (metallocene-produced polyethylene without polypropylene added), show that the addition of minor amounts of high MFR isotactic polypropylene simultaneously improves modulus, tensile strength, elongation at break, yield strength, and energy/thickness to more closely match those of comparative Example 6 (ZN-PE w/o iPP).

Comparative Examples 7-10 show similar improvements when adding the high-MFR polypropylene to Zeigler-Natta catalyzed polyethylene. However, none of the Zeigler-Natta catalyzed polyethylene samples have the superior optical properties or the lower extractables content of polyethylene produced using metallocene catalysts. It is well known that the narrow CD of polymers produced using single site catalysts have lower extractables content than their Zeigler-Natta catalyzed analogs. Since the polypropylene component of the invention will have a lower extractables content than the polyethylene component, the final blends in accordance with the invention will have lower extractables content than similar blends using Zeigler-Natta catalyzed polyethylene.

The results in Table 3 show the balance of properties for metallocene-produced polyethylene films both before and after the addition of high MFR polypropylene.

TABLE 3

Properties of Polymer Blend Components				
Example Type	11 Control	12 Invention	13 Control	14 Invention
FB-1	100	95	—	—
FE-3	—	—	100	95
PP-2	—	5	—	5
Ingonon-1010	0.2	0.2	0.2	0.2
Orange(ml)	1.3	1.2	1.1	1
Gloss	78.9	71.6	62.8	57.5
Haze	4.5	6.3	12.7	9.6

TABLE 3-continued

Properties of Polymer Blend Components				
Example Type	11 Control	12 Invention	13 Control	14 Invention
Tensile Tear, Y Mod. x 10 ⁴ psi (MPa)				
MD	1.23 (84.81)	1.32 (91.01)	1.25 (86.19)	1.43 (98.60)
TD	1.27 (87.57)	1.37 (94.46)	1.2 (82.74)	1.53 (105.5)
Notch Tensile Tear, Y Mod. psi x 10 ⁴ (MPa)				
MD	3.05 (210.3)	3.63 (250.3)	2.98 (205.5)	3.67 (253.1)
TD	2.7 (186.2)	3.44 (237.2)	3.19 (220.0)	3.88 (267.5)
Klimendorf Tear (g/ml)				
MD	265	351	231	307
TD	369	456	377	415

The gloss and haze test results summarized in Table 3 show that the addition of the polypropylene blend component has little impact on the superior optical properties of the polyethylene films. However, all of the tear test show a significant improvement in tear strength in both the machine direction and the transverse direction by the addition of a minor portion of high MFR polypropylene.

Various changes and modifications in the products and process of this invention can be made without departing from the spirit and scope thereof. The various embodiments which have been disclosed herein were for the purpose of further illustrating the invention but were not intended to limit it.

What is claimed is:

1. A composition comprising
 - a) a polyethylene polymer component having a melting temperature greater than or equal to about 75° C., an ethylene crystallinity level of 10 percent or more, a MWD of 4 or less, and a narrow compositional distribution; and
 - b) a polypropylene polymer component having a melt flow rate of 500 dg/min. or more at 230° C. and a melting temperature greater than or equal to about 125° C.
2. The composition of claim 1 wherein said ethylene polymer component is selected from a polyethylene

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homopolymer, a copolymer of ethylene and one or more comonomers, and combinations thereof.

3. The composition of claim 2 wherein said one or more comonomers are selected from C₃ to C₂₀ α-olefins and combinations thereof.

4. The composition of claim 1 wherein said polyethylene polymer component has a density of from 0.86 to 0.96 g/cc.

5. The composition of claim 4 wherein said polyethylene polymer component has a density of less than 0.93 g/cc.

6. The composition of claim 1 wherein said propylene polymer component is selected from an isotactic polypropylene homopolymer, a copolymer of propylene and one or more comonomers wherein the comonomer content does not exceed 20 mole percent.

7. The composition of claim 6 wherein said propylene polymer component has a heat of fusion of at least 10 J/g.

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8. The composition of claim 1 comprising from 90 to 99.9 weight percent of said ethylene polymer component and from 10 to 0.01 weight percent of said polypropylene, both based on the weight of said composition.

9. The composition of claim 8 further comprising one or more additional components selected from a slip agent, a stabilizer, an antioxidant, a filler, a dye, a pigment, and combinations thereof, and wherein the total of all blend components sums to 100 weight percent.

10. The composition of claim 1 having an extractables content of 2 wt. % or less.

11. An article of manufacture comprising the composition of claim 1.

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US006159566A

United States Patent [19]
Barre

[11] **Patent Number:** **6,159,566**
[45] **Date of Patent:** **Dec. 12, 2000**

[54] **FLEXIBLE THERMOPLASTIC AND COMPRESSIBLE TUBE MADE OF THIS MATERIAL**

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[75] **Inventor:** **Patrice Barre, Antony, France**

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[22] **Filed:** **Feb. 4, 1998**

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[51] **Int. Cl.⁷** **B65D 85/08; B65D 85/14; C08L 23/00; C08L 23/04**

[52] **U.S. Cl.** **428/35.7; 428/36.92; 525/88; 525/240; 206/277**

[58] **Field of Search** **428/35.7, 35.2, 428/36.92, 500, 521; 525/240, 88, 322, 323, 247, 249, 80; 526/124.7, 125.3, 126; 206/277**

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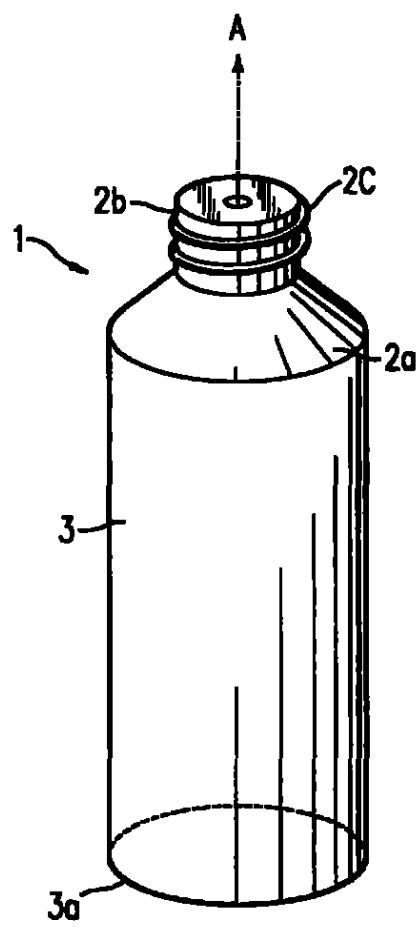
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Primary Examiner—Ellis Robinson
Assistant Examiner—John J. Figueroa
Attorney, Agent, or Firm—Obalon, Spivak, McClelland, Maier & Neustadt, P.C.

[57] **ABSTRACT**

A flexible package is provided made of plastic, having a wall made of a thermoplastic blend containing a first and of a second polymer, wherein the first polymer is a propylene homopolymer (PP) and the second polymer is a copolymer of propylene (PP) and of ethylene (PE), and a method for producing the package by injection molding of the blend in a suitable mold. The package can be an injection-moulded tube, and is particularly suitable for the packaging of small volumes of cosmetic and/or dermatological products.

11 Claims, 1 Drawing Sheet



12B
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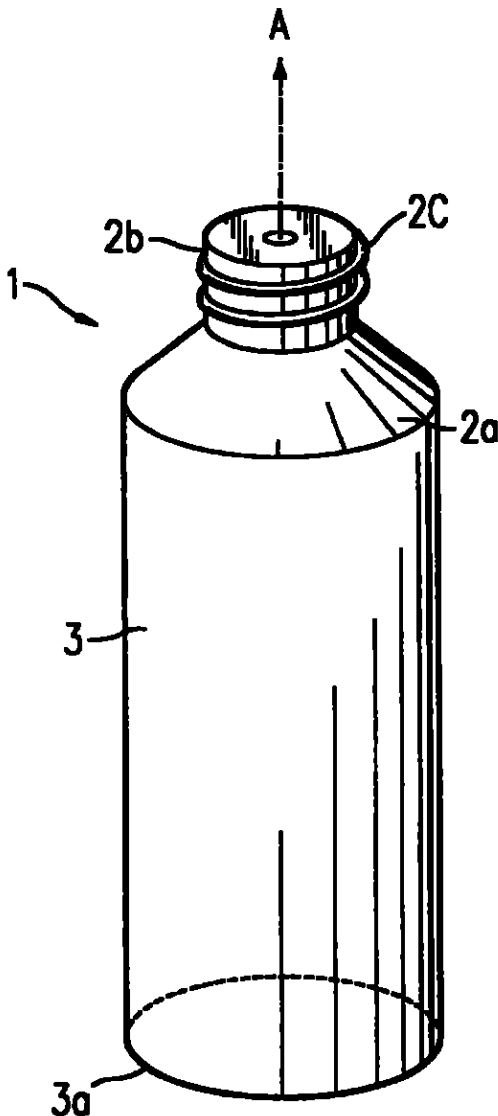


FIG. 1

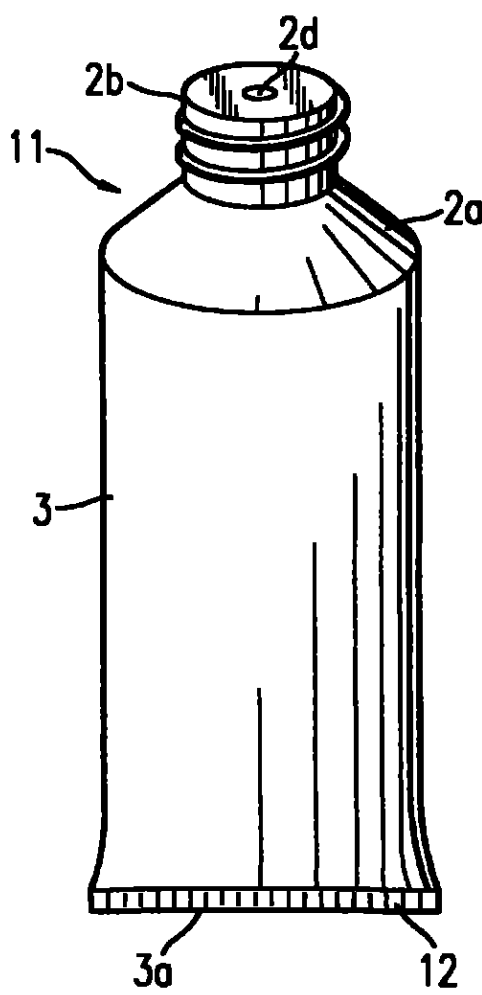


FIG. 2

FLEXIBLE THERMOPLASTIC AND COMPRESSIBLE TUBE MADE OF THIS MATERIAL

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a thermoplastic blend and to a compressible package of the tube type, obtained using this blend. The invention relates more particularly to the production of flexible plastic tubes by injection moulding, wherein the tubes are compatible with the product contained therein and the walls of which have sufficient flexibility to be compressed manually, without leaving folded areas after the compression. The package of the invention is intended, in particular, to contain a cosmetic, pharmaceutical, dermo-pharmaceutical product or certain food products.

2. Discussion of the Background

Currently, most of the packages used, particularly in the cosmetic field, such as tubes or bottles intended to contain a cream or a shampoo, are made of plastic. In order to manufacture them, thermoplastic polymers, such as suitable polyolefins, are generally used in an extrusion or extrusion blow-moulding process with the aid of conventional industrial equipment.

The thermoplastic polyolefins used are generally low-density polyethylenes, intended in particular for the manufacture of tubes, and high-density polyethylenes or polypropylenes which are intended for the manufacture of bottles. In particular, polypropylenes have good water-vapour impermeability properties, have the advantage of being compatible with most chemicals.

SUMMARY OF THE INVENTION

Accordingly, one object of the present invention is to provide a thermoplastic composition that is sufficiently fluid to allow the production, by injection moulding, of packages, such as compressible tubes, especially those having a wall that is thin and sufficiently flexible to be manually compressed in order to dispense the product.

Another object of the present invention is to provide a material that gives better resistance to creasing of the wall brought about by compressing the tube, and in reducing, or even eliminating, the formation of white regions in a previously creased wall region.

These and other objects of the present invention have been satisfied by the discovery of a combination of a particular copolymer with a conventional polypropylene homopolymer to form a thermoplastic blend that can be used for the manufacture, by injection moulding, of a package having the desired properties. This blend furthermore has good compatibility with the products intended to be stored in the package, in particular in the presence of certain surfactants.

BRIEF DESCRIPTION OF THE DRAWINGS

A more complete appreciation of the invention and many of the attendant advantages thereof will be readily obtained as the same becomes better understood by reference to the following detailed description when considered in connection with the accompanying drawings, wherein:

FIG. 1 represents a side view of a package according to the invention, before sealing the bottom.

FIG. 2 represents a side view of the package of FIG. 1, after sealing the bottom.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The packages provided by the present invention are generally of the type having a compressible peripheral

envelope open at a first free end, which, after filling with the product to be dispensed, is intended to be closed by pinching, followed by heat sealing of its free edges. Generally, the second end of the envelope is joined, for example by means of a region forming a shoulder, to a neck having a sufficient thickness to be rigid with a channel for dispensing the product passing through the neck. Usually the cross-section of the envelope is circular or oval, but other shapes are also possible, such as a polygonal shape. Preferably, the neck carries a closure means, such as a thread for fixing a closure cap, or a clip-on flange for fastening a dispensing capsule. The envelope must have, in its entirety, a shape suitable for it to be demoulded after injection moulding of the thermoplastic blend in a suitable mould.

The actual moulding of a package of the type mentioned above, by injection of a material such as polypropylene having a melt flow index suitable for injection moulding, causes no problems in practice. However, a package obtained in this way conventionally has two major drawbacks:

on the one hand, the walls of the envelope are not sufficiently flexible to be manually compressed, and it is therefore difficult to drain the tube, and,

on the other hand, the walls do not resume their initial shape after the envelope has been compressed and have undesirable visible folded regions which have, moreover, a whitish colour which is aesthetically unattractive.

The present invention therefore provides a flexible plastic package having a wall made of a thermoplastic blend comprising a first polymer and a second polymer, wherein the first polymer is a propylene homopolymer (PP) and, the second polymer is a copolymer of propylene (PP) and of ethylene (PE).

More particularly, the present invention provides a tube produced by injection-moulding the blend in a suitable mould.

According to one preferred embodiment of the present invention, the thermoplastic blend has a melt flow index (ISO 1133 standard, at 230° C., 2.16 kg) of approximately 25 g/10 min. Because of this relatively high flow index, the blend is particularly suitable for injection-moulding thin-walled articles.

According to another preferred embodiment of the present invention, the first polymer has a melt flow index (ISO 1133 standard) of from 20 g/10min to 200 g/10min (grades 20 to 200), preferably from 75 g/10 min. to 125 g/10 min., more preferably of 100 g/10 min. The first polymer is present in the mixture in a preferred amount of less than or equal to 50 wt. %, and preferably from 20 wt. % to 35 wt. %, with respect to the total weight of the blend.

Preferably, the second polymer (copolymer) has a melt flow index (ISO 1133 standard) of from 5 g/10 min to 20 g/10min (grades 5 to 20), more preferably from 6 g/10 min to 10 g/10 min, most preferably 8 g/10 min. The second polymer has a preferred flexural modulus, according to the ASTM D790 standard of less than or equal to 200 MPa. The second polymer is present in the blend in an amount of greater than or equal to 50 wt. %, preferably from 65 wt. to 80 wt. %, with respect to the total weight of the blend.

According to a particularly preferred embodiment of the present invention, the second polymer is a copolymer of propylene and of ethylene, having a flexural modulus, according to the ASTM D790 standard, of less than 200 MPa, such as the PP/PE copolymer sold by the company Montell under the brand name ADFLEX®.

The thermoplastic blend of the present invention can be used, in particular, for the injection moulding of any thin-walled plastic article which has to be flexible.

When this article is a flexible tube, it preferably has a relatively rigid head, consisting of a shoulder and a neck

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which is provided with a dispensing hole, and a compressible peripheral wall connected to the shoulder. The peripheral wall is flexible and forms a compressible body of the tube, in which the product is packaged. A cap may be provided in order to seal the dispensing orifice during the storage period. According to one preferred aspect of the present invention, the compressible wall is approximately cylindrical, or has an oval or polygonal cross-section. When the cross-section is circular, the external diameter of the tube is preferably from 10 mm to 50 mm, more preferably from 25 mm to 35 mm. Preferably, the wall has a thickness of from 0.2 mm to 1.0 mm, more preferably from 0.4 mm to 0.7 mm, most preferably approximately 0.5 mm.

Within the indicated flow index conditions of the blend, as well as of the above-noted wall thickness, it is easily possible to mould tubes of which the length of the compressible wall, measured along the axial dimension, is less than 15 cm. Preferably, the tube dimensions are chosen such that the wall length/wall diameter ratio of the tube is less than or equal to 4. According to the present invention, such a package is obtained by injecting the blend, when hot, into a suitable mould.

Thus, after pinching and sealing of that end of the compressible wall which is opposite the dispensing head, a volume is obtained which may range from approximately 5 ml to approximately 250 ml, preferably from 30 ml to 100 ml, and more preferably from 60 ml to 80 ml. This volume is intended to contain the product, such as a cosmetic or dermatological product. The volume can be varied depending on the cross-section of the tube and on its length.

The present invention is described below with respect to an illustrative embodiment, which is provided for improving understanding of the present invention and is not intended to be limiting thereof.

Denoted by the reference 1 in FIG. 1 is a packaging assembly according to the present invention, in the form of an open tube obtained by injection moulding. The tube 1, of axis A, has a cylindrical body formed by a cylindrical sidewall 3 provided with an open end 3a. On the opposite side from the end 3a, the body is surmounted by a dispensing head 2 having a frustoconical shoulder 2a which is extended by a cylindrical neck 2b having a smaller diameter than the diameter of the body 3. The neck 2b has an external thread 2c capable of engaging with a sealing cap (not shown). The head 2 is provided with a dispensing orifice 2d of smaller diameter than the diameter of the neck 2b.

In order to fill the tube 1, the neck 2 is closed off by a cap and the assembly is turned upside down so that the open end 3a is uppermost. A suitable amount of product is then poured into the tube. By means of a heated clamp, the free end 3a is pinched and, at the same time, a weld 12 is made, as shown in FIG. 2, in order to close off the bottom of the tube.

EXAMPLES

Having generally described this invention, a further understanding can be obtained by reference to certain specific examples which are provided herein for purposes of illustration only and are not intended to be limiting unless otherwise specified.

An open tube 1, as shown in FIG. 1, was obtained by injecting a molten blend of two polymers into a suitable mould. The injection-moulding temperature was approximately 220° C. This blend comprised:

20% of a polypropylene homopolymer, grade 100 (sold by the company Montell under the brand name MOPLEN EPN31MA), and

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80% of a copolymer of propylene and of ethylene, grade 8 (sold by the company Montell under the brand named ADFLEX X100G). This tube included the head 2 and the sidewall 3. The height of the wall 3, along the axis A, was approximately 9 cm, with the thickness of the said wall 3 being approximately 0.5 mm.

After filling the tube with the product, the open end 3a of the tube was pinched and is closed off by heat sealing. The tube 11 in its final form, as shown in FIG. 2, was then obtained. It may be seen that the end 3a, having a sealing strip 12, was now closed off. Because of the small thickness of the wall 3, the tube 11 would be easily deformed, by compressing it, by a user wishing to remove a dose of product.

The cost of manufacture of a tube according to the present invention is substantially less than the cost of a tube manufactured by extrusion.

The present application is based on French Priority Application Serial No. 97-01227, filed with the French Patent Office on Feb. 4, 1997, the entire contents of which are hereby incorporated by reference.

Obviously, additional modifications and variations of the present invention are possible in light of the above teachings. It is therefore to be understood that within the scope of the appended claims, the invention may be practised otherwise than as specifically described herein.

What is claimed as new and desired to be secured by Letters Patent of the United States is:

1. A single layer flexible plastic tube having a wall consisting essentially of a thermoplastic blend consisting essentially of a first polymer and a second polymer, wherein the first polymer is a propylene homopolymer (PP) and the second polymer is a copolymer of propylene (PP) and of ethylene (PE), and wherein said second polymer is present in an amount of at least 65 wt. %, with respect to the total weight of said thermoplastic blend.

2. The tube according to claim 1, wherein the tube is produced by injection-moulding the thermoplastic blend.

3. The tube according to claim 1, wherein the thermoplastic blend has a melt flow index (ISO 1133 standard) of approximately 25 g/10 min.

4. The tube according to claim 1, wherein the first polymer has a melt flow index (ISO 1133 standard) of from 20 g/10 min to 200 g/10 min.

5. The tube according to claim 1, wherein the second polymer has a melt flow index (ISO 1133 standard) of from 5 g/10 min to 20 g/10 min.

6. The tube according to claim 1, wherein the second polymer has a flexural modulus, according to the ASTM D790 standard, of less than or equal to 200 MPa.

7. The tube according to claim 1, wherein the wall has a thickness of from 0.2 mm to 1.0 mm.

8. The tube according to claim 1, wherein the thickness of the wall is from 0.4 mm to 0.7 mm.

9. The tube according to claim 1, wherein the wall has a length/diameter ratio of less than or equal to 4.

10. The tube according to claim 1, wherein the tube has a bottom obtained by pinching a free end of the wall, followed by heat sealing.

11. The tube according to claim 1, wherein the tube contains a cosmetic or dermatological product.

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Barre

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[45] **Date of Patent:** **Sep. 26, 2000**

[54] **INJECTED-MOLDED PACKAGE OF
BLENDED ETHYLENE/OLEFIN
COPOLYMERS**

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[75] **Inventor:** **Patrice Barre, Antony, France**

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[73] **Assignee:** **L'Oreal, Paris, France**

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[21] **Appl. No.:** **09/018,556**

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Maier & Neustadt, P.C.

[30] **Foreign Application Priority Data**

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[51] **Int. Cl.⁷** **B65D 35/08; C08F 210/16**

[52] **U.S. Cl.** **428/35.7; 222/107; 428/36.92;**
525/240

[58] **Field of Search** **428/34.1, 35.7,**
428/36.92; 525/240; 222/107

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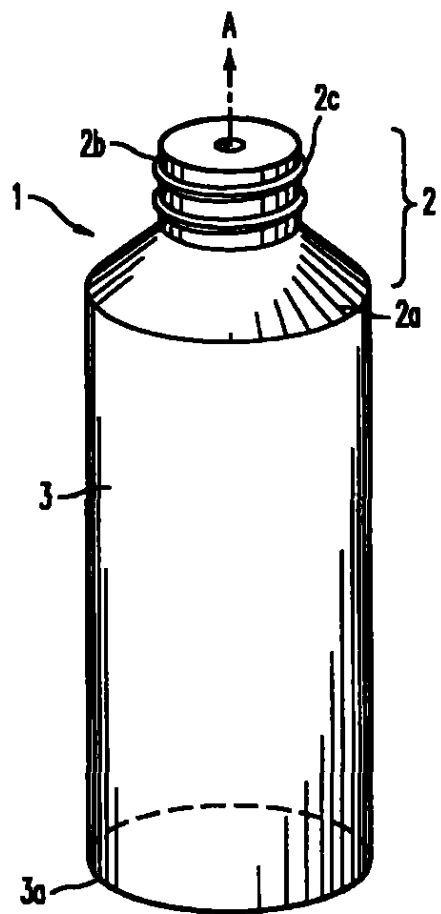
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[57] **ABSTRACT**

A package having improved resistance to stress-cracking due to chemical attack is provided having a wall made of a polymer blend containing:

- a) a first ethylene/C₄ to C₈ olefin copolymer and
 - b) a second ethylene/C₈ to C₁₀ olefin copolymer,
- wherein the package is obtained by injection-molding the blend in a suitable mold, preferably give a flexible tube, and a particular thermoplastic blend for producing the package.

12 Claims, 1 Drawing Sheet



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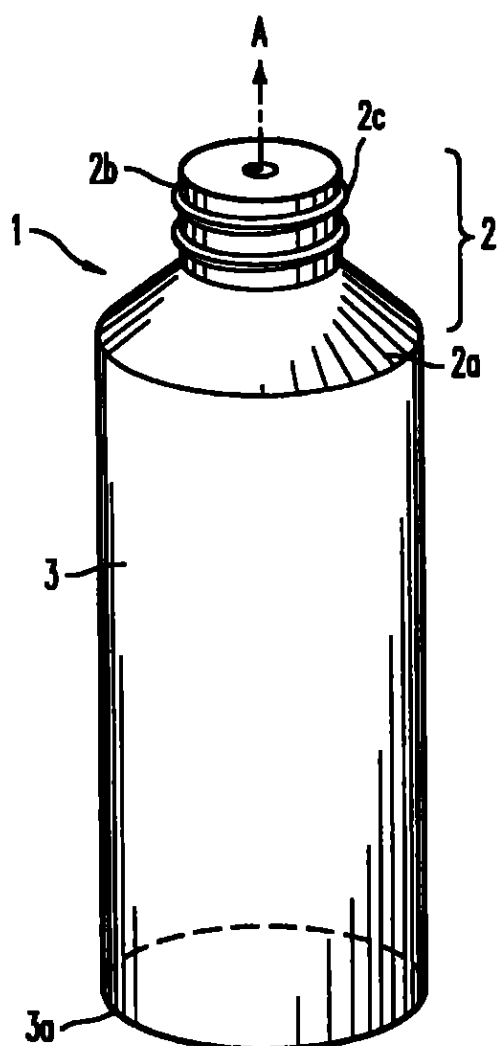


FIG. 1

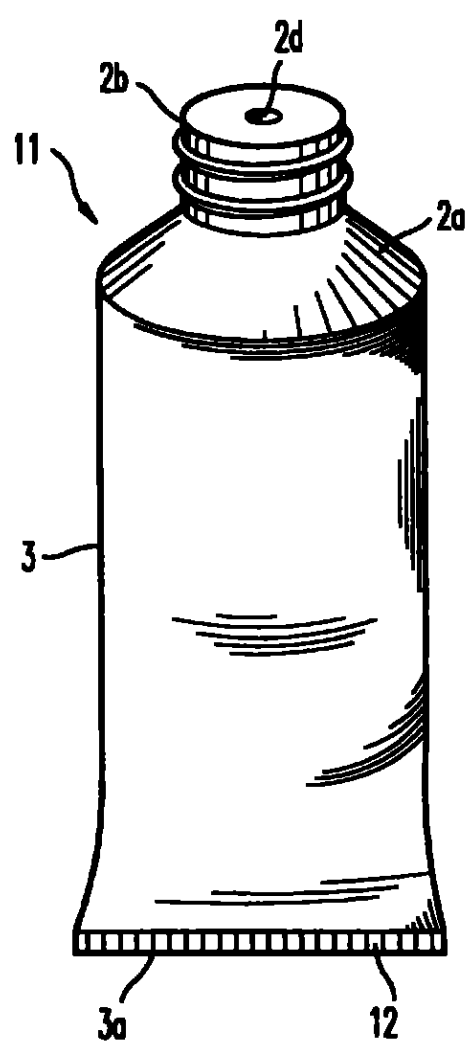


FIG. 2

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INJECTED-MOLDED PACKAGE OF BLENDED ETHYLENE/OLEFIN COPOLYMERS

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a thermoplastic blend and to a compressible package of the tube type, obtained using this blend. The invention relates more particularly to the production, by injection moulding, of plastic tubes having an improved stress-cracking resistance. The package of the invention is intended, in particular, to contain a cosmetic, pharmaceutical, dermo-pharmaceutical product or certain food products, and is particularly suitable for containing a product which contains one or more surfactants.

2. Discussion of the Background

Stress cracking is a term used to describe a phenomenon of chemical attack of a product acting on a polymeric material. The phenomenon is almost imperceptible when this material is not subjected to a mechanical stress. However, contact of the material with the product causes microcracks to form. When the material is then put under stress—for example, in the case of a plastic bottle containing a shampoo, by manually compressing the closed bottle—the microcracks propagate, leading to embrittlement of the material and to fracture of the polymeric wall. In the example in question, the bottle will therefore inevitably leak. The stress-cracking phenomenon occurs in particular in strongly folded regions or in heat-sealing regions, for example at the bottom of a tube which has been obtained by pinching the free end of the compressible wall of the tube, followed by heat sealing.

Currently, most of the packages used are made of plastic, particularly in the cosmetic field, such as tubes or bottles intended to contain a cream or a shampoo. In order to manufacture them, thermoplastic polymers, and more particularly suitable polyolefins, are generally used, prepared by an extrusion or extrusion blow-moulding process with the aid of conventional industrial equipment.

Among the known thermoplastic polyolefins used are low-density polyethylenes, intended in particular for the manufacture of tubes. Low-density polyethylene tubes are flexible, thereby allowing easy expulsion of the product contained in the tube by simply compressing it. However, this type of polyethylene is incompatible with many chemicals and the phenomenon of stress cracking is regularly observed in the case of low-density polyethylene tubes, in particular when they contain a product comprising one or more surfactants. As a consequence, it is not conceivable to use such a tube for packaging a shampoo or a body-care emulsion, which generally contain at least one surfactant. This stress-cracking phenomenon is even more pronounced when the tubes are produced by injection moulding.

A thermoplastic blend that can be used for producing articles resistant to stress cracking is known, for example, from document EP-A-0,530,782, this blend being composed of:

a) a linear low-density ethylene copolymer containing a C_4 to C_9 olefin having approximately 10 to 15 long-chain branches per 1000 carbon atoms and

b) a low-density polyethylene,

with the copolymer being present in the blend in a proportion of between 25% and 35%. According to the illustrative embodiments, this blend is used for the manufacture of articles moulded by the techniques of extrusion or of blow

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moulding. The melt flow indices of the materials mentioned in this reference do not allow these materials to be used for producing tubes using the technique of injection moulding.

Furthermore, EP-A-0,103,942 describes bags manufactured from a plastic film, the film being made of a blend comprising at least one ethylene/ C_8 to C_{10} olefin copolymer having a density of between 0.916 and 0.930 g/cm³ and an ethylene/ C_4 to C_{10} olefin copolymer having a density of between 0.916 and 0.924 g/cm³. This blend cannot be used for the injection moulding of thin-walled articles since, at the temperatures of injection moulding, it has too low a flow index.

Likewise, blends of ethylene/octene copolymers and ethylene/butene copolymers described in document EP-A-0,315,028 cannot be used since they have too low a flow index at the injection-moulding temperatures.

SUMMARY OF THE INVENTION

Accordingly, one object of the present invention is to provide the production of a compressible tube of the aforementioned type, made of plastic, that does not undergo the stress-cracking phenomenon and that can be injected, when hot, into a suitable mould by injection moulding of a thermoplastic.

A further object of the present invention is to find a thermoplastic that is sufficiently fluid to allow production, by injection moulding, of packages such as compressible tubes or bottle-tubes, in particular thin-walled tubes.

These and other objects of the present invention have been satisfied by the discovery of a package having improved stress-cracking resistance, having a wall made of a thermoplastic blend comprising:

(a) a first ethylene/ C_4 to C_9 olefin copolymer and

(b) a second ethylene/ C_8 to C_{10} olefin copolymer, wherein the package is obtained by injection-moulding the blend in a suitable mould, and the thermoplastic blend of (a) and (b).

BRIEF DESCRIPTION OF THE FIGURES

A more complete appreciation of the invention and many of the attendant advantages thereof will be readily obtained as the same becomes better understood by reference to the following detailed description when considered in connection with the accompanying drawings, wherein:

FIG. 1 represents a side view of a package according to the invention, before sealing the bottom.

FIG. 2 represents a side view of the package of FIG. 1, after sealing the bottom.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

After extensive research, the Applicant has discovered a blend of thermoplastics, the constituents of which are mutually compatible, wherein the blend is easy to inject into a mould for the production of tubes that have flexible walls and good stress-cracking resistance.

The present invention relates to a package having improved stress-cracking resistance, having a wall made of a thermoplastic blend comprising:

(a) a first ethylene/ C_4 to C_9 olefin copolymer and

(b) a second ethylene/ C_8 to C_{10} olefin copolymer, wherein the package is obtained by injection-moulding the blend in a suitable mould.

According to a preferred embodiment, the first copolymer is a linear low-density ethylene/butene copolymer (LLDPE).

Advantageously, the first polymer has a density of less than or equal to 0.910 g/cm^3 , preferably less than or equal to 0.900 g/cm^3 .

Preferably, a linear low-density ethylene/octene copolymer (LLDPE) is chosen as the second copolymer. Preferably, the second polymer has a density of between 0.915 g/cm^3 and 0.930 g/cm^3 .

In the case of the first copolymer, a linear low-density ethylene copolymer containing ethylene groups and butene groups is preferred, for example the product sold by the company Enichem under the brand name CLEARFLEX MQFO®, the density of which is less than 0.910 g/cm^3 .

In the case of the second copolymer, a linear low-density ethylene copolymer containing octene units is preferably used, such as the product DOWLEX 2035E® sold by the company Dow Chemical or the product STAMYLEX 08076F® sold by the company DSM.

In accordance with one preferred embodiment of the present invention, the blend formed by the first and second copolymers has a melt flow index (ISO 1133 standard) of approximately 10 g/10 min. Because of this relatively high flow index, the blend is particularly suitable for injection-moulding thin-walled articles.

The first copolymer of the present invention preferably has a melt flow index (ISO 1133 standard) of from 10 g/10 min to 20 g/10 min (grades 10 to 20), more preferably from 12 g/10 min to 15 g/min, most preferably approximately 13 g/10 min.

The second copolymer of the present invention preferably has a melt flow index (ISO 1133 standard) of from 4 g/10 min to 8 g/10 min (grade 4 to grade 8), more preferably from 5 g/10 min to 7 g/10 min, most preferably approximately 6 g/10 min. The thermoplastic blend of the invention can be used, in particular, for the injection moulding of any thin-walled plastic article which has to be flexible.

Thus, according to a preferred embodiment of the invention, the package is in the form of a tube. Advantageously, this tube has a relatively rigid head, consisting of a shoulder and a neck which is provided with a dispensing hole, and a compressible peripheral wall connected to the shoulder. The peripheral wall is flexible and forms a compressible body of the tube, in which the product is packaged. A cap may be provided in order to seal the dispensing orifice during the storage period. According to one preferred aspect of the invention, the compressible wall is approximately cylindrical, or has an oval or polygonal cross-section. When the cross-section is circular, the external diameter of the tube is preferably from 10 mm to 50 mm, more preferably from 25 mm to 35 mm. Preferably, the wall has a thickness of from 0.2 mm to 1.0 mm, more preferably from 0.4 mm to 0.7 mm and most preferably approximately 0.5 mm.

Within the indicated flow index conditions of the blend, as well as of the noted wall thickness, it is easily possible to mould tubes of which the length of the compressible wall, measured along the axial dimension, is less than 15 cm. Preferably, in respect of the compressible wall, dimensions are chosen such that the wall length/wall diameter ratio of the tube is less than or equal to 4. According to the present invention, such a package is obtained by injecting the polymer blend, when hot, into a suitable mould.

After pinching and sealing of the free end of the compressible wall which is opposite the dispensing head, a volume is obtained which may range from approximately 5 ml to approximately 250 ml, preferably from 30 ml to 100 ml, and more preferably from 60 ml to 80 ml. This volume is intended to contain the product, such as a cosmetic or

dermatological product. The volume can be varied depending on the cross-section of the tube and on its length.

The present invention also provides a thermoplastic blend that can be used for manufacturing, by injection moulding, articles that must resist stress cracking, such as tubes, comprising

- (a) a first ethylene/ C_4 to C_8 olefin copolymer and
- (b) a second ethylene/ C_8 to C_{10} olefin copolymer.

Preferably, the first copolymer is a linear low-density ethylene/butene copolymer (LLDPE) having a density of less than or equal to 0.910 g/cm^3 and the second copolymer is a linear low-density ethylene/octene copolymer (LLDPE) having a density of from 0.915 g/cm^3 to 0.930 g/cm^3 , with the proportion of the first copolymer in the blend being from 5% to 33% by weight and the proportion of the second copolymer being from 95% to 67% by weight, with respect to the total weight of the blend.

The present invention is described below with respect to an illustrative embodiment which is merely for improving understanding of the invention and is not intended to be limiting thereof.

Denoted by the reference 1 in FIG. 1 is a packaging assembly according to the present invention, in the form of an open tube, as obtained by injection moulding in a suitable mould. The tube 1, of axis A, has a cylindrical body formed by a cylindrical sidewall 3 provided with an open end 3a. On the opposite side from the end 3a, the body is surmounted by a dispensing head 2 having a frustoconical shoulder 2a which is extended by a cylindrical neck 2b having a smaller diameter than the diameter of the body 3. The neck 2b has an external thread 2c capable of engaging with a sealing cap (not shown). The head 2 is provided with a dispensing orifice 2d of smaller diameter than the diameter of the neck 2b.

In order to fill the tube 1, the neck 2 is closed off by a cap and the assembly is turned upside down so that the open end 3a is uppermost. A suitable amount of product is then poured into the tube. By means of a heated clamp, the free end 3a is pinched and, at the same time, a weld 12 is made, as shown in FIG. 2, in order to close off the bottom of the tube.

EXAMPLES

Having generally described this invention, a further understanding can be obtained by reference to certain specific examples which are provided herein for purposes of illustration only and are not intended to be limiting unless otherwise specified.

Open tubes 1, as shown in FIG. 1, were obtained by injecting a molten blend of two copolymers into a suitable mould. The injection-moulding temperature was approximately 200°C . This blend comprised:

33% of a linear low-density ethylene/butene copolymer, grade 13 (sold by the company Enichem under the brand name CLEARFLEX MQFO) and

66% of a linear low-density ethylene/octene copolymer, grade 6-7 (sold by the company Dow Chemicals under the brand name DOWLEX 2035E or the product STAMYLEX 08076F sold by the company DSM).

This tube included the head 2 and the sidewall 3. The height of the wall 3, along the axis A, was approximately 9 cm, with the thickness of the said wall 3 being approximately 0.5 mm.

After filling the tube with the product, the open end 3a of the tube was pinched and the end closed off by heat sealing. The tube 11 in its final form, as shown in FIG. 2, was then obtained. It may be seen that the end 3a, having a sealing strip 12, was now closed off. Because of the small thickness of the wall 3, the tube 11 can be easily deformed, by compressing it, by a user wishing to remove a dose of product.

MEASUREMENT OF THE STRESS-CRACKING RESISTANCE

Ten tubes 11, according to the present invention, as described above (see FIG. 2) were filled with a 0.3% aqueous solution of Antaron CO 630 (nonylphenol having 9 oxyethylene groups). The tube 11 was kept in an oven at 55° C. for a period of 24 hours. The sidewall 3 of the tube was then pressed manually, in a diametral manner, and it was noted whether there were leaks of liquid or not. In no case was a leak of product observed.

The cost of manufacture of a tube according to the present invention is substantially less than the cost of a tube manufactured by extrusion or extrusion blow moulding.

The present application is based on French Priority Application Serial No. 97-01228, filed in the French Patent Office on Feb. 4, 1997, the entire contents of which are hereby incorporated by reference.

Obviously, numerous modifications and variations of the present invention are possible in light of the above teachings. It is therefore to be understood that within the scope of the appended claims, the invention may be practiced otherwise than as specifically described herein.

What is claimed as new and desired to be secured by Letters Patent of the United States is:

1. A compressible tube having improved resistance to stress-cracking in the tube due to chemical attack, having a wall made of a thermoplastic polymer blend comprising:

- (a) a first ethylene/C₄ to C₈ olefin copolymer having a density of 0.910 gm/cm³ or less and
- (b) a second ethylene/C₄ to C₁₀ olefin copolymer having a density of 0.915 to 0.930 gm/cm³,

wherein the first copolymer (a) is present in the polymer blend in an amount of less than or equal to 50 wt. %, with respect to total weight of the polymer blend, and

the blend has a melt-flow index of about 10 gm/10 min. wherein the compressible tube is obtained by injection-molding the polymer blend.

2. The compressible tube according to claim 1, wherein the first copolymer is a linear low-density ethylene/butene copolymer.

3. The compressible tube according to claim 1, wherein the second copolymer is a linear low-density ethylene/octene copolymer.

4. The compressible tube according to claim 1, wherein the first polymer (a) has a density of less than or equal to 0.900 g/cm³.

5. The compressible tube according to claim 1, wherein the first copolymer (a) has a melt flow index (ISO 1133 standard) of from 10 g/10 min. to 20 g/10 min.

6. The compressible tube according to claim 1, wherein the second copolymer (b) has a melt flow index (ISO 1133 standard) of from 4 g/10 min. to 8 g/10 min.

7. The compressible tube of claim 1, wherein the first copolymer (a) is present in an amount of less than or equal to 33 wt. % based on total weight of the polymer blend.

8. The compressible tube according to claim 1, wherein the wall has a thickness of from 0.2 mm to 1.0 mm.

9. The compressible tube according to claim 8, wherein the thickness of the wall is from 0.4 mm to 0.7 mm.

10. The compressible tube according to claim 1, wherein the wall has a length/diameter ratio of less than or equal to 4.

11. The compressible tube according to claim 1, wherein the package has a bottom obtained by pinching a free end of the wall, followed by heat sealing.

12. The compressible tube according to claim 1, wherein the package contains a cosmetic or dermatological product.

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