61

CAVELIER
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SUPERINDUSTRIA Y COMERCIO
Radicacion : 04084709 0000000 Folios: 2
Fecha (AAAA): 2005-05-11 16:52:53
Tramite : 011 PCT-PATENT 378 FASE NACI 538 PETICION
Dependencia: 2020 DIVISION DE NUEVAS CREACIONES

Señora Jefe de la
DIVISION DE NUEVAS CREACIONES
Superintendencia de Industria y Comercio
E. S. D.

Tramite: 011
Evento: 379
Actuación: 538

Referencia	:	Expediente No. **04 – 084.709**
Asunto	:	Solicitud de patente para **"COMPOSICIONES DE COPOLÍMERO DE BLOQUE QUE TIENEN PROPIEDADES MECÁNICAS Y DE PROCESABILLIDAD MEJORADAS"**
Solicitante	:	**KRATON POLYMERS RESEARCH B.V.**
Fecha de Solicitud	:	30 de Agosto de 2004
Publicada en	:	Gaceta **546** del 30 de Noviembre de 2004

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 No. 05 – 15.247 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, 11 MAYO 2005
Señora Jefe,

EMILIO FERRERO
T.P.A. No. 31.929

COLO 14012 841 001 0
PRP/PRP/ID-000009/WPC14012

62

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO

NIT : 800176089-2

SUPERINDUSTRIA Y COMERCIO
Radicacion : 04084709 00000001
Folios: 2
Fecha (AMD): 2005-03-14 16:52:53
Tramite : 011 PCT-PATENT 378 FASE NACI 538 PETICION
Dependencia: 2020 DIVISION DE NUEVAS CREACIONES

RECIBO OFICIAL DE CAJA : 05 - 15,247
FECHA : FEBRERO 28 DE 2005

***** C O N S I G N A C I O N *****

DEPOSITANTE	TIPO PAGO	BANCO	CUENTA	No. PAGO	FECHA PGO	Vr. PAGO
CAVELIER ABOGADOS	CONSIGNACION	BANCO POPULAR	030-00110-6	23840360	28/02/2005	32,194,000.00

***** C O N C E P T O *****

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

SON: TRESCIENTOS SETENTA Y UNO MIL PESOS

RESPONSABLE : ______________________________

RECIBO DE CAJA APLICADO AL EXPEDIENTE No.______________________

Colo 14012-841-001-0

Industria y Comercio
SUPERINTENDENCIA

DIVISION DE NUEVAS CREACIONES

RADICACIÓN EXPEDIENTE No. **04-84709**

EL EXTRACTO DE LA PRESENTE SOLICITUD DE **PATENTE DE INVENCION - PCT** FUE PUBLICADO EN LA GACETA DE PROPIEDAD INDUSTRIAL No **546**, DE FECHA **30** DE **NOVIEMBRE** DE **2004**, EL TERMINO HABIL SEÑALADO POR LA LEY EXPIRA EL **24** DE **FEBRERO** DE **2005**.

NOTA: Dentro del plazo de los seis (6) meses siguientes a partir de la fecha de publicación en la gaceta de Propiedad Industrial, deberá solicitar y cancelar el examen de patentabilidad so pena de que la solicitud caiga en abandono, de acuerdo con lo establecido en el Artículo 44 de la Decisión 486/2000.

SE PRESENTARON OPOSICIONES POR PARTE DE TERCEROS.

SI ____ _____ NO ___ X ____

Carrera 13 No. 27-00 Piso 5 y 10
Conmutador: 554 12 21-2-3-4
Fax: 281 31 25 e-mail: info@sic.gov.co
Santa Fe de Bogotá D.C. - Colombia

SUPERINTENDENCIA DE INDUSTRIA Y C MERCI
DIVISIÓN DE NUEVAS CREACIONES

2020
Bogotá, D. C., 8 de Marzo de 2007

Doctor
EMILIO FERRERO
Representante **KRATON POLYMERS RESEARCH B. V.**

ASUNTO	Radicación No.	**04-84709**
	Trámite	002
	Evento	001
	Actuación	430
	Oficio	3666
	Folios	015

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 30 a 53 de la solicitud en estudio.

b) Para el presente estudio se tendrá en cuenta el capítulo reivindicatorio que comprende 8 reivindicaciones en los folios 54 a 57 de la solicitud en estudio.

c) 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 agosto de 2004, y en el momento de la radicación se presentó como solicitud PCT FASE NACIONAL y donde SI se reclamó prioridad de las primeras solicitudes presentadas en Europa EP02075463.6 y EP02079462.4

2) **Objeto de la Invención**

a) Las reivindicaciones 1 a 8 de la solicitud en estudio se refieren a una composición para ser utilizada para la elaboración de películas mono o multicapa para aplicaciones de envoltura de alimentos que comprende desde 5 a 40% en peso de un copolímero de bloque estirénico, que tiene una estructura molecular de acuerdo con la fórmula general

$$S\text{-}EB\text{-}S\ (1) \text{ o } (S\text{-}EB)_n X\ (2)$$

en donde cada S independientemente es un bloque de polímero de estireno predominantemente y ES es un bloque de polímero hidrogenado de butadieno predominantemente, n es un entero igual o mayor de 2, y X es el residuo de un agente de acoplamiento, que tiene un contenido de poli (estireno) de desde 10 a 29% en peso y preferiblemente desde 17 a 24% en peso, que tiene bloques de poli(estireno) (S) de un peso molecular cierto en el rango de desde 6,000 a 9,000, que tiene un peso molecular cierto del copolímero del bloque completo en el rango desde 80,000 a 150,000 que tiene un grado de adición 1, 2 (contenido de vinilo) en el precursor del bloque de poli (butadieno) (EB) en el rango de desde 60 a 80% (mol/mol), en donde el bloque EB tiene un grado de hidrogenación de al menos 80% y

preferiblemente apenas 90% y en donde el dibloque S-ES opcionalmente ocurre en un contenido de máximo 20 moles % y preferiblemente máximo 10 moles %, una poliolefina en una cantidad de al menos 40% en peso y opcionalmente una resina que es compatible con los bloques de poli(butadieno) hidrogenados en una cantidad de desde 0 a 25% en peso, en donde todos los porcentajes en peso son con relación al peso de la composición completa.

b) La anterior composición busca facilitar la elaboración de películas mono o multicapa

c) Según la Clasificación Internacional de Patentes, la codificación para esta solicitud corresponde a C 08 L 53/02

3) **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 **DOS** diferentes objetos. La definición de la materia que caracteriza a cada una de las reivindicaciones 1 y 5 es muy diferente entre sí. Esto permite afirmar que no se trata del mismo producto. Todo el problema radica en configurar varias reivindicaciones 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, está oficina procederá a estudiar solo el primer grupo de invenciones que conformen un único concepto inventivo.

4) **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".

La reivindicación 4 busca proteger el uso de la composición de las primeras reivindicaciones. 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 o su composición, 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.

Por lo anterior, la reivindicación 4 no es patentable de acuerdo al Art. 14 de la Decisión 486.

5) 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 53/02*** y las más cercanas a ellas, se encontró que antes del 13 de enero de 2003 (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 de copolímeros.

Teniendo en cuenta lo reportado por la Organización Mundial de Propiedad Intelectual, no es posible tomar en consideración la fecha de prioridad toda vez que existen impedimentos para ello. El solicitante podrá rebatir ante esta oficina, las razones por las cuales la OMPI realizó dicho análisis.

De acuerdo con o 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	US 5 346 964	(Modified) Hydrogenated diene block copolymer and composition comprising the same	1994.09.13
D2	EP 1 061 099	Polypropylene resin compositions and parking stretched and packaging stretched film made thereof	2000.12.20
D3	US 6 042 907	Coextrusion of multilayer film for container sleeve labels	2000.03.28
D4	WO 01 09239	Hydrogenated block polymers having elasticity and articles made therefrom	2001.02.08
D5	EP 0 863 193	Sealant compositions	1998.09.09
D6	US 4 970 259	Elastomeric film composition	1990.11.13
D7	EP 0 413262	Thermoplastic resin composition	1991.02.20
D8	US 5 777 031	High 1,2 content thermoplastic elastomer / oil /polyolefin composition	1998.07.07
D9	WO 02 28965	An Elastomeric film and fiber grade thermoplastic elastomer composition	2002.04.11

6) 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 de la novedad y el del Nivel Inventivo

El art. 16 de la Decisión 486 de la Comisión de la Comunidad Andina establece:

"Una invención se considerará nueva cuando no está comprendida en el estado de la técnica." "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 prioridad de la solicitud de patente que se estuviese examinando, siempre que dicho contenido esté incluido en la solicitud de fechas de prioridad cuando ella se publique o hubiese transcurrido el plazo previsto en el artículo 40."

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".

b) El informe de búsqueda hecho por la Oficina de Patentes Europea a la presente solicitud en trámite en su fase internacional, revela 7 documentos que afectarían directamente la patentabilidad de la misma. Estos son los documentos relacionados como D1 a D7 en el presente estudio. Esta oficina está de acuerdo con esa apreciación, dado que en esos documentos se revelan copolímeros de bloque estirénico, que tiene una estructura molecular de acuerdo con la fórmula general S-EB-S (1) o $(S\text{-}EB)_n X$ (2) y con las características esbozadas en el presente capítulo reivindicatorio. Además de lo anterior, esta oficina ha encontrado un documento adicional, el D8 US 5777031, que revela en esencia lo mismo que el solicitante desea proteger para Colombia. Aparte de los anteriores documentos, también se relaciona D9 WO0228965, que muestra todo lo que el solicitante quiere proteger, y dado que según relaciona la Oficina Internacional en su Informe de búsqueda no es posible aceptar la prioridad, D9 afecta directamente la presente solicitud. Por tanto, la presente solicitud carecería de los requisitos de patentabilidad para que se le conceda el privilegio solicitado.

c) Resumen

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

Nº	Documento	Reivindicaciones afectadas	Requisito que afecta
D1	US 5 346 964	1 - 8	Novedad Nivel inventivo
D2	EP 1 061 099	1 - 8	Novedad Nivel inventivo
D3	US 6 042 907	1 - 8	Novedad Nivel inventivo
D4	WO 01 09239	1 - 8	Novedad Nivel inventivo
D5	EP 0 863 193	1 - 8	Novedad Nivel inventivo
D6	US 4 970 259	1 - 8	Novedad Nivel inventivo
D7	EP 0 413262	1 - 8	Novedad Nivel inventivo
D8	US 5 777 031	1 - 8	Novedad Nivel inventivo
D9	WO 02 28965	1 - 8	Novedad Nivel inventivo

7) **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 Nº 10 de 2001

ALIX CARMENZA CÉSPEDES DE VERGEL
Jefe División de Nuevas Creaciones

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

23 MAR. 2007

Concepto Técnico Nº	EXAMINADOR TÉCNICO Código No.	EXAMINADOR JURÍDICO Código No.
424	202003	

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US005346964A

United States Patent [19]

Shibata et al.

[11] Patent Number: 5,346,964

[45] Date of Patent: Sep. 13, 1994

[54] (MODIFIED) HYDROGENATED DIENE BLOCK COPOLYMER AND COMPOSITION COMPRISING THE SAME

[75] Inventors: Tsuru Shibata; Toshio Tamamoto; Yoshiharu Hashiguchi; Kunio Goshima, all of Yokkaichi, Japan

[73] Assignee: Japan Synthetic Rubber Co., Ltd., Tokyo, Japan

[21] Appl. No.: 80,115

[22] Filed: Jun. 23, 1993

Related U.S. Application Data

[62] Division of Ser. No. 937,723, Sep. 1, 1992, which is a division of Ser. No. 524,809, May 18, 1990, Pat. No. 5,191,024.

[30] Foreign Application Priority Data

May 19, 1989 [JP] Japan 1-124429
May 19, 1989 [JP] Japan 1-124430

[51] Int. Cl.[5] C08F 297/04; C08F 287/00

[52] U.S. Cl. 525/314; 525/279; 525/282; 525/285; 525/286; 525/293; 525/301; 525/303; 525/312

[58] Field of Search 525/279, 282, 285, 286, 525/293, 301, 303, 312, 314

[56] References Cited

U.S. PATENT DOCUMENTS

4,628,072 12/1986 Shiraki et al. 525/84

Primary Examiner—Vasu S. Jagannathan
Attorney, Agent, or Firm—Oblon, Spivak, McClelland, Maier & Neustadt

[57] ABSTRACT

A hydrogenated diene block copolymer having a polystyrene-reduced number-average molecular weight of 50,000–600,000 which is a hydrogenation product of an (A)-(B) block copolymer in which (A) means an alkenyl aromatic compound polymer block and (B) means a conjugated diene homopolymer block wherein the vinyl content of the conjugated diene portion is more than 60%, or an alkenyl aromatic compound-conjugated diene random copolymer block wherein the vinyl content of the conjugated diene portion is 15% or more, an (A)-(B)-(C) block copolymer in which (A) and (B) are as defined above and (C) means an alkenyl aromatic compound-conjugated diene copolymer tapered block wherein the proportion of the alkenyl aromatic compound increases gradually, or an (A)-(B)-(A) block copolymer in which (A) and (B) are as defined above. Said hydrogenated diene block copolymer is useful as a modifier for polar resins, non-polar resins or both of them.

8 Claims, No Drawings

(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 1 061 099 A1

(12) **EUROPEAN PATENT APPLICATION**
published in accordance with Art. 158(3) EPC

(43) Date of publication:
20.12.2000 Bulletin 2000/51

(21) Application number: 99906528.5

(22) Date of filing: 26.02.1999

(51) Int. Cl.[7]: C08L 23/10, C08J 5/18, B32B 27/32

(86) International application number:
PCT/JP99/00853

(87) International publication number:
WO 99/45064 (10.09.1999 Gazette 1999/36)

(84) Designated Contracting States:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU MC NL PT SE

(30) Priority: 02.03.1998 JP 6622498

(71) Applicant:
Kureha Chemical Industry Co., Ltd.
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- FUNABASHI, Shinichiro
Niihari-gun Ibaraki 315-0054 (JP)

(74) Representative:
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14 South Square,
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London WC1R 5LX (GB)

(54) POLYPROPYLENE RESIN COMPOSITIONS AND PACKAGING STRETCHED FILM MADE THEREOF

(57) A polypropylene resin composition which contains 60 to 99 parts by weight of a polypropylene resin (A) having a crystalline melting point of 130°C or higher, 1 to 40 parts by weight of a hydrogenated copolymer (B) of an aromatic vinyl compound and a conjugated diolefin, 0.1 to 20 parts by weight of polybutene (C) having a kinematic viscosity as measured at 37.8°C in accordance with JIS K2283 of 10 to 2,000,000 cSt, 0.1 to 20 parts by weight of a tackifier (D), and 0 to 5 parts by weight of a tackifier aid (E), the amounts of components (C), (D), and (E) being on the basis of 100 parts by weight of the sum of components (A) and (B); a polypropylene resin composition which contains 95 to 100 parts by weight of component (A), 0 to 5 parts, excluding 5 parts, by weight of component (B), 5 to 20 parts by weight of component (C), 0.1 to 20 parts by weight of component (D), and 0.01 to 1 part by weight of component (E), the amounts of components (C), (D), and (E) being on the basis of 100 parts by weight of the sum of components (A) and (B); and a stretched film for packaging which is made of any of these polypropylene resin compositions.

Printed by Xerox (UK) Business Services
2.16.7 (HRS)/3.6

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US006042907A

United States Patent [19]

Blackwelder et al.

[11] **Patent Number: 6,042,907**

[45] **Date of Patent: Mar. 28, 2000**

[54] **COEXTRUSION OF MULTILAYER FILM FOR CONTAINER SLEEVE LABELS**

[75] Inventors: **Maurice W. Blackwelder; Louis M. DiBello**, both of Bardstown, Ky.

[73] Assignee: **Owens-Illinois Labels Inc.**, Toledo, Ohio

[21] Appl. No.: **08/919,371**

[22] Filed: **Aug. 28, 1997**

[51] Int. Cl.[7] B32B 27/32; B45D 23/08

[52] U.S. Cl. 428/35.2; 428/35.7; 428/36.91; 428/195; 428/213; 428/517; 428/519; 428/910; 215/386

[58] Field of Search 428/517, 519, 428/521, 215, 910, 35.7, 36.91, 34.9, 36.5, 35.2, 213, 195; 215/386

[56] **References Cited**

U.S. PATENT DOCUMENTS

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4,049,768	9/1977	Luthra	264/45.5
4,386,125	5/1983	Shiraki et al.	428/910
4,486,366	12/1984	Reddy	264/416
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4,585,679	4/1986	Karabedian	428/34.7
4,626,455	12/1986	Karabedian	428/34.7
4,883,697	11/1989	Dornbusch et al.	428/35.7
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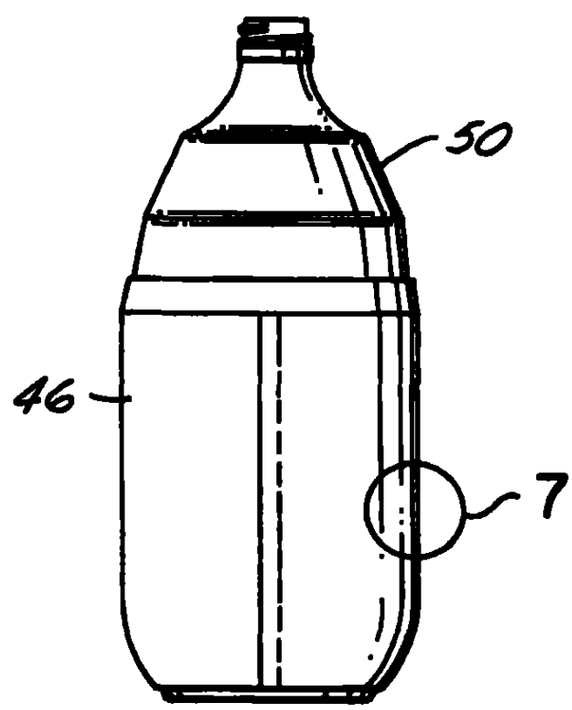
5,516,393	5/1996	Freedman	156/229
5,753,326	5/1998	Blackwelder	428/34.9
5,861,201	1/1999	Blackwelder et al.	428/36.91
5,891,537	4/1999	Yoshii et al.	428/35.7

Primary Examiner—Rena L. Dye

[57] **ABSTRACT**

A multilayer sheet, which is particularly well adapted for use as as a label sleeve on carbonated beverage containers, includes first and second coextruded unfoamed layers of polymer compositions each consisting essentially of polyolefin, polystyrene and a compatibility agent. The polyolefin and polystyrene are in a weight ratio in the range of about 30/70 to 70/30, and the compatibility agent is in the amount of about 5% to 10% by total weight. A pigment in the amount of about 10% to 15% by total weight may be included in one or both of the coextruded layers. The polyolefin preferably is selected from the group consisting of polypropylene, polyethylene and mixtures thereof, and the compatibility agent preferably comprises a styrene-ethylene/butylene-styrene block copolymer. One of the unfoamed layers preferably is thicker and of higher strength than the other layer, while the other layer has a smooth uniform exterior surface.

14 Claims, 2 Drawing Sheets



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(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
8 February 2001 (08.02.2001)

PCT

(10) International Publication Number
WO 01/09239 A1

(51) International Patent Classification⁷: C08L 53/02, B32B 27/00, A61L 15/58, A43B 13/14

(21) International Application Number: PCT/US00/20826

(22) International Filing Date: 28 July 2000 (28.07.2000)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:

60/146,008	28 July 1999 (28.07.1999)	US
60/197,161	13 April 2000 (13.04.2000)	US
60/203,538	11 May 2000 (11.05.2000)	US

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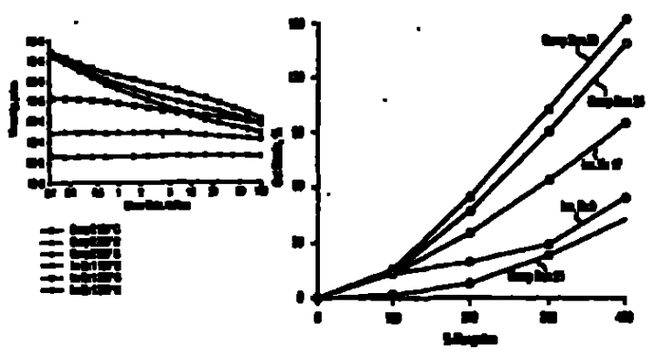
[Continued on next page]

(54) Title: HYDROGENATED BLOCK POLYMERS HAVING ELASTICITY AND ARTICLES MADE THEREFROM



(57) Abstract: The present invention relates to an elastic article comprising at least one hydrogenated block polymer and, optionally, at least one other polymer selected from the group consisting of a reactive tailored liquid polyurethane, an elastomeric or unhydrated ethylene/vinyl aromatic interpolymer, an elastomeric ethylene/C_3-C_{20} α-olefin interpolymer, a C_3-C_{20} α-olefin/conjugated diene interpolymer, an elastic polypropylene polymer, an enhanced polypropylene polymer, an elastomeric thermoplastic polyurethane, an elastic copolyester, a partially hydrogenated block polymer, an elastic polyamide, a hydroxyl functionalized polyether (or polythioether), a styrene/conjugated diene interpolymer, and an elastomeric metallocene-catalyzed synthetic polymer or a blend or formulated system thereof. In particular, the invention pertains to elastic shaped articles such as, for example, but not limited to, elastic fibers, elastic fabric, and elastic film as well as composites comprising the same, especially a composite absorbent item comprising at least one elastic shaped article. Innovative composite items include, but are not limited to, feminine hygiene napkins, incontinence pads, disposable diapers, and training pants. The term "elastic article" is used in reference to shaped items, while the term "elastic material" is used in reference to the novel compositions of the invention.

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Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

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United States Patent [19]

Mitchell et al.

[11] **Patent Number: 4,970,259**

[45] **Date of Patent: Nov. 13, 1990**

[54] **ELASTOMERIC FILM COMPOSITION**

[75] Inventors: Neil F. Mitchell, Santa Barbara, Calif.; Lin K. Djiauw, Houston, Tex.

[73] Assignee: Shell Oil Company, Houston, Tex.

[21] Appl. No.: 394,611

[22] Filed: Aug. 16, 1989

[51] Int. Cl.[5] C08K 53/00; C08L 53/00

[52] U.S. Cl. 524/505; 524/481; 525/89; 525/99; 525/316

[58] Field of Search 524/505, 484, 487; 525/89, 99

[56] **References Cited**

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Primary Examiner—Joseph L. Schofer
Assistant Examiner—Mark D. Sweet
Attorney, Agent, or Firm—Del S. Christensen

[57] **ABSTRACT**

A composition is provided which is suitable for extrusion blowing to form an elastomeric film. The film produced from this composition has a very low modulus, high elongation and excellent elastic recovery. The composition comprises: two hydrogenated block copolymers each comprising at least two blocks containing predominantly polymerized alkene arene monomer units and at least one block containing predominantly polymerized conjugated diene monomer units, the first hydrogenated block copolymer having a molecular weight between about 55,000 and about 200,000 and the second hydrogenated block copolymer having a molecular weight between about 15,000 and about 85,000, the ratio of the molecular weight of the first of the second being greater than 1.1:1, and each hydrogenated block copolymer being present in an amount of greater than 15 parts by weight for each 100 parts by weight of the total amount of the two hydrogenated block copolymers; between about 5 parts by weight and about 100 parts by weight of a polymer which is compatible with the polymerized vinyl arene blocks of the hydrogenated block copolymer; and between about 5 parts by weight and 200 parts by weight of a non-aromatic processing oil.

15 Claims, No Drawings

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(54) Thermoplastic resin composition

Thermoplastische Harzzusammensetzung

Composition de résine thermoplastique

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Remark:
The file contains technical information submitted after the application was filed and not included in this specification

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United States Patent [19]

Djiauw et al.

[11] Patent Number: 5,777,031

[45] Date of Patent: Jul. 7, 1998

[54] HIGH 1,2 CONTENT THERMOPLASTIC ELASTOMER/OIL/POLYOLEFIN COMPOSITION

[75] Inventors: Lie Khong Djiauw; Michael John Modic, both of Houston, Tex.

[73] Assignee: Shell Oil Company, Houston, Tex.

[21] Appl. No.: [illegible]

[22] Filed: Jul. [illegible], 1997

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. [illegible], Jul. 3, 1996, abandoned.

[51] Int. Cl.⁶ C08L 53/02; C08L 9/06; C08L 47/00

[52] U.S. Cl. .... [illegible]; 525/98; 525/99; 525/232; 525/240; 525/241

[58] Field of Search 525/88, 98, 99, 525/232, 240, 241

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Primary Examiner—Fred Zitomer

Attorney, Agent, or Firm—Beverlee G. Steinberg

[57] ABSTRACT

A thermoplastic elastomer composition comprising a block copolymer having at least two resinous endblocks and a high 1,2-addition butadiene midblock, a paraffin oil and a crystalline polyolefin. The composition exhibits greater softness, better processability and better elastic properties as compared with similar compositions made with normal amounts of a 1,2-addition. Compositions are useful for articles such as overmolding [illegible] substrates, grips, medical tubing and miscellaneous rubbery articles.

[illegible] Claims, No Drawings

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HIGH 1,2 CONTENT THERMOPLASTIC ELASTOMER/OIL/POLYOLEFIN COMPOSITION

This application is a continuation-in-part of U.S. patent application Ser. No. [illegible], filed Jul. 3, 1996, now abandoned.

BACKGROUND OF THE INVENTION

This invention relates to thermoplastic elastomer compositions containing oil and a polyolefin.

It is well known to incorporate olefin polymers into thermoplastic elastomer compositions to improve processability and to otherwise enhance the mechanical and chemical properties. For instance, high melting olefin polymers such as polypropylene improve the upper service temperature and ozone resistance of the compositions. It is also known to use paraffinic oils, alone or in combination with olefin polymers, to soften thermoplastic elastomer compositions and also to improve processability. However, increasing the amount of oil is a limited option because, at high oil levels, oil migration occurs which results in surface tackiness.

In many utilities, however, greater softness would be desirable.

SUMMARY OF THE INVENTION

It is an object of this invention to provide thermoplastic elastomers having greater softness; and

It is yet a further object of this invention to provide thermoplastic elastomers with lower hardness and improved melt flow without an increase in the amount of oil.

In accordance with this invention, a high 1,2-content butadiene/monovinyl aromatic block copolymer elastomer is combined with a paraffinic oil and an olefin polymer.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Surprisingly, it has been found that the use of high 1,2-addition (high vinyl) thermoplastic elastomer in a rubber/oil/polyolefin composition results in greater softness as compared with similar compositions using elastomers where the 1,2-addition is in the usual 15 to 50 mole percent range. Furthermore, these novel compositions also have improved processability and better elastic properties as measured by, for instance, by compression set.

Thermoplastic Elastomer

By thermoplastic elastomer is meant a block copolymer having at least two end-blocks made of polymerized monovinyl aromatic compound, thus giving a glassy, aromatic segment, and a mid-block made up at least predominantly of polymerized 1,3-butadiene monomer, thus giving an amorphous elastomeric segment. The copolymers can be linear, A-B-A, radial, $(A\text{-}B)_nX$, or mixtures thereof. Some A-B diblock polymer can be present but preferably at least 70 weight percent of the block copolymer is A-B-A or radial (or otherwise branched so as to have 2 or more terminal resinous blocks per molecule) so as to impart strength. Generally, 80 to 100 weight percent of the block copolymer has 2 or more terminal resinous blocks per molecule and it is preferred to have essentially no diblock. In the above radial formula the n is an integer of at least 3, generally 3 to 50, more generally 6 to 13, and the X is the remnant of a coupling agent.

The A-B-A compositions can be made by either sequential polymerization or coupling. In the sequential polymerization

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technique, the monovinyl aromatic monomer is first introduced to produce an aromatic block followed by the introduction of the butadiene monomer to produce the rubbery midblock followed by additional monovinyl aromatic compound to produce the other terminal aromatic block. This is broadly disclosed in Holden, U.S. Pat. No. 3,231,635 (Jan. 25, 1966), the disclosure of which is hereby incorporated by reference. The production of such polymers and also radial polymers is broadly disclosed in Stevens et al. U.S. Pat. No. 5,194,530 (Mar. 16, 1993), the disclosure of which is hereby incorporated by reference. Another patent broadly disclosing the anionic polymerization of thermoplastic elastomers using an organo alkali metal initiator is Bean, U.S. Pat. No. 4,764,572 (Aug. 16, 1988), the disclosure of which is hereby incorporated by reference.

It is well known in the art to drive the polymerization toward the 1,2-addition of butadiene. Broadly, this can be done by utilizing an organic polar compound such as an ether, including cyclic ethers, polyethers and thioethers or an amine including secondary and tertiary amines. Preferred are chelating ethers and amines. By chelating ether is meant an ether having more than one oxygen as exemplified by the formula $R(OR')_m(OR'')_oOR$ where each R is individually selected from 1 to 8, preferably 2 to 3, carbon atom alkyl radicals; R' and R'' are individually selected from 1 to 6, preferably 2 to 3, carbon atom alkylene radicals; and m and o are independently selected integers of 1–3, preferably 1–2. Examples of preferred ethers include diethoxypropane, 1,2-dioxyethane (dioxo) and 1,2-dimethoxyethane (glyme). Other suitable materials include $CH_3\text{—}OCH_2\text{—}CH_2\text{—}OCH_2\text{—}CH_2\text{—}OCH_3$ (diglyme) and $CH_3\text{—}CH_2\text{—}OCH_2\text{—}CH_2\text{—}OCH_2\text{—}CH_2\text{—}OCH_2\text{—}CH_3$. By chelating amine is meant an amine having more than 1 nitrogen such as N,N,N',N'-tetramethylethylene diamine. Monoamines are operable but less preferred. Less preferred also (but still operable) are straight chain and cyclic monoethers such as dimethylether, diethylether, anisole, and tetrahydrofuran.

This microstructure promoter is used in an amount of at least 0.1 moles per mole of lithium compound, preferably 1–50, more preferably 2–25, moles of promoter per mole of the lithium compound. Alternatively, the concentration can be expressed in parts per million by weight based on the total weight of solvent and monomer. Based on this criteria from 10 parts per million to about 1 weight percent, preferably 100 parts per million to 2000 parts per million are used. This can vary widely, however, since extremely small amounts of some of the preferred promoters are very effective. At the other extreme, particularly with less effective promoters, the promoter itself can be the solvent. Again, these techniques are well known in the art, disclosed for instance in Winkler, U.S. Pat. No. 3,686,366 (Aug. 22, 1972), Winkler, U.S. Pat. No. 3,700,748 (Oct. 24, 1972) and Koppes et al., U.S. Pat. No. 5,194,535 (Mar. 16, 1993), the disclosures of which are hereby incorporated by reference.

The resulting vinyl content for the polymers useful in this invention is greater than 50 mole percent, preferably 50–90, more preferably 65–90, most preferably 65–80.

The thermoplastic elastomer as it is actually used in this invention is hydrogenated and hence there is little or no vinyl unsaturation left. Nonetheless, it is still a high 1,2 addition polymer (from a high vinyl precursor). Even the hydrogenated product may be loosely referred to as "high vinyl" because of its origin.

The thermoplastic elastomers utilized in the compositions of this invention are selectively hydrogenated so as to remove most of the vinyl unsaturation and any ethylenic

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unsaturation in the polymer backbone from the monomer which did not polymerize in the 1,3 manner. By selective hydrogenation is meant that the aliphatic unsaturation is significantly removed while leaving unaffected most of the aromatic unsaturation. Suitable known catalysts for accomplishing this include nickel compounds in combination with a reducing agent such as an aluminum alkyl. Hydrogenation is taught in Shore, U.S. Pat. No. 3,634,549 (Jan. 11, 1972), De la Mare, U.S. Pat. No. 3,670,054 (Jan. 13, 1972), Wald et al, U.S. Pat. No. 3,700,633 (Oct. 24, 1972) and Jones, Re 27,145 (Jan. 22, 1971), the disclosures of which are hereby incorporated by reference.

Each individual styrenic endblock must have a molecular weight of at least about 20,000. Preferably the endblocks have a molecular weight within the range of 20,000 to 50,000, more preferably 25,000 to 40,000, most preferably 25,000 to 37,000.

The thermoplastic elastomers utilized in this invention have a total molecular weight which is relatively high compared with thermoplastic elastomers in general. The molecular weight will generally be at least 130,000. For linear A-B-A polymers, the molecular weight will generally be within the range of 150,000 to 300,000. Actually, the upper limit is dictated by viscosity considerations and can be as high as can be tolerated and still be processible. The most preferred molecular weight for linear A-B-A polymers is 180,000 to 250,000. With radial polymers, the molecular weight can be much higher since these polymers have a lower viscosity for a given total molecular weight. Thus, for radial polymers the molecular weight generally will be in the range of 150,000 to 1 million, preferably 150,000 to 500,000.

The total styrenic content of the block copolymer will generally be within the range of 20 to 45 weight percent based on the total weight of the block copolymer, preferably 25 to 45, more preferably 25 to 35 weight percent. The upper limit is set by the maximum which can be tolerated such that the material is still elastomeric as opposed to rubbery. At about 50 weight percent and higher the material is rubbery.

Since the block copolymers utilized in this invention are hydrogenated to remove the aliphatic unsaturation or central backbones, they can be viewed as S-EB-S polymers, the S referring to the monovinyl aromatic generally styrene, endblocks. The EB represents ethylene/butylene which is the structure resulting from the hydrogenation of polymerized 1,3-butadiene.

Oil

The oil is one which is compatible with the elastomeric mid-block segment of the elastomeric block copolymer and which does not tend to go into the aromatic endblock portions to any significant degree. Thus, the oils can be viewed as paraffinic. Paraffinic oils which may be used in the elastomeric composition should be capable of being melt processed with other components of the elastomeric composition without degrading. Particularly important is the ability of the final composition to be melt extruded. An exemplary processing oil is a white mineral oil available under the trade designation DRAKEOL® 34 from the Pennzoil Company, Pennzoil Division. DRAKEOL® 34 has a specific gravity of 0.864–0.878 at 60° F., a flashpoint of 460° F., and a viscosity of 370–430 SUS at 100° F. Suitable vegetable oils and animal oils or their derivatives may also be used as the processing oil. Suitable oils also include hydrogenated materials, i.e. hydrogenated naphthenics, hydrogenated materials which were initially aromatic in nature are hydrogenated to the point where they exhibit no significant levels of aromatic unsaturation or of usual, very low levels.

Polyolefin

The polyolefins utilized in this invention are crystalline polyolefins. That is, polyolefins having a crystallinity of at least 50% (i.e. at least 50 weight percent is crystalline). Most preferred are high density polyethylene, which has a crystallinity of about 80 to 90%, and crystalline polypropylene, the crystalline polypropylene being most preferred in many applications because of the improved high temperature properties it imparts. Other suitable polyolefins include polybutene, ethylene/higher α-olefin copolymers, propylene copolymers and butylene copolymers or mixtures of any of the above-described polyolefins. Most preferred is an injection molding grade crystalline polypropylene such as Polypropylene 5A15 homopolymer (melt flow rate 5 g/10 min. from Shell Chemical Co.).

Compounding

The thermoplastic elastomers of this invention may be viewed as comprising a hydrocarbon component made up of the elastomeric block copolymer, the paraffinic oil and the crystalline polyolefin. To this hydrocarbon component can be added other ingredients such as typically found in elastomeric compositions.

Other ingredients which do not affect the essential elastomeric characteristics of the composition may be present including pigments, fungicides, stabilizers, flame retardants, antistatic, waxes, flow promoters, extenders, and materials added to enhance processibility and pellet handling of the composition. The composition can also contain 5 to 40 weight percent based on the weight of hydrocarbon component of a filler such as a hard inorganic mineral filler.

The stabilizer can be any conventional stabilizer or stabilizer system and is frequently simply an antioxidant such as a hindered phenol. Particularly preferred is IRGANOX® 1010 alone or in combination with a thiosynergist such as DLTDP. IRGANOX® 1010 is tetrakis[methylene(3,5 -di-t-butyl-4-hydroxyhydrocinnamate)] methane. DLTDP is dilauryl thiodipropionate. Suitable stabilizers are shown in Alper et al, U.S. Pat. No. 5,149,741 (Sep. 22, 1992) and St. Clair, U.S. Pat. No. 4,838,200 (May 30, 1989), the disclosures of which are hereby incorporated by reference. More volatile materials such as 2,6-di-tert-butylphenol are less preferred because of the volatility.

The stabilizer present is generally present in an amount within the range of 0.01 to 4, preferably 0.5 to 1 weight percent based on the weight of the base composition.

The composition of this invention may be thought of in terms of

(a) a base composition comprising

(i) the elastomeric block copolymer,

(ii) the oil,

(iii) the crystalline polyolefin, and

(b) the other ingredients.

The base composition comprises 15 to 55, preferably 25 to 50, more preferably, 25 to 45 weight percent of the hydrogenated high 1,3 elastomeric block copolymer; 5 to 80 preferably 25 to 65, more preferably 25 to 60 weight percent of said paraffinic oils; and 5 to 20, preferably 5 to 15, more preferably 10 to 15 weight percent of the crystalline polyolefin. All of the percentages are based on the total weight of the base composition, i.e. the block copolymer, oil and polyolefin.

The ingredients preferably are compounded by contacting the block copolymer with the oil and allowing time for the oil to be absorbed into the copolymer. Generally, the copolymer will absorb the oil to the appearance of dryness. Therefore the oil/block copolymer composition is generally dry blended in a tumble blender with the polyolefin and extruded after which the blend is reextruded further and extruded.

Definitions

As used herein, the term "tensile strength" or "TS" refers to the resistance of an elastic material to being elongated as determined in accordance with ASTM D-412 using 0.125 inch wide and 0.020 inch thick dumbbell samples that are cut from injection molded plaques. Tensile testing is performed on an INSTRON® Model 1123 Universal Test Machine utilizing a crosshead speed of 10 inch/min.

As used herein, the term "elongation" or "El" refers to the percent extension of an elastic material until breakage as determined in accordance with ASTM-D-412 as described above. A mechanical extensometer is used during the testing to obtain a more accurate elongation. The gap distance for the extensometer is 1 inch.

As used herein, the term "compression set" or "CS" refers to a value determined according to ASTM-D-395, Method A, Type 1. Disks of 1 inch diameter are cut out of injection molded plaques. These disks are stacked to approximately 0.5 inches in height and compressed between two flat chrome plates. The degree of compression is controlled by the use of standard metal spacers. The disk stacks are placed under compression for 22 hours at room temperature or 70° C., and then allowed to recover for 30 minutes before their final thickness is measured.

As used herein, the term "hardness" refers to a value determined according to ASTM D2240 after 10 seconds of indentation on the Shore A hardness scale. The hardness value is the average of five measurements taken at different locations around a 4 inch by 2 inch injection molded plaque.

As used herein the melt flow index ("MFI") is an indication of melt viscosity determined according to ASTM D1238 Procedure A at a temperature of 230° C. and 2.16 kg piston loading (Old Condition 1). The procedure utilizes a dead-weight piston plastometer.

By "molecular weight" as used herein is meant the following. Molecular weights of linear block copolymers are conveniently measured by Gel Permeation Chromatography (GPC), where the GPC system has been appropriately calibrated. Polymers of known molecular weight are used to calibrate and these must be of the same molecular structure and chemical composition as the unknown linear polymers or segments that are to be measured. For substantially polystyrene linear polymers, the polymer is conveniently measured and it is both convenient and adequately descriptive to report the "peak" molecular weight of the narrow molecular weight distribution observed. Hence, this is what is meant with regard to reference herein to molecular weight of linear polymers. This is also what is meant with regard to reference herein to molecular weight of linear polymers. This is also what is meant by the reference herein to the molecular weight of the styrenic endblocks A block. Polystyrene is used to calibrate, then directly giving the absolute molecular weight of polystyrene endblocks. From this and the known percent styrene, the absolute molecular weight of the midblock is calculated. That is, an aliquot is removed after the first step of the polymerization, terminated to deactivate the initiator and the molecular weight measured.

Measurement of the true molecular weight of final coupled star polymer is not as straightforward or as easy to make using GPC. This is because the star shaped molecules do not separate and elute through the packed GPC columns in the same manner as do the linear polymers used for the calibration, and, hence, the time of arrival at a UV or refractive index detector is not a good indicator of the molecular weight. A good analytical method to use for a star polymer is to measure the weight average molecular weight by light scattering techniques. The sample is dissolved in a suitable solvent at a concentration less than 1.0 gram of sample per 100 milliliters of solvent and filtered using a syringe and porous membrane filters of less than 0.5 micron pore size directly into the light scattering cell. The light scattering measurements are performed as a function of scattering angle and of polymer concentration using standard procedures. The differential refractive index (DRI) of the sample is measured at the same wavelength and in the same solvent used for the light scattering. Then, the relation to molecular weight in reference to linear star or radial polymers across molecular weight determined in this fashion. Moreover, even with the star polymers, the endblocks are still measured by taking an aliquot and using GPC as described for the linear polymers.

Example

In the following example polymers of high and normal vinyl content were utilized. The high vinyl content blends, designated "A," "C," "D," "E," "F," "G" and "H," were produced as follows. Utilizing the conventional secondary butyllithium initiator, styrene, then 1,3-butadiene, then styrene were sequentially introduced to give an A-B-A polymer. Polymerization of the butadiene segment was carried out at 30° C. and cyclohexane solvent utilizing 300 parts per million based on the weight of solvent and monomer of glyme so as to induce high 1,3-addition. The resulting polymers had 1,3-additions as shown in Table 1. The polymers were then hydrogenated utilizing a conventional chlorohydrosilane, hydrogenation catalyst to give the S-EB-S structure.

Polymer "B" was a sequentially polymerized polymer prepared in a similar manner except glyme was not utilized, instead 6 weight percent diethylether, based on the weight of solvent and monomer, was used. The polymer was hydrogenated in the same manner as Polymer A.

TABLE 1

HYDROGENATED BLOCK COPOLYMERS

Block	MW (S, EB, S) (×1,000)	Polymer Content (% w)	1,3-addition of Butadiene (% mol)
A	15-142-15	20	72.1
B	15-122-15	25	35
C	15-104-15	30.1	71
D	15-83-15	35.1	77
E	15-67-15	40	69+
F	15-125-15	20.0	72.1
G	15-125-15	25.0	72.1
H	15-125-15	30.0	72.1

Three aliquots of conventional Polymer B and four aliquots of the high vinyl Polymers were separately compounded with various amounts of oil and polyolefin as set out in Table 2. Compounding was carried out by contacting the oil and the block copolymer and allowing 8 hours for absorption of the oil into the block copolymer. Thereafter the composition was tumbled with the polyolefin for 15 minutes and then extruded at a temperature of 225° C. From this extrudate tensile specimens and compression set specimens were molded and the melt flow determined. The results are set out in Table 2.

TABLE 2

[illegible]

Blend #	SBC[a]	SBC (% w)	Oil[b] (% w)	PP[c] (% w)	Hardness (Shore A)	TS (RT) (psi)	Eb (RT) (%)	TS (70C) (psi)	Eb (70C) (%)	CS (70C) (%)	MFI (230C/2.16) (g/10 min)
8	C	35	50	15	[illegible]	680	780			48.1	21.6
9	D	35	50	15	[illegible]	680	735			37.8	41.9
1	A	40	50	10	[illegible]	525	880	121	307	48.6	3.13
2	B	40	50	10	[illegible]	697	824	182	760	35.8	1.39
10	B	45	45	10	[illegible]	646	730			34.1	0.16
11	C	45	45	10	[illegible]	429	680			32.1	0.57
12	F	45	45	10	[illegible]	546	656			32.4	0.4
13	G	45	45	10	[illegible]	586	586			34.1	0.12
14	H	45	45	10	[illegible]	570	580			32.2	0.33
3	A	45	45	10	[illegible]	705	970	115	380	46	2.58
4	A	45	45	10	[illegible]	520	901	121	335		1.76
15	D	45	45	10	[illegible]	606	614			30.6	5
5	B	45	45	10	[illegible]	745	705	185	885	31.7	0.1
6	A	55	35	10	[illegible]	550	851	160	370	30.9	<0.05
7	B	55	35	10	[illegible]	765	650	200	677	40	<0.01

[a] Styrenic Block Copolymer (SBC)
[b] [illegible]
[c] Polypropylene sold under the trade designation [illegible] from Shell Oil Company

As can be seen comparing the similar blends, significantly lower hardness (greater softness) was obtained with the high-vinyl SBCs as compared with the comparable Control SBC (B). As can be seen further, this was achieved with better set, the lower number indicating better elasticity, i.e. less permanent deformation. Finally, a comparison of the melt flow index shows that all of these beneficial results were obtained with an improvement rather than a sacrifice in melt flow.

Similarly, a comparison of the blends at slightly lower oil ratios shows the same lower hardness (softer softness), and the same improvement in compression set and melt flow.

While this invention has been described in detail for the purpose of illustration, it is not to be construed as limited thereby but is intended to cover all changes and modifications within the spirit and scope thereof.

I claim:

1. A thermoplastic elastomer composition comprising:

(A) a base composition comprising:

(I) 15 to 35 weight percent of a block copolymer having at least two resinous polymerized monovinyl aromatic endblocks and a midblock of hydrogenated polymerized butadiene wherein at least 51 mole percent of said butadiene has polymerized at the 1,2-position,

(II) 5 to 80 weight percent of a paraffinic oil, and

(III) 5 to 20 weight percent of a crystalline polyolefin; and

(B) a stabilizer, each stabilizer being present in an amount within the range of 0.01 to 4 weight percent based on the weight of said base composition.

2. A composition according to claim 1 wherein said end-blocks each have a molecular weight of at least 20,000 and wherein said block copolymer has a molecular weight of at least 130,000.

3. A composition according to claim 2 wherein said block copolymer comprises 20–40 weight percent of said monovinyl aromatic compound.

4. A composition according to claim 3 wherein said block copolymer is an A-B-A block copolymer wherein each A represents polymerized styrene and wherein said crystalline polyolefin is polypropylene, said block copolymer further being defined by a molecular weight within the range of 180,000–250,000.

5. A composition according to claim 4 wherein said block copolymer has a styrene content within the range of 25–35 weight percent.

6. A composition according to claim 1 wherein said block copolymer is an A-B-A block copolymer having a molecular weight within the range of 150,000–300,000.

7. A composition according to claim 1 wherein said block copolymer has a monovinyl aromatic content within the range of 22–45 weight percent.

8. A composition according to claim 1 wherein said monovinyl aromatic compound is styrene.

9. A composition according to claim 1 wherein said polyolefin is polypropylene.

10. A composition according to claim 1 wherein said block copolymer has a monovinyl aromatic content within the range of 25–35 weight percent.

11. A composition according to claim 1 wherein said stabilizer comprises a hindered phenol antioxidant and a thiosynergist.

12. A composition according to claim 11 wherein said hindered phenol is tetrakis[methylene(3,5-di-t-butyl-4-hydroxyhydrocinnamate)] methane and said thiosynergist is dilaurylthiodipropionate.

13. A composition according to claim 1 comprising in addition a flame retardant.

14. A composition according to claim 1 comprising in addition a filler.

15. A composition according to claim 1 wherein said oil is a white mineral oil having a specific gravity within the range of 0.864–0.878 at 60° C. and a viscosity of 370–420 sus at 100° F. and wherein said polyolefin is polypropylene.

16. A composition comprising 25 to 45 weight percent of a styrene-ethylene/butylene-styrene block copolymer wherein at least 51 mole percent of said butylene block is derived from 1,2-butadiene polymerization; 35 to 60 weight percent of a paraffinic oil; and 10 to 15 weight percent of a crystalline polyolefin.

17. A composition according to claim 16 wherein said ethylene-butylene block is derived from butadiene in which 65–80 mole percent polymerized at the 1,2 position.

18. A process comprising:

combining a block copolymer having at least two resinous polymerized monovinyl aromatic compound endblocks and a midblock of hydrogenated polymerized butadiene wherein at least 51 mole percent of said butadiene has polymerized at the 1,2-position with a paraffinic oil;

allowing time for said block copolymer to absorb said paraffinic oil to give an oil-containing block copolymer composition;

tumble blending said oil-containing block copolymer composition with a crystalline polyolefin to give a block copolymer/oil/polyolefin mixture;

melt extruding said mixture, wherein said block copolymer is present in an amount within the range of 15 to 35 weight percent, said oil is present in an amount within the range of 5 to 80 weight percent, and said crystalline polyolefin is present in an amount within the range of 5 to 20 weight percent based on the total weight of said block copolymer, oil and polyolefin.

19. A method according to claim 18 wherein said monovinyl aromatic compound is styrene, said block copolymer is of a linear A-B-A configuration, 65–80 mole percent of said butadiene has polymerized at the 1,2-position, and wherein said block copolymer is present in an amount within the range of 25 to 45 weight percent, said oil is present in an amount within the range of 35 to 60 weight percent and said crystalline polyolefin is polypropylene present in an amount within the range of 10 to 15 weight percent, and wherein a stabilizer is also present during said tumble blending.

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(54) Title: AN ELASTOMERIC FILM AND FIBER GRADE THERMOPLASTIC ELASTOMER COMPOSITION

(57) Abstract: In one embodiment, the present invention provides an elastomeric composition which is useful as an elastic film and fiber grade compound. These compositions contain at least one [illegible] block copolymer having a vinyl content of 60 percent or greater and a molecular weight of 40,000 to 110,000 and a styrene block molecular weight of 5,000 to 15,000. The composition will comprise from 60 to 85 percent by weight of the block copolymer, from 5 to 25 percent by weight of a tackifying resin, and from 5 to 25 percent by weight of a low molecular weight, low density polyethylene. In a second embodiment of the present invention, an elastic film and fiber grade compound is provided which does not contain a tackifying resin. The composition is comprised of from 15 to 30 percent by weight of a low molecular weight, low density polyethylene and the balance is comprised of the block copolymer described above. A third embodiment of this invention provides another elastic film and fiber grade compound. This compound also contains no tackifying resin. It is comprised of from 2 to 60 percent by weight of a metallocene polyethylene elastomer polymer and the balance is the block copolymer described above.

AN ELASTOMERIC FILM AND FIBER GRADE THERMOPLASTIC ELASTOMER COMPOSITION

CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims benefit of United States provisional patent application serial number 60/237,533, filed October 4, 2000, which is herein incorporated by reference.

FIELD OF THE INVENTION

This invention relates to elastomeric polymer compositions that can be extruded into fibers or films. More specifically, the invention relates to new high vinyl styrene-diene block copolymer compositions for use in making film or spun bond fiber for elastic nonwovens laminates.

BACKGROUND OF THE INVENTION

Extrudable elastomeric compositions which can be easily compression molded or melt blown into elastic fibers or films having low stress relaxation, low hysteresis, and high recoverable energy are known. The elastomeric fibers or films are useful in making a variety of applications such as diaper waistbands and non-woven fabrics.

A number of thermoplastic elastomer compositions have been developed for making film or spun bond fiber nonwovens laminate for personal hygiene applications. U.S. Patent 4,789,699 disclosed such compositions based on styrene-ethylene/butylene-styrene (SEBS) polymers the incorporate additional tackifier and polyolefin resins. One of the drawbacks of this composition was the relatively poor elastic recovery performance. U.S. Patent No. 5,093,422 disclose composition based on styrene-propylene/ethylene styrene (SEPS) polymers which are said to improve the elastic properties of the materials. However, the flow behavior of these compositions was reduced. U.S. Patent No. 5,332,613 discloses a composition based on styrene-ethylene/propylene-styrene-ethylene/propylene (SEPSep) four-block polymers as a way to balance the hysteresis and flow performance. However, none of the above technologies provide a desirable balance of important properties:

elastic hysteresis, stress relaxation at body temperature and ease of flow characteristics. The stress relaxation at body temperature tends to be the most critical shortcoming in these compositions.

SEBS elastomeric block copolymers and SEPS elastomeric block copolymers have been blended as discussed above to form extrudable elastomeric compositions which can be formed into elastic fibers or films. While the additives, tackifying resins or polyolefins, improve the extrusion properties of the compositions and the processing and/or bonding properties of the elastic fibers or films, such additives have an adverse affect on the elastic properties of the resulting fiber or film, especially at temperatures above 25°C.

It can be seen that it would be advantageous to provide an elastomeric composition which overcomes the drawbacks of the above prior art compositions. An elastomeric composition which maintained or improved the elastic performance of the products made therefrom and which also exhibits improved flow behavior which is highly desirable in film and fibers applications would be particularly advantages. The present invention provides such an elastomeric composition.

SUMMARY OF THE INVENTION

In one embodiment, the present invention provides an elastomeric composition which is useful as an elastic film and fiber grade compound. These compositions contain at least one SEBS block copolymer having a vinyl content of 60 percent or greater and a number average molecular weight of 40,000 to 110,000, preferably 60,000 to 100,000, and a styrene block molecular number average weight of 5,000 to 15,000. The composition will comprise from 60 to 85 percent by weight of the block copolymer, from 5 to 25 percent by weight of a tackifying resin, and from 10 to 35 percent by weight of a polyethylene.

In a second embodiment of the present invention, an elastic film grade compound is provided which does not contain a tackifing resin. The composition is comprised of from 5 to 35 percent by weight of a polyethylene and the balance is comprised of the block copolymer described above.

A third embodiment of this invention provides another elastic film grade compound. This compound also contains no tackifying resin. It is comprised of from

2 to 60 percent by weight of a metallocene polyethylene elastomer polymer and the balance is the block copolymer described above.

The term "vinyl content" refers to the fact that a conjugated diene is polymerized via 1,2-addition (in the case of butadiene - it would be 3,4-addition in the case of isoprene). Although a pure "vinyl" group is formed only in the case of 1,2-addition polymerization of 1,3-butadiene, the effects of 3,4-addition polymerization of isoprene (and similar addition for other conjugated dienes) on the final properties of the block copolymer will be similar. The term "vinyl" refers to the presence of a pendent vinyl group on the polymer chain.

DETAILED DESCRIPTION OF THE INVENTION

The extrudable elastomeric composition of the present invention is an improvement of the extrudable compositions described in United States Patents Nos. 4,970,259, 5,093,422, and 5,332,613 which descriptions are incorporated by reference herein. The known compositions include one or more styrenic block copolymers, typically an SEBS or an SEPS or an SEPSep elastomeric block copolymer which is produced by hydrogenating a polystyrene-polybutadiene-polystyrene or polystyrene-polyisoprene-polystyrene or polystyrene-polyisoprene-polystyrene-polyisoprene block copolymer. The SEBS block copolymers which were specifically discussed and utilized in the above patents all had vinyl contents in the "normal" range of 35 to 55 percent by weight.

In the present invention, the compositions contain at least one hydrogenated polystyrene-polybutadiene-polystyrene block copolymer (S-EB-S) having a vinyl content in the saturated block of polybutadiene of at least 60 percent by weight and preferably from 60 to 85 percent by weight in comparison to the conventional block copolymers used to make elastomeric films and fibers commercially and described in the above patents. This change in microstructure results in improved elastic performance and flow behavior while maintaining the stress relaxation properties of the conventional block copolymers. The S-EB-S block copolymer may be blended with other hydrogenated block copolymers, such as the SEPS or the SEPSep elastomeric block copolymers, or the butadiene may be co-polymerized with other conjugated dienes, such as isoprene, in amounts that retain improved elastomeric properties.

The styrenic block copolymers have at least two poly(monoalkenylarene) blocks, preferably two polystyrene blocks, separated by a saturated block of a poly(conjugated diene), preferably a saturated polybutadiene. The preferred block copolymers comprise two polystyrene blocks, at least one block having a number average molecular weight from 5,000 to 15,000, and one saturated polybutadiene midblock, each having a number average molecular weight from 30,000 to 85,000. The saturated polybutadiene blocks preferably have at least 60 percent by weight 1,2-configuration (vinyl content) and preferably from 60 to 85 percent. The total number average molecular weight of the block polymer is from 40,000 to 110,000, preferably 60,000 to 100,000, and the block copolymers preferably have an average polystyrene content from 12% to 25% by weight.

These polymers may be prepared using free-radical, cationic and anionic initiators or polymerization catalysts. Such polymers may be prepared using bulk, solution or emulsion techniques. In any case, the polymer containing at least ethylenic unsaturation will, generally, be recovered as a solid such as a crumb, a powder, a pellet, or the like.

In general, when solution anionic techniques are used, conjugated diolefin polymers and copolymers of conjugated diolefins and alkenyl aromatic hydrocarbons are prepared by contacting the monomer or monomers to be polymerized simultaneously or sequentially with an organoalkali metal compound in a suitable solvent at a temperature within the range from about -150°C to about 300°C, preferably at a temperature within the range from about 0°C to about 100°C. Particularly effective anionic polymerization initiators are organolithium compounds having the general formula:

$$RLi_n$$

wherein R is an aliphatic, cycloaliphatic, aromatic, or alkyl-substituted aromatic hydrocarbon radical having from 1 to about 20 carbon atoms; and n is an integer of 1 to 4.

In addition to sequential techniques to obtain triblocks, tetrablocks, and higher orders of repeating structures, anionic initiators can be used to prepare diblocks of polystyrene-polydiene having a reactive ("live") chain end on the diene block which

can be reacted through a coupling agent to create, for example, $(S\text{-}I)_xY$ or $(S\text{-}B)_xY$ structures wherein x is an integer from 2 to about 30, Y is a coupling agent, I is isoprene, B is butadiene and greater than 85 percent of S-I or S-B diblocks are chemically attached to the coupling agent. Y usually has a molecular weight which is low compared to the polymers being prepared and can be any of a number of materials known in the art, including halogenated organic compounds; halogenated alkyl silanes; alkoxy silanes; various esters such as alkyl and aryl benzoates, difunctional aliphatic esters such as dialkyl adipates and the like; polyfunctional agents such as divinyl benzene (DVB) and low molecular weight polymers of DVB. Depending on the selected coupling agent the final polymer can be a fully or partially coupled linear triblock polymer (x=2), i.e., SIYIS; or branched, radial or star configurations. The coupling agent, being of low molecular weight, does not materially affect the properties of the final polymer. DVB oligomer is commonly used to create star polymers, wherein the number of diene arms can be 7 to 20 or even higher.

The styrenic block copolymers must be hydrogenated. In general, the hydrogenation or selective hydrogenation of the polymer may be accomplished using any of the several hydrogenation processes known in the prior art. For example the hydrogenation may be accomplished using methods such as those taught, for example, in U.S. Patent Nos. 3,494,942; 3,634,594; 3,670,054; 3,700,633; and Re. 27,145, the disclosure of which patents are incorporated herein by reference. The methods known in the prior art and useful in the present invention for hydrogenating polymers containing ethylenic unsaturation and for hydrogenating or selectively hydrogenating polymers containing aromatic and ethylenic unsaturation, involve the use of a suitable catalyst, particularly a catalyst or catalyst precursor comprising an iron group metal atom, particularly nickel or titanium or cobalt, and a suitable reducing agent such as an aluminum alkyl. The amount of ethylenic unsaturation remaining after hydrogenation is typically less than 20%. The level of saturation achieved by hydrogenation is desirably greater than about 85%. For example, the level of saturation achieved by hydrogenation is desirably greater than about 98%. More desirably, the level of saturation achieved by hydrogenation is greater than about 99%.

In general, the hydrogenation will be accomplished in a suitable solvent at a temperature within the range from about 20°C to about 100°C and at a hydrogen partial pressure within the range from about 100 psig (8 bar) to about 5,000 psig (350 bar), preferably about 100 psig (8 bar) to 1,000 psig (70 bar). Catalyst concentrations within the range from about 10 ppm (wt) to about 500 ppm (wt) of metal based on total solution are generally used and contacting at hydrogenation conditions is generally continued for a period of time within the range from about 60 to about 240 minutes. After the hydrogenation is completed, the hydrogenation catalyst and catalyst residue will, generally, be separated from the polymer.

The compositions of the present invention may include from 5 to 35 percent by weight of one or more polyolefins. The polyolefins which may be utilized in the extrudable composition must be polyolefins which, when blended with the elastomeric block copolymer or a mixture of elastomeric block copolymers and subjected to an appropriate combination of elevated pressure and elevated temperature conditions, is extrudable, in blended form, with the elastomeric block copolymer or a mixture of elastomeric block copolymers. In particular, preferred polyolefin materials include low molecular weight low density polyethylene with a density of less than 0.92 grams per cubic centimeter and a melt index greater than 30 grams/10 minutes, and linear low density polyethylene, metallocene linear low density polyethylene, various ethylene copolymers, such as low vinyl acetate polyethylene, ethylene methyl acrylate copolymer, ethylene acrylic acid, ethylene methacrylic acid resins etc. Blends of two or more of the polyolefins may be utilized.

An example of a low molecular weight, low density polyethylene is Petrothene NA 601-04 (also referred to herein as PE NA 601) obtained from Equistar Chemical. Information obtained from Equistar Chemical states that PE NA 601 is a low molecular weight, low density polyethylene for application in the areas of hot melt adhesives and coatings. PE NA 601 exhibits following key characteristics: (1) a density of 0.903 grams per cubic centimeter when measured in accordance with ASTM D 1505; and (2) an equivalent Melt Index of 2,000 grams per 10 minutes when measured in accordance with ASTM D 1238.

In another embodiment of this invention, the above block copolymers are blended with a metallocene polyolefin having a density from 0.86 to 0.91, a

molecular weight distribution less than 3, and from 8% to 30% by weight of an α-olefin comonomer having from 4 to 12 carbon atoms, preferably from 4 to 8 carbon atoms. The metallocene polyolefins are polyolefins produced with a metallocene catalyst as described in United States Patents No. 5,322,728 and 5,272,236 which are descriptions are incorporated by reference herein. Such elastomeric polyolefins are available from DuPont Dow Elastomers under the trademark ENGAGE (ethylene/octene copolymers), from Dow Chemical Company under trademark AFFINITY, and from Exxon Chemical Company under the trademark EXACT (ethylene/butene copolymers). The metallocene polyolefins have low crystallinity when ethylene is copolymerized with from 8% to 30% by weight of an α-olefin comonomer having from 4 to 12 carbon atoms.

Various tackifying resins can be used in at least one of the embodiments of the present invention. In particular, the purpose of the tackifying resin is to allow elastomeric film or fiber to act as a pressure sensitive adhesive, e.g., to allow elastomeric film or fiber to bond to another web or layer of material. Of course, various tackifying resins are known, and are discussed, e.g., in U.S Patent Nos. 4,789,699; 4,294,936; and 3,783,072, the contents of which, with respect to the tackifier resins, are incorporated herein by reference. Any tackifier resin can be used which is compatible with the elastomeric polymer and the polyolefin, and can withstand the high processing (e.g., extrusion) temperatures. Generally, hydrogenated hydrocarbon resins are preferred tackifying resins, because of their better temperature stability. The following paragraphs disclose information on three specific tackifying resins, two of which (REGALREZ® and ARKON®P series tackifiers) are examples of hydrogenated hydrocarbon resins, and the ZONATAC®501 Lite is a terpene hydrocarbon. Of course, while the three tackifying resins are specifically discussed, the present invention is not limited to use of such three tackifying resins, and other tackifying resins which are compatible with the other components of the composition and can withstand the high processing temperatures, and can achieve the objectives of the present invention, can also be used.

REGALREZ® hydrocarbon resins, a product of Hercules, Incorporated, are fully hydrogenated α-methylstyrene, low molecular weight hydrocarbon resins, produced by polymerization and hydrogenation of pure monomer hydrocarbon feed stocks.

Grades 1094, 3102, 6108, and 1128 are highly stable, light-colored low molecular weight, nonpolar resins suggested for use in plastics modification, adhesives, coatings, sealants, and caulks. The resins are compatible with a wide variety of oils, waxes, alkyds, plastics, and elastomers and are soluble in common organic solvents.

ZONATAC®501 Lite resin, a product of Arizona Chemical Co., has a softening point of 106°C, a Gardner color (50% in heptane) of 1—and a Gardner color neat (pure) of 2+; (a Gardner color of 1—(50% in heptane) is approximately equal to APHA color = 70) a specific gravity (25°/25°C) of 1.02 and a flash point (closed cup, °F) of 480°F.

In one embodiment of the present invention, a composition according to the present invention is provided as an elastic fiber grade compound. This composition comprises from 60 to 85 percent by weight of the above-described high vinyl content block copolymer, from 5 to 25 percent by weight of one of the above-described tackifying resins, and from 10 to 35 percent by weight of one of the above-described polyethylene resin. These compounds show excellent hysteresis recovery and good stress relaxation properties at body temperature. Increasing the vinyl content improves both of these properties as compared to the same polymer with a lower vinyl content. Additionally, these compounds exhibit improved melt flow characteristics and elasticity over compounds comprising similar polymers with lower vinyl contents.

In another embodiment of the present invention, a composition is provided which is a low molecular weight, low density polyethylene containing film compound. This compound does not contain any tackifying resin in order to minimize the softening effect of the tackifying resin. It will comprise from 15 to 35 percent of the low molecular weight, low density polyethylene material described above and the balance will be comprised of the high vinyl block copolymer described above. Within this composition range, these compounds exhibit improved elastic behavior and improved melt flow compared to compounds made from a similar polymer with a lower vinyl content. If the amounts of low molecular weight, low density polyethylene is increased to 60 percent, the compatibility of the high vinyl block

copolymer and the polyethylene is poor. Also, such compounds exhibit poor tensile elongation and cannot sustain the stress relaxation test.

In a third embodiment of this invention, another film grade compound is provided. This compound also contains no tackifying resin and it contains a metallocene elastomer polymer which is used instead of the low molecular weight, low density polyethylene or the combination of lw. This composition will contain from 2 to 60 percent by weight of the metallocene polyolefin and the balance is comprised of the high vinyl block copolymer described above. The compatibility of these polymers within this composition range is good. The blends are homogeneous and they exhibit excellent elastic properties even at the 60/60 blend ratio.

While the principal components of the extrudable elastomeric composition used to form the elastic sheet have been described in the foregoing, such extrudable elastomeric composition is not limited thereto, and can include other components not adversely affecting the extrudable elastomeric composition attaining the stated objectives. Exemplary materials which could be used as additional components would include, without limitation, pigments, antioxidants, stabilizers, surfactants, waxes, flow promoters, solvents, particulates, and materials added to enhance processability and pellet handling of the composition.

The term "elastic" is used herein to mean any material which, upon application of a biasing force, is stretchable, that is, elongatable at least about 60 percent (i.e., to a stretched, biased length which is at least about 160 percent of its relaxed unbiased length) and which, will recover at least 55 percent of its elongation upon release of the stretching, elongating force. A hypothetical example would be a one (1) inch sample of a material which is elongatable to at least 1.60 inches (4.06 cm) and which, upon being elongated to 1.60 inches (4.06 cm) and released, will recover to a length of not more than 1.27 inches (3.23 cm). Many elastic materials may be elongated by much more than 60 percent (i.e., much more than 160 percent of their relaxed length), for example, elongated 100 percent or more, and many of these will recover to substantially their initial relaxed length, for example, to within 105 percent of their initial relaxed length, upon release of the stretching force.

As used herein, the term "stress relaxation" refers to the percent loss of tension or load between the maximum load or force encountered after elongating an elastic material at a specified rate of extension to a predetermined length (or the load or force measured at some initial length) and the remaining load or force measured after the sample has been held at that length for a specified period of time, for example, from about 10 minutes to about 30 minutes. Except where otherwise noted for the present invention, stress relaxation is expressed as a percentage loss of the initial load encountered at a specified extension of an elastic material. The stress relaxation is determined by calculating the difference between the initial maximum load measured after elongating an elastic material at a rate of 20 inches (50.8 cm) per minute to an elongation of 160 percent (i.e., to 260 percent of the material's initial length) and the remaining load measured after that sample was held at that length for 30 minutes divided by the initial maximum load at that length. Testing may be performed on an Instron Model 5565 Universal Test Machine using ASTM microtensile specimens. Stress relaxation after 30 minutes at, for example, an elongation of 160 percent (i.e., to 260 percent of the material's initial length - from 100 mm to 260 mm) may be expressed as a percentage utilizing the following equation: stress relaxation = (peak $load_{max}$ - $load_{max}$ @30 min)/(peak $load_{max}$)*100.

As used herein, the term "tensile strength" refers to the resistance of an elastic material to being elongated as determined in accordance with ASTM 412 Method using microtensile specimens that are cut from films. Films formed from a blend of an elastomeric block copolymer and other materials such as, for example, a polyolefin (metallocene and/or crystalline), a tackifier, and/or an extending oil were compression molded. Tensile testing may be performed on an Instron Model 5565 Universal Test Machine.

As used herein, the term "recoverable energy" refers to the energy stored by an elastic material when it is elongated to a specified length. Recoverable energy is measured utilizing a tensile testing apparatus such as, for example, an Instron Model 5565 Universal Test Machine by elongating a sample of an elastic material sample at 1 inch/minute to 160 percent elongation (i.e., to 260 percent of the material's initial relaxed length) and cycling back to zero load for 1 hysteresis loop. The percent recoverable energy is determined by dividing the area under the

retraction curve of the first hysteresis loop by the area under the elongation curve of the first hysteresis loop and then multiplying by 100.

As used herein, the "number average molecular weight" was determined utilizing gel permeation chromatography techniques for linear anionic polymers. All molecular weights are measured prior to hydrogenation which will increase the molecular weights by a small amount. The molecular weights of linear polymers or unassembled linear segments of polymers such as mono-, di-, triblock, etc., arms of star polymers before coupling are conveniently measured by Gel Permeation Chromatography (GPC), where the GPC system has been appropriately calibrated. For anionically polymerized linear polymers, the polymer is essentially monodisperse (weight average molecular weight/number average molecular weight ratio approaches unity), and it is both convenient and adequately descriptive to report the "peak" molecular weight of the narrow molecular weight distribution observed. Usually, the peak value is between the number and the weight average. The peak molecular weight is the molecular weight of the main species shown on the chromatograph. For polydisperse polymers the weight average molecular weight should be calculated from the chromatograph and used. For materials to be used in the columns of the GPC, styrene-divinyl benzene gels or silica gels are commonly used and are excellent materials. Tetrahydrofuran is an excellent solvent for polymers of the type described herein. A refractive index detector may be used.

EXAMPLES

SEBS block copolymers of varying 1,2-vinyl content were made for these experiments. The conventional SEBS polymers of standard vinyl content (35 to 45 percent) were synthesized with diethylether as the structure modifier. The higher vinyl content polymers were synthesized with 1,2-diethoxy propane as the structure modifier. The first group of polymers, which are described in Table I, consists of SEBS polymers with about 100,000 overall total number average molecular weight, 13 to 21 percent polystyrene content, and vinyl contents ranging from 38 to 78 percent. The referenced conventional SEBS polymer (vinyl content of 38 percent) is typically used in high performance elastic SEBS polymer blends for film and fibers applications.

The compound samples were prepared by melt blending the raw ingredients in a small Brabender Kneader at 400°F (204°C). Test samples were compression molded into 25 mil, 4 in. (10.2 cm) by 4 in. (10.2 cm) rectangular plaques at 380°F (193°C). ASTM micro tensile test specimens were die cut from the test plaques.

The stress-strain properties of the pressed films were determined in accordance with ASTM D-412 utilizing a Constant Rate of Extension Tester, Instron Model 5565 Universal Testing Instrument. Each sample was placed lengthwise in jaw faces, with a jaw span of 0.75 inches (1.9 cm). The Instron Model 5565 Universal Test Instrument crosshead speed was set at 2 inches per minute for the first series of tests measuring the Stress-Strain properties. In addition, stress relaxation and hysteresis tests were measured using the Instron Model 5565 Universal Test Machine and determined as previously described. The specimens were cut orthogonally and the results were reported based on the average of both directions.

Table I lists the characteristics and physical properties of the three polymers which were used to make the compounds which are evaluated in Tables II and III. It can be seen that the melt flow of the higher vinyl polymers is significantly higher than that of the standard vinyl content SEBS block copolymer and the rubber moduli of the higher vinyl polymers are lower than the referenced polymer (Polymer A). The elastic recovery behavior of the higher vinyl polymers is significantly better than the reference polymer while their stress relaxation properties at body temperature remain unchanged.

Example 1

Elastic fiber grade compounds containing the SEBS polymers of Table I were made and their corresponding physical properties are shown in Table II. Two types of elastic film formulations were used in this example. The first type of formulation (compounds 1, 2 and 3 in Example 1, Table II) contains SEBS block copolymer, tackifying resin, and a low density polyethylene resin. The polyethylene resin used was Equistar NA 601-04 which is described in detail above. This type of compound also exhibits hot melt adhesive behavior with the plasticization of the midblock by the tackifying resin. These compounds show excellent hysteresis recovery and

good stress relaxation properties at body temperature. Increasing the vinyl content in the midblock improves both the hysteresis recovery and the stress relaxation. Of most interest is the improvement of stress relaxation of the high vinyl polymer compounds at body temperature. Elastic recovery and stress relaxation behavior of the compounds made from the high vinyl SEBS block copolymers B and C are the best among these compounds and thus compounds 2 and 3 with their improved melt flow and elasticity are preferred.

Table I

Polymer Number	A	B	C
Characteristics			
1,2 Vinyl Content, % by weight	37.5	60.6	76
Block Molecular Weight by GPC	8.9-52.5-8.4	7.6-63.8-8.4	9/8-80-12.6
Hydrogenated Total Molecular Weight	87,000	100,000	103,800
Polystyrene Content, % by weight	12.8	15	20.8
Properties of Polymer			
Melt Flow @ 230°C/5.0 Kg, grams/10 min.	<1.0	5.3	4.25
Mechanical Properties at 23°C			
Stress Relax., % 30 min., 150%	17	17	20
Stress Strain Properties			
100% modulus, psi (Kg/cm²)	228 (16.0)	150 (10.5)	176 (12.4)
300% modulus, psi (Kg/cm²)	370 (26.0)	230 (16.2)	307 (21.6)
500% modulus, psi (Kg/cm²)	627 (44.1)	345 (24.3)	448 (31.5)
Tensile Strength, psi (Kg/cm²)	1555 (109)	1230 (86.5)	*>1223 (>86)
Elongation at Break, psi (Kg/cm²)	787 (55.3)	1070 (75.2)	*>1114 (>78)
Hysteresis to 150%			
Hysteresis to 150% elongation	248	170	235
% Recovery	77.5	88	80.3
% Set	11	12	10
Stress Relaxation at 40°C			
% Stress Relax., 30 min., to 150% extension	24	23	22

* No break

Example 2

The second type of compounds described in Table II are binary blends of SEBS block copolymer and the same low density polyethylene resin used above.

The compounds were prepared with SEBS/PE blend ratios of 85/15, 70/30, and 50/50 levels. The results are shown in Table II (Example 2, compounds 4 to 16). At blend ratios between 85/15 and 70/30, the high vinyl polymer compounds exhibit improved elastic behavior and improved melt flow compared to compounds from the reference polymer. The compatibility of the high vinyl SEBS polymer with low molecular weight, low density polyethylene is poor at the higher polyethylene content. Also, the 50/50 blend exhibited poor tensile elongation and could not sustain the stress relaxation test.

Example 3

Several film grade compounds utilizing a metallocene polyethylene elastomer were made. The particular metallocene was Dow Affinity® resin having a density of 0.885 and a melt index of 30. The compatibility of this metallocene polymer with the high vinyl SEBS polymers is good. The blends appear homogeneous and exhibit excellent elastic properties at a 50/50 blend ratio. Table III shows the comparison of physical properties of blends of polymer A,B and C with low density polyethylene and metallocene linear low density polyethylene at 30 and 50% polyethylene level.

The blends of high vinyl polymers B and C, formulation 12, 13, 17 and 18, exhibit better flow than formulations 7 and 8 made with "normal" vinyl polymer A while maintaining equivalent or better recoverable energy, permanent set and stress relaxation.

Table II

	Example 1			Example 2								
Formulation	-1	-2	-3	-6	-7	-8	-11	-12	-13	-16	-17	-18
Composition, % wt												
Polymer A, 33% vinyl SEBS	67.5			84.5	69.5	49.5						
Polymer B, 60% vinyl SEBS		67.5					84.5	69.5	49.5			
Polymer C, 78% vinyl SEBS			67.5							84.5	69.5	49.5
[illegible]	20	20	20									
PE NA601-04	12	12	12	15	30	50	15	30	50	15	30	50
AO 330	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Total, % wt	100	100	100	100	100	100	100	100	100	100	100	100
Properties of Compound												
Melt Flow @ 190°C/2.16 kg, gms/10 min	<1.0	3.15	1.38	<1.0	<1.0	4.7	<1.0	4.34	>20	<1.0	4.86	>20
Mechanical Properties at 23°C, [illegible]	22.7	20.9	24.9	22.9	27.4	37.2	17.8	28.5	38.5	23.9	31.9	Sample Broke
Stress Strain Properties												
100% modulus, [illegible]	14.1	[illegible]	9.40	14.7	21.9	31.1	13.0	17.8	27.1	11.7	17.0	23.4
200% modulus, [illegible]	21.0	14.1	[illegible]	[illegible]	[illegible]	41.7	[illegible]	[illegible]	33.4	[illegible]	[illegible]	-
300% modulus, [illegible]	[illegible]	21.0	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	-	[illegible]	34.1	-
Tensile Strength, [illegible]	57.2	[illegible]	>31.7	[illegible]	[illegible]	[illegible]	>[illegible]	72.0	38.7	[illegible]	51.4	[illegible]
Elongation at Break, [illegible]	[illegible]	>[illegible]	>31.7	[illegible]	[illegible]	[illegible]	>[illegible]	61.9	[illegible]	[illegible]	[illegible]	[illegible]
Hysteresis to 100% extension												
[illegible]	16.3	10.2	7.5	21.6	[illegible]	[illegible]	14.6	[illegible]	[illegible]	14.3	19.0	Broke
[illegible]	71	[illegible]	[illegible]	70	[illegible]	[illegible]	[illegible]	67	42	[illegible]	[illegible]	-
[illegible]	10.8	12.1	11.9	13.7	17.7	[illegible]	11.3	16.8	27.1	12.3	15.3	-
Relaxation at 40°C												
[illegible]	44	[illegible]	25.4	21.1	22.2	48.8	21.1	38	Broke	[illegible]	Broke	Broke

Note: ">" symbol indicates sample did not break at that elongation.

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Table III

Formulation	-5	-6	-7	-8	-10	-11	-12	-13	-15	-16	-17	-18
Composition, % wt												
Polymer A, 38% vinyl SEBS	69.8	49.8	69.8	49.8								
Polymer B, 60% vinyl SEBS					69.8	49.8	69.8	49.8				
Polymer C, 78% vinyl SEBS									69.8	49.8	69.8	49.8
PE, NA601-04	30	50			30	50			30	50		
AFFINITY® Resin, 30 MI			30	50			30	50			30	50
AO 330	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Total, % wt	100	100	100	100	100	100	100	100	100	100	100	100
Properties of Compound												
Melt Flow @ 190°C/2.16 Kg, grams/10 min.	<1.0	4.89	<1.0	1	4.34	>20	<1.0	4.04	4.89	>20	<1.0	2.34
Mechanical Properties at 23°C, % Stress Relax., 150 % extension for 30 min.	27.4	37.2	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	29.1	31.9	Broke	25.6	30.7
Stress Strain Properties												
100% modulus, Kg/cm²	21.9	31.1	20.3	[illegible]	17.8	27.1	18.5	22.6	17.0	23.4	18.7	20.8
300% modulus, Kg/cm²	32.0	41.7	30.6	[illegible]	[illegible]	33.4	25.0	31.5	25.3	–	[illegible]	30.4
500% modulus, Kg/cm²	49.5	69.0	47.1	81.9	[illegible]	–	34.9	41.9	34.1	–	[illegible]	40.1
Tensile Strength, Kg/cm²	136.9	78.3	123.7	123.1	72.0	A	>112	108.0	81.4	A	>91	>92.1
Elongation at Break, Kg/cm²	84.9	46.6	84.8	94.8	91.8	< 35.2	>78.7	78.1	68.6	< 21.1	>77.8	>
Hysteresis to 150%												
Peak Stress, Kg/cm²	23.9	32.6	22.3	25.8	20.2	25.8	18.4	24.0	18.0	–	18.8	24.8
% Recovery	82	42	67	67	67	48	73	69	65	–	68	[illegible]
% Set	17.7	[illegible]	17.4	31	18.9	37.1	18.6	19.5	18.3	–	18	20.6
Properties at 40°C, % Stress Relax., 150% extension for 30 min.	33.2	48.8	30.6	33.4	36	B	30.1	38.4	B	B	23.6	28.3

Note: " > " symbol indicates sample did not break at that elongation. A, B denotes samples failed prematurely during the test.

WE CLAIM:

1. An elastomeric film and fiber grade thermoplastic elastomer composition comprising

(a) a block copolymer having at least two polystyrene endblocks and a midblock of hydrogenated polymerized butadiene which has a vinyl content of at least 60 percent by weight, a number average molecular weight of 40,000 to 110,000 and a styrene block number average molecular weight of 5,000 to 15,000;

(b) optionally a tackifying resin;

(c) optionally a low molecular weight polyolefin; and

(d) optionally a polyolefin made with a metallocene catalyst having a density of 0.86 to 0.91, a molecular weight distribution of less than 3, and from 5 percent to 30 percent by weight of an α-olefin comonomer having from 4 to 12 carbon atoms;

wherein the composition comprises either:

(i) from 50 to 85 percent by weight of component (a), from 5 to 30 percent by weight of component (b), and from 10 to 35 percent by weight of component (c); or

(ii) from 65 to 95 percent by weight of component (a) and from 5 to 35 percent by weight of component (c); or

(iii) from 40 to 98 percent by weight of component (a) and from 2 to 60 percent by weight of component (d).

2. The composition of claim 1 where the block copolymer is a hydrogenated styrene-butadiene-styrene triblock copolymer with a polystyrene content of 12 to 25%.

3. The composition of claim 1 where the block copolymer is a hydrogenated styrene-butadiene-styrene triblock copolymer with a number average molecular weight of 60,000 to 100,000.

4. The composition of claim 1 where the tackifying resin is a fully hydrogenated hydrocarbon resin.

5. The composition of claim 1 where the low molecular weight polyolefin is a low density polyethylene with a density of less than 0.92 grams per cubic centimeter and a melt index greater than 30 grams/10 minutes.

6. The composition of claim 1 wherein the vinyl content of the block copolymer is from 60 to 85 percent by weight.

7. The composition of claim 1 wherein the midblock of the block copolymer further comprises hydrogenated isoprene or wherein the block copolymer is blended with another block copolymer comprising hydrogenated isoprene.

8. Elastomeric fibers or films from the extruded composition of claim 1.

INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08L5/02 C08F297/04

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B. FIELDS SEARCHED
Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C08L C08D C08J C08F C08K

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

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 709 413 A (JAPAN SYNTHETIC RUBBER CO LTD) 1 May 1996 (1996-05-01) * page 3,line 1-4 ; page 3,line 21-23 ; page 5,line 45-46 ; page 5,line 27-28 ; page 6,line 25-26 ; page 6,line 55-58 ; page 7,line 22-25 ; page 9,line 11-20 ; claim 11 * page 8, line 56 -page 9, line 3	1-8
X	US 5 346 964 A (SHIRATA TOORU ET AL) 13 September 1994 (1994-09-13) * column 2,line 58-62 ; column 3,line 45-50 ; column 7,line 27-30 ; column 7,line 44-53, 64-66 ; column 10,line 3-10 ; column 10,line 51-58 ; column 13,line 39-54 * column 14, line 1-6; claim 1	1-8

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[X] Further documents are listed in the continuation of box C. [X] Patent family members are listed in annex.

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
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For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: BLOCK COPOLYMER COMPOSITIONS, HAVING IMPROVED MECHANICAL PROPERTIES AND PROCESSABILITY

(57) Abstract: A composition to be used for the manufacture of mono-or multilayer films for food-wrap applications comprising from 5 to 40 wt% of a styrenic block copolymer, a polyolefin in an amount of at least 40 wt% and optionally a resin which is compatible with the hydrogenated poly(butadiene) blocks of the styrenic block copolymer in an amount of from 0 to 25 %wt, wherein all weight percentages are relative to the weight of the complete composition; a styrenic block copolymer to be used in said composition, and mono-or multi-layer films comprising said composition.

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INTERNATIONAL SEARCH REPORT

International application No. PCT/EP 03/00278

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EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	WO 02 28965 A (KRATON POLYMERS RES B V ;HANDLIN DALE LEE JR (US); DJIAUW LIE KHON) 11 April 2002 (2002-04-11) * (same applicant,same invention - invalid present application priority date) ;pg.2,line 30- pg.3,line 2 ;claims 1-8 ;pg.5,line 16-32 ;pg.4,line 29- pg.5,line 16 ;examples ;pg.10,line 22-23 * page 6, line 22 -page 8, line 5; claim 8	1-4
X	US 5 346 964 A (SHIBATA TOORU ET AL) 13 September 1994 (1994-09-13) * column 7, line 30, particularly "films,sheets" ; column 1, line 61 - column 2, line 1; column 2, line 31-38; column 3, line 9-12, 40-44; column 3, line 56 - column 4, line 6 ; abstract * column 7, line 44-49,51-59	1-4

Sin equivalente en Colombia

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Date of the actual completion of the international search	Date of mailing of the international search report
8 January 2004	18.01.2004
Name and mailing address of the ISA: European Patent Office, P.B. 5818 Patentlaan 2, NL - 2280 HV Rijswijk, Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer: Hammond, A

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/EP 03/00278

C. (Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 1 061 099 A (KUREHA CHEMICAL IND CO LTD) 20 December 2000 (2000-12-20) * claims 1,2,4,3-17, particularly films and laminated films ; page 4, line 9-31, 42-57 ; page 2, line 1-8 * abstract	1-4
X	US 6 042 907 A (BLACKHELDER MAURICE W ET AL) 28 March 2000 (2000-03-28) * abstract ; claims 1-5 * column 5, line 41-43	1-4
P,X	US 6 406 653 B1 (BLACKHELDER MAURICE W ET AL) 18 June 2002 (2002-06-18) * abstract ; claims 7,9,10 * column 5, line 43-45	1-4
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Y	EP 0 413 262 A (KURARAY CO) 20 February 1991 (1991-02-20) * abstract * page 3, line 1-50	1-4
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A	US 5 627 235 A (HIMES GLENN R) 6 May 1997 (1997-05-06) * column 1, line 10-13; column 1, line 60 - column 2, line 5 ; column 2, line 55-65* abstract; table 1	1-3

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/EP 03/00278

C. (Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 01 19910 A (SHELL INT RESEARCH) 22 March 2001 (2001-03-22) * abstract ; claims *	1-3
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Form PCT/ISA/210 (continuation of second sheet) (July 1998)

INTERNATIONAL SEARCH REPORT

International Application No.
PCT/EP 03/00276

Box I Observations where certain claims were found unsearchable (Continuation of Item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claim Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claim Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:

3. ☐ Claim Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of Item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☒ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

1-4

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☒ No protest accompanied the payment of additional search fees.

Form PCT/ISA/210 (continuation of first sheet (1)) (July 1998)

International Application No. PCT/EP 03 00276

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. Claims: 1-3

   A composition suitable for the manufacture of a monolayer, or of multilayer films for food-wrap applications.The said composition comprising from 5 to 40 wt.% of a styrenic block copolymer of either molecular structure S-EB-S ...(1), or of molecular structure (S-EB)nX ...(2) as described in the application claim 1 ; a polyolefin in an amount of at least 40 wt.% ; and optionally 0-25 %wt. of a resin which is compatible with the hydrogenated poly(butadiene) blocks, wherein all wt.% are relative to the weight of the complete composition.

2. Claim : 4

   A monolayer film, or a multilayer film comprising at least one layer based on a composition according to any one of the claims 1-3.

3. Claims: 5-8

   A styrenic block copolymer as described in application claims 5-8.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP 03/00278

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International application No.
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— *of inventorship (Rule 4.17(iv)) for US only*

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WO 02/28965 A1

(54) Title: AN ELASTOMERIC FILM AND FIBER GRADE THERMOPLASTIC ELASTOMER COMPOSITION

(57) Abstract: In one embodiment, the present invention provides an elastomeric composition which is useful as an elastic film and fiber grade compound. These compositions contain at least one SEBS block copolymer having a vinyl content of 60 percent or greater and a molecular weight of 40,000 to 110,000 and a styrene block molecular weight of 5,000 to 15,000. The composition will comprise from 60 to 85 percent by weight of the block copolymer, from 5 to 25 percent by weight of a tackifying resin, and from 5 to 35 percent by weight of a low molecular weight, low density polyethylene. In a second embodiment of the present invention, an elastic film and fiber grade compound is provided which does not contain a tackifing resin. The composition is comprised of from 15 to 30 percent by weight of a low molecular weight, low density polyethylene and the balance is comprised of the block copolymer described above. A third embodiment of this invention provides another elastic film and fiber grade compound. This compound also contains no tackifying resin. It is comprised of from 2 to 60 percent by weight of a metallocene polyethylene elastomer polymer and the balance is the block copolymer described above.