

CAVELIER

ABOGADOS

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

64
SUPERINTENDENCIA Y COMERCIO
Radicación: 0404710 0000001 Folios: 2
Fecha (Act): 2005-05-11 16:35:21
Trámite: 011 PCT-PAT/MI 378 FASE NNCI 538 PETICION
Dependencia: 2020 DIVISION DE NUEVAS CREACIONES

Trámite: 011
Evento: 379
Actuación: 538

Referencia : Expediente No. 04 – 084.710
Asunto : Solicitud de patente para **"COMPOSICIONES DE COPOLÍMERO QUE TIENEN PROPIEDADES MECÁNICAS Y DE PROCESABILIDAD MEJORADAS Y COPOLÍMEROS DE BLOQUE ESTIRÉNICOS PARA SER USADOS EN ELLOS"**
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 ple 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 – 15.248 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 841 002 8
PRP/PRP/ID-000010/WPC14012

68

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO

MIT : 000176009-2

SUPERINDUSTRIA Y COMERCIO
Radiacion : 04004710 00000001 Folios: 2
Fecha (ORA): 2005-02-11 16:53:21
Tramite : 011 PCT-PATENT 370 FASE NACI 530 PETICION
Dependencia: 2020 DIVISION DE NUEVAS CREACIONES

RECIBO OFICIAL DE CAJA : 05 - 15,248
FECHA : FEBRERO 28 DE 2005

***** CONSIGNACION *****

DEPOSITANTE	TIPO PAGO	BANCO	CUENTA	No. PAGO	FECHA PGO	Vr. PAGO
CAVELIER ABOGADOS	CONSIGNACION	BANCO POPULAR	050-00110-6	23840360	28/02/2005	32,194,000.00

***** CONCEPTO *****

CANT.	RENTISTICO	CONCEPTO	TOTAL CONCEPTO
1	50003-01-01 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. _____

006 14012-841-002-8

DIVISION DE NUEVAS CREACIONES

RADICACIÓN EXPEDIENTE No. 04-84710

**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**

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

2020

Bogotá, D. C., 13 de Marzo de 2007

Doctor

EMILIO FERRERO

Representante **KRATON POLYMERS RESEARCH B. V.**

ASUNTO

Radicación No.	04-84710
Trámite	002
Evento	001
Actuación	430
Oficio	3667
Folios	054

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 31 a 55 de la solicitud en estudio.
- b) Para el presente estudio se tendrá en cuenta el capítulo reivindicatorio que comprende 10 reivindicaciones en los folios 56 a 60 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 EP02079638.9

2) Objeto de la Invención

- a) Las reivindicaciones 1 a 10 de la solicitud en estudio se refieren a una composición para ser usada en la fabricación de fibras, filamentos, no tejidos soplados por fusión o pegados por hilado o películas fundidas o sopladas, comprende por lo menos 50% en peso de un copolímero de bloque estirénico, que tiene una estructura molecular de acuerdo con las fórmulas generales



en donde cada S independientemente es un bloque de polímero de estireno predominantemente y EB 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, y preferiblemente entre 7000 a 8500, que tiene un peso molecular aparente del copolímero del bloque completo en el rango desde 80,000 a 150,000 que tiene un grado de 1, 2 adición (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 por lo menos 80% y preferiblemente por lo menos 90% y en donde el dibloque S-ES opcionalmente ocurre en un contenido a lo sumo del 20 % moles y preferiblemente a lo sumo 10 % en moles, una poliolefina en una cantidad de 10 a 30% en peso; una resina que es compatible con los bloques de poli(estireno) en una cantidad de desde por lo menos 5% en peso, y una resina que es compatible con los bloques de polibutadieno hidrogenado en una cantidad de por lo menos 3% en peso, en donde todos los porcentajes en peso son con relación al peso de la composición completa.

- b) El anterior producto busca obtener composiciones para ser usadas en la fabricación de fibras, filamentos, no tejidos por fusión soplados o hilados por pegado o películas tendidas o sopladas.
- c) Según la Clasificación Internacional de Patentes, la codificación para esta solicitud corresponde a C 08 L 53/02

3) Claridad de la Solicitud

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

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

La descripción no es clara toda vez que la redacción y traducción son sumamente deficientes. Por ejemplo, la frase "...copolímero de bloque de estireno butadieno hidrogenado modificados..." es inexacta y no corresponde al nombre técnico real en español del compuesto. Tampoco lo es "polímero hidrogenado de butadieno" o "un grado 1,2 de adición (contenido de vinilo)..." y un muy largo etcétera. No existe el "p-test.butil estireno" no los "bloques vivientes", o los "tetametoxisilano". Los compuestos de formula general R11 del folio 44 también son inexistentes. Además, de esto hay un sinnúmero de errores.

En general, la solicitud es todo un caos. Deberá presentarse nueva solicitud en español, con una correcta traducción y redacción, y que sea revisada por un técnico que conozca de la materia. .

Además de lo anterior, el solicitante deberá recordar que todas las composiciones enumeradas con su nombre comercial, deberán acompañarse de su composición química.

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

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

El capítulo reivindicatorio no es claro toda vez que:

- i) Todas las objeciones planteadas en el punto 3) a) aquí son aplicables también, por lo que el solicitante deberá cambiar toda su solicitud.
- ii) No se precisa la materia sobre la cual se solicita protección. Como se explicará en el punto 4), la presente solicitud no posee unidad de invención, por lo que no está definida la materia sobre la cual se solicita protección.

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

4) Evaluación de la Unidad de Invención

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

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

La presente solicitud carece de unidad de invención toda vez que configura DOS diferentes objetos. La definición de la materia que caracteriza a cada una de las reivindicaciones independientes 1 y 7 es muy diferente entre sí. Esto permite afirmar que no se trata del mismo producto. Todo el problema radica en configurar varias reivindicaciones independientes con materia diferente. El solicitante debe establecer una sola reivindicación independiente dirigida al producto en la forma más simple de la solicitud de invención. Partiendo de allí establecer reivindicaciones dependientes que amplíen esa forma más simple hasta su forma más compleja.

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

5) Reivindicaciones de uso

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

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

La reivindicación 6 se refiere al uso que se le va a dar a la composición de las primeras reivindicaciones. Tal como está contemplado en la legislación el uso no se protege. Se protegen los productos o procedimientos, donde el producto esté 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 6 no es patentable de acuerdo al Art. 14 de la Decisión 486, y deberá eliminarse.

6) Determinación del Estado de la Técnica

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

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

"Sólo para el efecto de la determinación de la novedad, también se considerará dentro del estado de la técnica, el contenido de una solicitud de patente en trámite ante la oficina nacional competente cuya fecha de presentación o de prioridad fuese anterior a la fecha de presentación o de prioridad de la solicitud de patente que se estuviese examinando, siempre que dicho contenido esté 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 lo establecido en el artículo 16 se determinó el estado de la técnica y se encontró el siguiente antecedente:

Nº	Documento	Título	Fecha de Publicación
D1	WO 02 28965	An Elastomeric film and fiber grade thermoplastic elastomer composition	2002.04.11
D2	US 5 346 964	Hydrogenated diene block copolymer and composition comprising the same	1994.09.13
D3	WO 01 09239	Hydrogenated block copolymers	2001.02.08
D4	EP 0 863 193	Sealant compositions	1998.09.09
D5	EP 1061099	Polypropylene resin composition and packing stretched film made thereof	2000.12.20
D6	US 6 406 653	Coextrusion of multi-layer film for container sleeve labels	2002.06.18
D7	US 5 777 043	Sealant formulations containing high vinyl content hydrogenated styrene butadiene styrene block copolymers	1998.07.07
D8	US 6 042 907	Coextrusion of multilayer film for container sleeve labels	2000.03.28

7) Evaluación de los requisitos de patentabilidad

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

"Los Países Miembros otorgarán patentes para las invenciones, sean de producto o procedimiento, en todos los campos de la tecnología, siempre que sean nuevas tengan nivel inventivo y sean susceptibles de aplicación industrial". En cumplimiento con este artículo, se procedió a evaluar los requisitos de novedad, nivel inventivo y aplicación industrial con el fin de establecer la patentabilidad de la invención reivindicada en la solicitud en estudio.

a) Evaluación 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".

El informe de búsqueda hecho por la Oficina de Patentes Europea a la presente solicitud en trámite en su fase internacional, revela varios documentos que afectarían directamente la patentabilidad de la misma. D1 WO0228965, muestra todo lo que el solicitante quiere proteger, y

dado que no es posible aceptar la prioridad según relaciona la Oficina Internacional en su informe de búsqueda, afectaría directamente la presente solicitud. Esta oficina está de acuerdo con la apreciación de la autoridad encargada de búsqueda con este y los restantes documentos, dado que allí se revelan copolímeros de bloque estirénico, que tiene una estructura molecular de acuerdo con la fórmula general S-EB-S (1) o (S-EB)_n X (2) y con las características esbozadas en el presente capítulo reivindicatorio. Además de lo anterior, esta oficina ha encontrado documentos adicionales, que revelan en esencia lo mismo que el solicitante desea proteger para Colombia. Por tanto, la presente solicitud carecería de los requisitos de patentabilidad para que se le conceda el privilegio solicitado.

b) Resumen

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

Nº	Documento	Reivindicaciones afectadas	Requisito que afecta
D1	WO 02 28965	1 - 10	Novedad
			Nivel inventivo
D2	US 5 348 964	1 - 10	Novedad
			Nivel inventivo
D3	WO 01 09239	1 - 10	Novedad
			Nivel inventivo
D4	EP 0 863 193	1 - 10	Novedad
			Nivel inventivo
D5	EP 1061099	1 - 10	Novedad
			Nivel inventivo
D6	US 6 408 853	1 - 10	Novedad
			Nivel inventivo
D7	US 5 777 043	1 - 10	Novedad
			Nivel inventivo
D8	US 6 042 907	1 - 10	Novedad
			Nivel inventivo

8) Notificación

En cumplimiento del artículo 45 de la Decisión 486 de la Comisión de la Comunidad Andina, se le indica que dentro del término de sesenta días contados a partir de la fecha de la notificación de la presente comunicación debe responder a la notificación. En caso de no dar respuesta al presente requerimiento, o si a pesar de la respuesta subsistieran los impedimentos para la concesión, se denegará la patente. Notifíquese el presente oficio conforme a lo dispuesto por el numeral 5.2, literal e) del capítulo quinto del título primero de la Circular Única N° 10 de 2001



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 N°	EXAMINADOR TÉCNICO	EXAMINADOR JURÍDICO
430	Código No. 202003	Código No.

(19) World Intellectual Property Organization
International Bureau



(18) International Publication Number
WO 02/28965 A1

(43) International Publication Date
11 April 2002 (04.04.2002)

PCT

(61) International Patent Classification
C08L 53/04

(64) International Application Number
PCT/US99/1134

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(63) Filing Language
English

(64) Publication Language
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4 October 1999 (04.10.1999) US

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(81) Designated States (national): AR, AG, AL, AM, AT, AU,
AZ, BA, BB, BG, BR, BY, BE, CA, CH, CN, CO, CR, CU,
CZ, DE, DK, DM, DO, EC, EE, EG, ES, FI, FR, GB, GR, GT,
HA, HN, HU, ID, IL, IN, IS, JP, KE, KG, KH, KR, KZ, LC,
LK, LR, LS, LU, LV, LY, MA, MD, MG, MK, MN, MW,
MX, MY, NZ, NI, NO, PA, PE, PG, PH, PK, PL, PT, RO, RU, SD,
SE, SI, SK, TM, TR, TT, TZ, UA, UG, US, UZ, VE, YU,
ZA, ZW.

(82) Designated States (epigraphic): ARIPO patent (CF, GM,
KE, LS, MW, NZ, SD, SE, SG, TZ, UG, ZW), Eurasian
patent (AM, AZ, BY, BG, CY, CZ, DE, EE, FI, FR, GB, GR, HU,
IE, IL, IN, JP, KG, MD, MG, MK, MN, MW, MY, NZ, NI, NO,
PA, PE, PG, PH, PK, PL, PT, RO, RU, SD, SE, SI, SK, TM, TR,
TT, TZ, UA, UG, UZ, VE, YU, ZA, ZW).

Publication under Rule 4.17:
— of transmittal (Rule 4.17(b)) for US only

Publication:
— with international search report
— before the expiration of the time limit for amending the
claims and to be published in the event of receipt of
amendments

For two-letter codes and other abbreviations, refer to the "Glossary
of Symbols on Codes and Abbreviations" appearing at the beginning
of each regular issue of the PCT Gazette.

AN ELASTOMERIC FILM AND FIBER GRADE
THERMOPLASTIC ELASTOMER COMPOSITION

5 CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims benefit of United States provisional patent application
serial number 00/237,633, filed October 4, 2000, which is herein incorporated by
reference.

10 FIELD OF THE INVENTION

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

15 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 4,789,880 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. 5,083,422 discloses composition
based on styrene-propylene/ethylene styrene (SEPES) polymers which are used 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 (SEPEP) 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:

25 polyolefin resins. One of the drawbacks of this composition was the relatively poor
elastic recovery performance. U.S. Patent No. 5,083,422 discloses composition
based on styrene-propylene/ethylene styrene (SEPES) polymers which are used 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 (SEPEP) 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:

WO 02/28965 A1 94 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 1,000,000 and a styrene block molecular weight of 3,000 to 15,000. The composition will
contain from 60 to 95 percent by weight of the block copolymer, from 5 to 25 percent by weight of a tackifying resin, and from 3
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 tackifying resin. The composition is comprised of from
15 to 95 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 methacrylic polyethylene derivative polymer and
the balance to the block copolymer described above.

88

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 SEP8 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 effect 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 advantageous. 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 80 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 16,000. The composition will comprise from 80 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 tackifying 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 80 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 pendant 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. 4,970,288, 5,083,422, 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 SEP8 or an SEP8ep elastomeric block copolymer which is produced by hydrogenating a polystyrene-polybutadiene-polystyrene or polystyrene-polyisoprene-polystyrene or polystyrene-polyisoprene-polystyrene 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 85 to 86 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 80 percent by weight and preferably from 80 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 SEP8 or the SEP8ep 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(monosubstyrenic) 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 8,000 to 18,000, and one saturated polybutadiene midblock, each having a number average molecular weight from 30,000 to 68,000. The saturated polybutadiene blocks preferably have at least 60 percent by weight 1,2-configuration (vinyl content) and preferably from 80 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 28% 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 allyl/aromatic hydrocarbons are prepared by contacting the monomer or monomers to be polymerized simultaneously or sequentially with an organolithium 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:



wherein R is an aliphatic, cycloaliphatic, aromatic, or allyl-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, (B-I)_xY or (B-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 65 percent of B-I or B-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 alkenes; alkoxy alkenes; various esters such as alkyl and aryl benzoates, difunctional aliphatic esters such as diallyl-sebacate 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., BVI8; 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. 3,484,842; 3,634,584; 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 98%. 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%.

76

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 8 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 801-04 (also referred to herein as PE NA 801) obtained from Equistar Chemical. Information obtained from Equistar Chemical states that PE NA 801 is a low molecular weight, low density polyethylene for application in the areas of hot melt adhesives and coatings. PE NA 801 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 6% to 30% by weight of an α -olefin comonomer having from 4 to 12 carbon atoms, preferably from 4 to 6 carbon atoms. The metallocene polyolefins are polyolefins produced with a metallocene catalyst as described in United States Patents No. 6,322,728 and 6,272,238 which are descriptions are incorporated by reference herein. Such elastomeric polyolefins are available from DuPont Dow Elastomers under the trademark ENGAGE (ethylene/octane copolymers), from Dow Chemical Company under trademark AFFINITY, and from Exxon Chemical Company under the trademark EXACT (ethylene/butane copolymers). The metallocene polyolefins have low crystallinity when ethylene is copolymerized with from 6% 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. 4,789,898; 4,294,938; and 3,763,072, 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 ARCON® series tackifiers) are examples of hydrogenated hydrocarbon resins, and the ZONATAC® 8601 L 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 1084, 3102, 6108, and 1126 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.

ZONATAC8501 Lila resin, a product of Arizona Chemical Co., has a softening point of 105°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 AFHA 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 80 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 resins. 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 amount 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 the two. 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 80/60 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 tensile 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 65 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 180 percent (i.e., to 280 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 8806 Universal Test Machine using ASTM microtensile specimens. Stress relaxation after 30 minutes at, for example, an elongation of 180 percent (i.e., to 280 percent of the material's initial length - from 100 mm to 280 mm) may be expressed as a percentage utilizing the following equation: stress relaxation = (peak load_{max} - load_{rem} @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 8806 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 8806 Universal Test Machine by elongating a sample of an elastic material sample at 1 inch/minute to 180 percent elongation (i.e., to 280 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

relaxation 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 technique for linear atactic 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 atactically 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.

EXAMPLE

SEBS block copolymers of varying 1,2-vinyl content were made for these experiments. The conventional SEBS polymers of standard vinyl content (38 to 48 percent) were synthesized with diethylether as the structure modifier. The higher vinyl content polymers were synthesized with 1,2-dichloro 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.

15 The stress-strain properties of the pressed film were determined in accordance with ASTM D-412 utilizing a Constant Rate of Extension Tester, Instron Model 5585 Universal Testing Instrument. Each sample was placed lengthwise in jaw faces, with a jaw span of 0.78 inches (1.9 cm). The Instron Model 5585 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 5585 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.

15 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).
20 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 801-04 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	37.8	80.8	78
Block Molecular Weight by GPC	6.9-92.5-6.4	7.5-83.6-6.4	8.8-80-12.6
Hydrogenated Total Molecular Weight	97,000	100,000	103,600
Polyethers Content, % by weight	12.8	16	20.8
Properties of Polymer			
Melt Flow @ 230°C/30.0 Kg. pressure/10 min.	<1.0	6.3	4.38
Mechanical Properties at 23°C			
Stress Relax., % 30 min., 100%	17	17	20
Stress Relax. Examples			
100% modulus, psi (Koblen*)	228 (16.8)	150 (10.6)	178 (12.4)
500% modulus, psi (Koblen*)	370 (26.6)	239 (16.2)	307 (21.9)
800% modulus, psi (Koblen*)	627 (44.1)	345 (24.3)	448 (31.9)
Tensile Strength, psi (Koblen*)	1688 (108)	1230 (86.6)	>1238 (>86)
Elongation at Break, psi (Koblen*)	787 (55.3)	1070 (75.2)	>1114 (>78)
Hysteresis to 100%			
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 100% 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.

13

Table III

[illegible]

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 80 percent by weight, a number average molecular weight of 40,000 to 110,000 and a styrene block number average molecular weight of 8,000 to 16,000;
- (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 2, and from 8 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 60 to 95 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 95 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 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.
- 10 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.
- 15 8. Elastomeric fibers or films from the extruded composition of claim 1.

82

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When the amount is less than 0.01 part by weight, there can be obtained an excellent improvement in impact resistance, electrical resistance and heat resistance. When the amount is more than 10 parts by weight, there appears deterioration in electrical properties, mechanical resistance, etc. The addition amount of functional group-containing monomer component in hydrogenated diene block copolymer of this invention can be effected within the amount described in Japanese Patent Publication No. 53-4004. That is, a hydrogenated diene block copolymer of this invention is used in place of an olefin rubber; the copolymer and a functional group-containing monomer component are subjected to mixing-kneading in a melt state, whereby addition reaction can be effected between them. The mixing-kneading can be effected between using a closed type kneader, or continuously using an extruder or the like. In this case, it is possible to add a possible to enhance the reaction rate, or, in summary, to add a stabilizer. To the (modified) hydrogenated diene block copolymer of this invention can be added conventional additives, for example, an antioxidant, a heat stabilizer, an ultraviolet absorber, a lubricant, a coloring agent and a flame retardant. The (modified) hydrogenated diene block copolymer of this invention can be used as it is or as a modifier for various uses and is useful as a material for automobile parts, electric or electronic parts, films, sheets, etc. The (modified) hydrogenated diene block copolymer (I) of this invention can be used alone, or can be used as a blend with a non-polymer resin (II) and/or a polymer resin (III) and, as necessary, other copolymer rubbers. The properties of the resin to be blended with the (modified) hydrogenated diene block copolymer of this invention is 1-99% by weight, preferably 1-50% by weight. The optimum proportion is varied depending on the application purpose of the resulting blend. The modification of resin by the (modified) hydrogenated diene block copolymer of this invention is undetectable when the copolymer is added in an amount of less than 10% by weight. The non-polymer resin (II) used in this invention is: olefin polymers, high-molecular polyethylene, high-density polyethylene, medium-density polyethylene, low-density polyethylene, LLDPE (linear low-density polyethylene), polypropylene, polybutylene, polyisobutylene, polyethylene, etc. The olefin non-polymer resin (II) are polypropylene, polyethylene and polybutylene. The properties of the polymer (modified) hydrogenated diene block copolymer/non-polymer resin (II) is 1-99% by weight/99-1% by weight. In order to obtain sufficient modification of the component (II) by addition of the component (I), the proportion of the component (I) is preferably 1-50% by weight, more preferably 1-20% by weight. When the proportion of the component (I) is too low, no sufficient modification is obtained. When the proportion is too high, the inherent properties of the component (II) are modified. The (modified) hydrogenated diene block copolymer to be blended with the non-polymer resin (II) is preferably the (modified) hydrogenated diene block copolymer. This (modified) hydrogenated diene block copolymer has good compatibility with the non-polymer resin (II),

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polymer segment (V) consisting mainly of an aliphatic polyether or aliphatic polyester unit.

The weight ratio of (V)/(IV) is the thermoplastic polymer content is 30-95/70-70.

The high-melting crystalline segment (V) consists of at least one diisocyanate unit having a molecular weight of less than 300 and at least one aliphatic glycol or epoxide glycol having a molecular weight of less than 300.

The low-melting polymer segment (V) consists of at least one long-chain glycol unit having a molecular weight of 400-4,000, or of at least one solid long-chain glycol and at least one diisocyanate unit having a molecular weight of less than 300.

The component (V) can be replaced by (V') a thermoplastic polyamide and/or a thermoplastic polyamide derivative.

The thermoplastic polyamide is, for example, a polyamide obtained by condensation of (i) a linear diamine represented by $H_2N-(CH_2)_n-NH_2$ (n is an integer of 4-12) and (ii) a linear diisocyanate unit represented by $HOOC-(CH_2)_m-COOH$ (m is an integer of 2-12) and a polyamide obtained by ring-opening polymerization of lactams. Particular examples of these polyamides are nylon 6,6, nylon 6,8, nylon 6,10, nylon 6,12, nylon 6,14, nylon 12, nylon 12,12, nylon 4,6, etc.

There can also be used copolyamide polyamides such as nylon 6,6/6,10, nylon 6,6/12, nylon 6,12/12, nylon 6,6/6,12 and the like.

The polyamide derivative used in the component (V') can be an esteramide synthesized by a condensation reaction between a polyamide and a polyether having a hydroxyl group at the chain terminal.

The polyether having a hydroxyl group at the chain terminal can be a straight chain or branched chain polyoxyethylene glycol (e.g., polyoxyethylene glycol, polyoxypropylene glycol, polyoxytetraethylene glycol), their isomers, or a copolyether derived from the polyoxyethylene glycol. The average molecular weight of the polyether is generally 200-4,000, preferably 400-3,000.

The content of the polyoxyethylene glycol in the total component is usually 5-50% by weight, preferably 10-30% by weight.

The polyether includes a lactam whose hydroxamate chain has 4-16 carbon atoms and an amino acid condensation product.

(V') A polyoxyethylene ether can be used in place of the component (V).

Specific examples of the polyoxyethylene ether are polyethylene glycol, polypropylene glycol, polytetraethylene glycol, polyoctaethylene glycol, and a copolymer obtained from 2,6-diethylphenol and 2,2,4,4-tetraethylphenol.

The intrinsic viscosity $[\eta]$ of the polyoxyethylene ether (V') as measured at 30° C. in chloroform is not related but is preferably 0.3 dl/g, more preferably 0.25-0.7 dl/g.

The other thermoplastic polymer (V) is a thermoplastic resin, thermoplastic elastomer or rubbery polymer other than mentioned above. The component (V) is preferably 5-40% by weight, more preferably 10-30% by weight based on the total amount of the components (i) to (v).

When the content is 5% by weight or more, the resulting composition has excellent heat resistance, but when the content is more than 90% by weight, the resulting

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composition is inferior in impact resistance, surface appearance of molded article and moldability.

In the above composition, the total amount of the components (ii) and (iv) and is 50-100% by weight, preferably 50-90% by weight, more preferably 70-80% by weight. When the total amount is more than 90% by weight, the resulting composition is inferior in impact resistance. By setting the total amount 100% by weight or more, there can be obtained a composition having excellent impact resistance and surface appearance of molded article.

The ratio of the component (ii)/the component (iv) is preferably 50-90% by weight/10-50% by weight, more preferably 50-30% by weight/20-50% by weight, particularly preferably 70-30% by weight/30-70% by weight.

To the above thermoplastic resin composition can be applied the same copolymerization method as mentioned above concerning the composition of the unsaturated hydroxyfunctional diamine block copolymer (i) and the thermoplastic polyamide (V'), for improving the moldability.

For the purpose of improvement of compatibility and/or processability, there may be added to the composition at the time of its production, the same unsaturated component having a functional group as mentioned above is substituted, as necessary, with an organic particle.

Particular results are obtained in some cases when a crosslinking agent is used in addition to the above composition at the time of its production in order to crosslink the rubbery polymer used in the component (V), etc.

The crosslinking agent can be an organic particle along its combination with a crosslinking aid such as benzoinethers crosslinking aid, diacetylacetonate crosslinking aid, diethyl acetylacetonate, benzoinethers crosslinking aid, when composed or the like, or other crosslinking agents composed of silane (e.g., hexamethyldisiloxane) crosslinking aid in combination with a vulcanization crosslinking agent.

The above thermoplastic resin composition can be formed into various molded articles by injection molding, hot molding, vacuum molding, profile molding, sheet molding, blow molding, compression molding, etc.

The molded article can be used as a material for automobile exterior or interior parts, electric or electronic parts, housings, etc., for their excellent properties.

Next, a description is made on the composition comprising the (modified) hydroxyfunctional diamine block copolymer (i) of this invention and a thermoplastic polyamide (V). The (modified) hydroxyfunctional diamine block copolymer (i) of this invention, when blended with a thermoplastic polyamide (V), can give a composition having excellent strength and impact resistance, excellent heat resistance and chemical resistance. This composition is highly improved as compared with conventional allyl and acrylate-butadiene rubber, carboxyl group-containing acrylate-butadiene rubber, etc.

When in production of a composition of the (modified) hydroxyfunctional diamine block copolymer (i) and the thermoplastic polyamide (V), there is used a modified hydroxyfunctional diamine block copolymer in the component (i), the resulting composition has excellent compatibility and exhibits the effects as intended by this invention, at a higher level. Therefore, a modified hydroxyfunctional

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diamine block copolymer is preferable in the component (i). The functional group-containing unsaturated compound used as a graft monomer (a modifying agent) in the production of the modified hydroxyfunctional diamine block copolymer, is preferably an allyl acrylate group- or carboxyl group-containing unsaturated compound because it can be easily grafted. An allyl acrylate group-containing compound is particularly preferable because this compound is widely used as a coating agent for thermoplastic resins such as epoxy resin and the like, even if partially reaction occurred, it gives no adverse effect on thermoplastic resin.

Adding the (modified) hydroxyfunctional diamine block copolymer (i) with the thermoplastic polyamide (V) has no restriction, and it can be obtained using a closed type mixer (e.g., Banbury mixer), rolls, an extruder or the like depending upon the mixing ratio of the components (i) and the component (V).

The composition of the (modified) hydroxyfunctional diamine block copolymer (i) of this invention and the thermoplastic polyamide (V) can comprise, as necessary, an antioxidant, a stabilizer, a plasticizer, a coloring agent, inorganic and organic fillers, a reinforcing agent, a crosslinking agent, etc.

The composition comprising, as such component, the (modified) hydroxyfunctional diamine block copolymer (i) of this invention and the thermoplastic polyamide (V) is widely used mainly in electronic parts, and also in coating material, casting material, molding material, adhesive, paint, etc.

In the above description, the composition of the (modified) hydroxyfunctional diamine block copolymer (i) and a resin has been explained referring to the composition of the component (i) and the non-polymer resin (V) and the composition of the component (i) and the polyamide resin (V). However, the composition of this invention includes also a composition of the component (i), the component (ii) and the component (V).

This invention is described in more detail referring to Examples. However, this invention is not restricted to these Examples.

In the Examples, parts and % are by weight unless otherwise specified. Various properties are mentioned in the Examples were measured by the following methods.

Radial dyescent was measured by an infrared analysis, based on the phenyl group absorption at 679 cm^{-1} .

Viscosity content was calculated according to the Huggins method using an infrared analysis.

Hydroxylation degree was calculated from the 10-1000 cm^{-1} spectrum obtained at 300 MHz using tetramethylsilane as a solvent.

Molecular weight was obtained as a polystyrene-methyl methacrylate weight, by gel permeation chromatography at 135° C. using tetrahydrofuran as a solvent.

Heat flow rate was measured at 230° C. under a load of 15.5 kg, 3 kg or 2.16 kg in accordance with JIS K 7210.

Molding viscosity of pellets was measured by preparing round pellets using a 25-mm single-orifice extruder and a hot cutter, placing them in a constant temperature bath of 40° C. under a load of 30 g/cm² for 24 hours to allow them to stick to each other and form blocks, and using the blocks as follows.

① Blocks can be disintegrated very easily.
② Blocks can be disintegrated relatively easily.
③ Blocks are difficult to disintegrate.

5,346,964

18

Heat impact strength was measured according to JIS K 7110, using an isothermally-molded article with notch. Heat impact strength after thermal aging was measured by placing an isothermally-molded article with notch in a Chair oven set at 150° C. for 240 hours or 70 hours, then cooling the article to room temperature and subjecting the article to the above test according to JIS K 7110.

Flame retardant was measured in accordance with JIS K 7203.

Surface gloss was measured in accordance with JIS K 7105.

Film peeling strength was measured by depositing a 2-mm thick sheet obtained by injection molding, with solvent, subjecting the sheet to a machine treatment by ultrasonic waves, cooling the resulting sheet film with a polymer (DIBSOL) manufactured by Mitsui Chemicals K.K. and then with a polyethylene type resin (DIBSOL) manufactured by the same company) so that the film thickness (in μm) of the sheet became about 50 μm , and after the film has been cooled, peeling the film at 100° at a drawing speed of 20 mm/min.

Amount of functional group-containing unsaturated compound (modifying monomer) added was measured by measuring η_{inh} (intrinsic viscosity of solution) using the calibration curve method by infrared absorption spectrum.

Appearance of molded article was evaluated visually in accordance with the following rating standard.

○ Appearance is good.

△ Not poor appearance as represented by blotches, holes, flow marks, surface roughness, etc.

Tensile strength (T_g) was obtained by measuring a breaking strength (kg/cm²) at a drawing speed of 20 mm/min using a JIS No. 3 specimen.

Tensile elongation (E_g) was obtained by measuring an elongation (%) up to breaking under the same test conditions as used for the above tensile strength.

Thermal aging resistance was obtained by placing a JIS No. 3 specimen to stand in a Chair oven at 150° C. for 160 hours and then subjecting the resulting sample to measurement of tensile strength (T_g) and tensile elongation (E_g).

Hardness was measured as a JIS hardness.

Tensile air was obtained by drawing a JIS No. 3 specimen by 100%, maintaining the condition for 10 minutes, then measuring the length after 10 minutes, and calculating the tensile air. A larger tensile air indicates that the product is inferior in properties as thermoplastic elastomer.

Temperature was obtained by visually evaluating the transparency of a molded article (JIS No. 3 described) according to the following rating standard.

○ Good transparency.

△ Transparency.

○ Copied.

Volume shrinkage was measured in accordance with ASTM D 2974-61.

EXAMPLE 1
(Preparation of hydroxyfunctional diamine block copolymer I-1)

Into a 5-liter methanol were fed 3.500 g of diisocyanate and dihydroxybutanediol and 50 g of toluene. Thereafter, 0.5 g of triethylamine and 0.5 g of a base-catalyst. The mixture was subjected to further

87

19
and polymerization at 107°C. One-stage polymerization was conducted at 107°C while continuously adding A. When the conversion reached 100%, further polymerization was conducted at 107°C while continuously adding a mixture of 200 g of 1,3-butadiene and 100 g of styrene at a rate of 75 g per 10 minutes (second-stage polymerization stage).

Sampling was made at intervals of 10 minutes in the course of the polymerization and the polymers obtained at each sampling during were measured for bound oxygen content and other properties of 1,3-butadiene.

When the conversion of the monomers added reached approximately 100%, the reaction mixture was cooled to 70°C. Thereafter, 0.5 g of *n*-butylthiol, 0.5 g of 2,6-di-*tert*-butyl-*p*-cresol, 0.5 g of diisopropylamine, 0.5 g of diisobutylamine, and 1.1 g of diisopropylamine were added. The resulting mixture was subjected to reaction for 1 hour with the reaction pressure being maintained at 10.0 kg/cm² with hydrogen gas.

The reaction mixture was cooled to room temperature, taken out of the autoclave, subjected to steam stripping to remove the solvent, and dried on a 100°C rack to obtain a hydrogenated diene block copolymer (hereinafter referred to as Copolymer P-3).

The resulting hydrogenated diene block copolymer was measured for properties in accordance with the above-mentioned test methods. As a result, the total bound oxygen content in the copolymer before hydrogenation was 30% by weight, the bound oxygen content in the polymer block obtained in the first-stage polymerization was 100% by weight, and from the monomer conversion and the amount of the finally obtained copolymer, the properties of the bound oxygen content of the polymer block obtained in the first-stage polymerization in the final copolymer before hydrogenation was calculated to be 100% by weight. The polymer block formed in the first-stage polymerization is referred to as Block (A).

Successive analysis indicated that the second-stage polymerization proceeded so that the reaction product at each sampling during had a constant styrene/1,3-butadiene ratio. Measurement by GPC indicated that with the proceeding of the reaction the molecular weight of polymer increased gradually without partial formation of low-molecular polymer and the flow reaction proceeded as desired. The vinyl content of the 1,3-butadiene portion was found to be 40% by analysis. The polymerization reaction in the second stage polymerization is referred to as Block (B).

By sampling the amount of the residual double bond in the hydrogenated diene portion in Copolymer P-3, the hydrogenation degree of Copolymer P-3 was found to be 90%.

The hydrogenated diene block copolymer had a molecular weight of 150,000 and a melt flow rate of 45 g/10 min at 230°C under a load of 5 g.

EXAMPLE 2

(Preparation of hydrogenated diene block copolymer P-5)

The same procedure as in Example 1 was repeated, except that the following polymerization recipe was used, to obtain a hydrogenated diene block copolymer (hereinafter referred to as Copolymer P-5).

First-stage polymerization
Styrene 50 g
Tetrahydrofuran 0.5 g

3,346,964

Second-stage polymerization

Styrene 50 g

1,3-Butadiene 400 g

The properties of Copolymer P-5 are shown in Table 1.

EXAMPLE 3

(Preparation of hydrogenated diene block copolymer P-6)

The same procedure as in Example 1 was repeated, except that the following polymerization recipe was used, to obtain a hydrogenated diene block copolymer (hereinafter referred to as Copolymer P-6).

First-stage polymerization
Styrene 50 g

Tetrahydrofuran 0.5 g

Second-stage polymerization

Styrene 50 g

1,3-Butadiene 200 g

The properties of Copolymer P-6 are shown in Table 1.

EXAMPLE 4

(Preparation of hydrogenated diene block copolymer P-9)

The same procedure as in Example 1 was repeated, except that the following polymerization recipe was used, to obtain a hydrogenated diene block copolymer (hereinafter referred to as Copolymer P-9).

First-stage polymerization
Styrene 100 g

Tetrahydrofuran 0.5 g

Second-stage polymerization

Styrene 70 g

1,3-Butadiene 200 g

The properties of Copolymer P-9 are shown in Table 1.

COMPARATIVE EXAMPLE 1

(Preparation of hydrogenated diene block copolymer P-7)

First-stage polymerization
Styrene 100 g
1,3-Butadiene 200 g
Tetrahydrofuran 0.5 g

Only the first-stage polymerization was effected, followed by the same hydrogenation reaction as in Example 1, to obtain a hydrogenated diene block copolymer (hereinafter referred to as Copolymer P-7).

The properties of Copolymer P-7 are shown in Table 1.

COMPARATIVE EXAMPLE 2

(Preparation of hydrogenated diene block copolymer P-8)

The same procedure as in Example 1 was repeated, except that the hydrogen gas pressure during the hydrogenation reaction was changed to 5 kg/cm² to obtain a hydrogenated diene block copolymer (hereinafter referred to as Copolymer P-8).

The properties of Copolymer P-8 are shown in Table 1.

21

COMPARATIVE EXAMPLE 3

(Preparation of hydrogenated diene block copolymer P-7)

First-stage polymerization

Styrene 70 g

Tetrahydrofuran 10 g

Second-stage polymerization

1,3-Butadiene 200 g

A hydrogenated diene block copolymer (hereinafter referred to as Copolymer P-7) was obtained by repeating the same procedure as in Example 1, except that the above polymerization recipe was used and, when the conversion in the second-stage polymerization reached approximately 100%, 70 g of additional styrene was added and subsequent polymerization was effected. The properties of Copolymer P-7 are shown in Table 1.

The copolymer prepared in Examples 1-4 which are the hydrogenated diene block copolymers of this invention, were so blended in polymerization and, when blended with other resins, gave modifications effects as intended in this invention, as shown in Example 5 of the following. Copolymer P-5 of Comparative Example 1 causes blocking between plates. Copolymer P-6 and P-7 of Comparative Examples 2 and 3 cause no blocking between plates but, as shown in Comparative Example 5 of the following, give modifications effects inferior to those of the hydrogenated diene block copolymers of Examples 1 to 4 when blended with other resins.

3,346,964

22

out of the autoclave, and poured into water with stirring. The solvent was removed by steam distillation to obtain a hydrogenated polymer (hereinafter referred to as Copolymer Q-1). This hydrogenated polymer had a hydrogenation degree of 90%, a polystyrene-reduced number-average molecular weight of 200,000 and a melt flow rate of 2.5 g/10 min at 230°C under a load of 15.5 kg.

The vinyl content of the butadiene portion of the polymer before hydrogenation was 61%.

EXAMPLE 6

(Preparation of hydrogenated diene block copolymer Q-2)

Into a 10-liter autoclave were fed 5,000 g of degraded and dehydrochlorinated cyclohexene, 500 g of 1,3-butadiene, 100 g of styrene, and 50 g of styrene. Thereafter, 200 g of tetrahydrofuran and 0.5 g of *n*-butylthiol, and diisobutylamine were added, and the mixture was stirred for 10 minutes at 107°C. After 40 minutes, 40 g of styrene was added and further polymerization was effected. Then, hydrogenation was effected in the same manner as in Example 5.

The resulting hydrogenated polymer (hereinafter referred to as Copolymer Q-2) had a hydrogenation degree of 90%, a polystyrene-reduced number-average molecular weight of 150,000 and a melt flow rate of 2.5 g/10 min at 230°C under a load of 15.5 kg. The vinyl content of the butadiene portion of the polymer before hydrogenation was 60%.

TABLE 1

	Block				Copolymer			
	1	2	3	4	5	6	7	8
Hydrogenated diene block copolymer	Copolymer P-5	Copolymer P-6	Copolymer P-9	Copolymer P-7	Copolymer P-8	Copolymer P-7	Copolymer P-7	Copolymer P-7
Block (A) content (%)	100	100	100	100	100	100	100	100
Block (B) content (%)	0	0	0	0	0	0	0	0
Block (C) content (%)	0	0	0	0	0	0	0	0
Block (D) content (%)	0	0	0	0	0	0	0	0
Block (E) content (%)	0	0	0	0	0	0	0	0
Block (F) content (%)	0	0	0	0	0	0	0	0
Block (G) content (%)	0	0	0	0	0	0	0	0
Block (H) content (%)	0	0	0	0	0	0	0	0
Block (I) content (%)	0	0	0	0	0	0	0	0
Block (J) content (%)	0	0	0	0	0	0	0	0
Block (K) content (%)	0	0	0	0	0	0	0	0
Block (L) content (%)	0	0	0	0	0	0	0	0
Block (M) content (%)	0	0	0	0	0	0	0	0
Block (N) content (%)	0	0	0	0	0	0	0	0
Block (O) content (%)	0	0	0	0	0	0	0	0
Block (P) content (%)	0	0	0	0	0	0	0	0
Block (Q) content (%)	0	0	0	0	0	0	0	0
Block (R) content (%)	0	0	0	0	0	0	0	0
Block (S) content (%)	0	0	0	0	0	0	0	0
Block (T) content (%)	0	0	0	0	0	0	0	0
Block (U) content (%)	0	0	0	0	0	0	0	0
Block (V) content (%)	0	0	0	0	0	0	0	0
Block (W) content (%)	0	0	0	0	0	0	0	0
Block (X) content (%)	0	0	0	0	0	0	0	0
Block (Y) content (%)	0	0	0	0	0	0	0	0
Block (Z) content (%)	0	0	0	0	0	0	0	0

1. Hydrogenation degree (%)

2. Polystyrene-reduced number-average molecular weight

3. Melt flow rate (g/10 min) at 230°C under a load of 15.5 kg

4. Vinyl content (%) of butadiene portion

5. Hydrogenation degree (%)

6. Polystyrene-reduced number-average molecular weight

7. Melt flow rate (g/10 min) at 230°C under a load of 15.5 kg

8. Vinyl content (%) of butadiene portion

9. Hydrogenation degree (%)

10. Polystyrene-reduced number-average molecular weight

11. Melt flow rate (g/10 min) at 230°C under a load of 15.5 kg

12. Vinyl content (%) of butadiene portion

13. Hydrogenation degree (%)

14. Polystyrene-reduced number-average molecular weight

15. Melt flow rate (g/10 min) at 230°C under a load of 15.5 kg

16. Vinyl content (%) of butadiene portion

17. Hydrogenation degree (%)

18. Polystyrene-reduced number-average molecular weight

19. Melt flow rate (g/10 min) at 230°C under a load of 15.5 kg

20. Vinyl content (%) of butadiene portion

21. Hydrogenation degree (%)

22. Polystyrene-reduced number-average molecular weight

23. Melt flow rate (g/10 min) at 230°C under a load of 15.5 kg

24. Vinyl content (%) of butadiene portion

25. Hydrogenation degree (%)

26. Polystyrene-reduced number-average molecular weight

27. Melt flow rate (g/10 min) at 230°C under a load of 15.5 kg

28. Vinyl content (%) of butadiene portion

29. Hydrogenation degree (%)

30. Polystyrene-reduced number-average molecular weight

31. Melt flow rate (g/10 min) at 230°C under a load of 15.5 kg

32. Vinyl content (%) of butadiene portion

33. Hydrogenation degree (%)

34. Polystyrene-reduced number-average molecular weight

35. Melt flow rate (g/10 min) at 230°C under a load of 15.5 kg

36. Vinyl content (%) of butadiene portion

37. Hydrogenation degree (%)

38. Polystyrene-reduced number-average molecular weight

39. Melt flow rate (g/10 min) at 230°C under a load of 15.5 kg

40. Vinyl content (%) of butadiene portion

41. Hydrogenation degree (%)

42. Polystyrene-reduced number-average molecular weight

43. Melt flow rate (g/10 min) at 230°C under a load of 15.5 kg

44. Vinyl content (%) of butadiene portion

45. Hydrogenation degree (%)

46. Polystyrene-reduced number-average molecular weight

47. Melt flow rate (g/10 min) at 230°C under a load of 15.5 kg

48. Vinyl content (%) of butadiene portion

49. Hydrogenation degree (%)

50. Polystyrene-reduced number-average molecular weight

51. Melt flow rate (g/10 min) at 230°C under a load of 15.5 kg

52. Vinyl content (%) of butadiene portion

53. Hydrogenation degree (%)

54. Polystyrene-reduced number-average molecular weight

55. Melt flow rate (g/10 min) at 230°C under a load of 15.5 kg

56. Vinyl content (%) of butadiene portion

57. Hydrogenation degree (%)

58. Polystyrene-reduced number-average molecular weight

59. Melt flow rate (g/10 min) at 230°C under a load of 15.5 kg

60. Vinyl content (%) of butadiene portion

61. Hydrogenation degree (%)

62. Polystyrene-reduced number-average molecular weight

63. Melt flow rate (g/10 min) at 230°C under a load of 15.5 kg

64. Vinyl content (%) of butadiene portion

65. Hydrogenation degree (%)

66. Polystyrene-reduced number-average molecular weight

67. Melt flow rate (g/10 min) at 230°C under a load of 15.5 kg

68. Vinyl content (%) of butadiene portion

69. Hydrogenation degree (%)

70. Polystyrene-reduced number-average molecular weight

71. Melt flow rate (g/10 min) at 230°C under a load of 15.5 kg

72. Vinyl content (%) of butadiene portion

73. Hydrogenation degree (%)

74. Polystyrene-reduced number-average molecular weight

75. Melt flow rate (g/10 min) at 230°C under a load of 15.5 kg

76. Vinyl content (%) of butadiene portion

77. Hydrogenation degree (%)

78. Polystyrene-reduced number-average molecular weight

79. Melt flow rate (g/10 min) at 230°C under a load of 15.5 kg

80. Vinyl content (%) of butadiene portion

81. Hydrogenation degree (%)

82. Polystyrene-reduced number-average molecular weight

83. Melt flow rate (g/10 min) at 230°C under a load of 15.5 kg

84. Vinyl content (%) of butadiene portion

85. Hydrogenation degree (%)

86. Polystyrene-reduced number-average molecular weight

87. Melt flow rate (g/10 min) at 230°C under a load of 15.5 kg

88. Vinyl content (%) of butadiene portion

89. Hydrogenation degree (%)

90. Polystyrene-reduced number-average molecular weight

91. Melt flow rate (g/10 min) at 230°C under a load of 15.5 kg

92. Vinyl content (%) of butadiene portion

93. Hydrogenation degree (%)

94. Polystyrene-reduced number-average molecular weight

95. Melt flow rate (g/10 min) at 230°C under a load of 15.5 kg

96. Vinyl content (%) of butadiene portion

97. Hydrogenation degree (%)

98. Polystyrene-reduced number-average molecular weight

99. Melt flow rate (g/10 min) at 230°C under a load of 15.5 kg

100. Vinyl content (%) of butadiene portion

molecular weight of 200,000 and a melt flow rate of 1.3 g/10 min as measured at 230° C. under a load of 12.5 kg. The vinyl content of the butadiene portion of the polymer before hydrogenation was 77%.

EXAMPLE 3

Preparation of hydrogenated diene block copolymer Q-3

Into a 10-liter autoclave were fed 5,000 g of degassed and dehydrated cyclohexane and 40 g of styrene. Thereafter were added 200 g of isobutylene and 0.5 g of n-butyllithium. The resulting mixture was subjected to adiabatic polymerization for 30 minutes starting from 50° C. The reaction mixture was cooled to 10° C. and 600 g of 1,3-butadiene and 170 g of styrene were added. The resulting mixture was subjected to polymerization. 50 g of styrene and 90 g of 1,3-butadiene were further added, and the polymerization was continued. Then, the reaction mixture was subjected to the same hydrogenation reaction as in Example 1.

The resulting hydrogenated copolymer (hereinafter referred to as Copolymer Q-3) had a hydrogenation degree of 99%, a polyisoprene-estimated number-average molecular weight of 200,000 and a melt flow rate of 1.5 g/10 min as measured at 230° C. under a load of 12.5 kg. The vinyl content of the butadiene portion of the copolymer before hydrogenation was 77%.

EXAMPLE 4

Preparation of hydrogenated diene block copolymer Q-4

Into a 10-liter autoclave were fed 5,000 g of degassed and dehydrated cyclohexane and 150 g of styrene. Thereafter were added 150 g of isobutylene and 0.5 g of n-butyllithium. The resulting mixture was subjected to adiabatic polymerization for 30 minutes starting from 50° C. The reaction mixture was cooled to 10° C. 700 g of 1,3-butadiene was added and polymerization was effected. Further, 150 g of styrene was added and polymerization was effected. Then, the reaction mixture was subjected to the same hydrogenation reaction as in Example 1.

The resulting hydrogenated copolymer (hereinafter referred to as Copolymer Q-4) had a hydrogenation degree of 99%, a polyisoprene-estimated number-average molecular weight of 110,000 and a melt flow rate of 0.7 g/10 min as measured at 230° C. under a load of 12.5 kg. The vinyl content of the butadiene portion of the copolymer before hydrogenation was 67%.

Preparation of hydrogenated diene block copolymer Q-9

Into a 10-liter autoclave were fed 5,000 g of degassed and dehydrated cyclohexane and 150 g of styrene. Thereafter were added 200 g of isobutylene and 0.5 g of n-butyllithium. The mixture was subjected to adiabatic polymerization for 30 minutes starting from 50° C. The reaction mixture was cooled to 10° C. 700 g of 1,3-butadiene and 50 g of styrene were added and polymerization was effected. Further, 150 g of styrene was added and polymerization was effected. Then, the reaction mixture was subjected to the same hydrogenation reaction as in Example 1.

The resulting hydrogenated copolymer (hereinafter referred to as Copolymer Q-9) had a hydrogenation degree of 97%, a polyisoprene-estimated number-average molecular weight of 110,000 and a melt flow rate of 1.1 g/10 min as measured at 230° C. under a load of 12.5 kg. The vinyl content of the butadiene portion of the copolymer before hydrogenation was 77%.

EXAMPLE 11

Preparation of hydrogenated diene block copolymer Q-7

Into a 10-liter autoclave were fed 5,000 g of degassed and dehydrated cyclohexane and 150 g of styrene. Thereafter were added 200 g of isobutylene and 0.5 g of n-butyllithium. The resulting mixture was subjected to adiabatic polymerization for 30 minutes starting from 50° C. The reaction mixture was cooled to 10° C. 700 g of 1,3-butadiene was added and polymerization was effected. Further, 150 g of styrene was added and polymerization was effected. Then, the reaction mixture was subjected to the same hydrogenation reaction as in Example 1.

The resulting hydrogenated copolymer (hereinafter referred to as Copolymer Q-7) had a hydrogenation degree of 99%, a polyisoprene-estimated number-average molecular weight of 110,000 and a melt flow rate of 2.5 g/10 min as measured at 230° C. under a load of 12.5 kg. The vinyl content of the butadiene portion of the copolymer before hydrogenation was 97%.

In Table 2, there are shown the physical properties of the hydrogenated copolymers prepared in Examples 3-11. As is clear from Table 2, the hydrogenated diene block copolymers of this invention are particularly distinguished and suitably have excellent properties.

TABLE 2

	Sample						
	3	4	7	8	9	10	11
Hydrogenated diene block copolymer							
Estimated							
Type	Copolymer Q-1	Copolymer Q-2	Copolymer Q-3	Copolymer Q-4	Copolymer Q-5	Copolymer Q-6	Copolymer Q-7
1 Tensile strength (kg)	1	2	2.5	2.5	2.5	2	2
2 Elongation at break (%)	1	4.5	21	22.5	25	25	25
3 Tensile strength (kg) (at break)							
4 Vinyl content of butadiene portion in block (%)	77	77	77	77	77	77	77
5 Hydrogenation degree (%)	99	99	99	99	99	99	99
6 Molecular weight (g/mol)	200,000	200,000	200,000	200,000	200,000	200,000	200,000
7 Melt flow rate (g/10 min)	1.3	1.5	1.5	1.5	1.5	1.5	1.5
8 Nature of polymerization	O	O	O	O	O	O	O

TABLE 3-continued

1	Sample						
	3	4	7	8	9	10	11
2 Tensile strength of polymer	O	O	O	O	O	O	O

EXAMPLES 12-20 AND COMPARATIVE EXAMPLES 4-6

Preparation of compositions of hydrogenated diene block copolymer and non-polymer units

20 parts of one of the copolymers obtained in Examples 1-4 and 75 parts of a polypropylene resin (polypropylene MC4 manufactured by Mitsubishi Petrochemical Co., Ltd.) were melt-blended using a 4-liter Banbury mixer.

Nine kinds of the melt-blended products were prepared and then subjected to laboratory testing to prepare test pieces for measurement of physical properties. The results of measurement of physical properties are shown in Tables 3 and 4.

copolymer rubber widely used (JBR EP607 manufactured by Japan Synthetic Rubber Co., Ltd.) was subjected to the same melt-blending with polypropylene as above. Four kinds of the melt-blended products and a polypropylene resin alone were tested in the same manner as above to prepare test pieces for measurement of physical properties. The results of measurement of physical properties are shown in Tables 3 and 4.

The compositions of Examples 12-20 are superior in tensile strength, elongation and modulus to the comparative examples.

TABLE 3

Composition ratio	Sample						
	12	13	14	15	16	17	18
Copolymer Q-1							
Type	Copolymer Q-1	Copolymer Q-2	Copolymer Q-3	Copolymer Q-4	Copolymer Q-5	Copolymer Q-6	MC4
1 Tensile strength (kg)	15	15	15	15	15	15	15
2 Elongation at break (%)	15	15	15	15	15	15	15
3 Tensile strength (kg) (at break)	15	15	15	15	15	15	15
4 Vinyl content of butadiene portion in block (%)	15	15	15	15	15	15	15
5 Hydrogenation degree (%)	15	15	15	15	15	15	15
6 Molecular weight (g/mol)	15	15	15	15	15	15	15
7 Melt flow rate (g/10 min)	15	15	15	15	15	15	15
8 Nature of polymerization	15	15	15	15	15	15	15
9 Tensile strength of the polymer	15	15	15	15	15	15	15

For comparison, one of the copolymers obtained in Comparative Examples 1-3 or an ethylene-propylene

TABLE 4

Composition ratio	Sample						
	19	20	21	22	23	24	25
Copolymer Q-1							
Type	Copolymer Q-1	Copolymer Q-2	Copolymer Q-3	Copolymer Q-4	Copolymer Q-5	Copolymer Q-6	MC4
1 Tensile strength (kg)	15	15	15	15	15	15	15
2 Elongation at break (%)	15	15	15	15	15	15	15
3 Tensile strength (kg) (at break)	15	15	15	15	15	15	15
4 Vinyl content of butadiene portion in block (%)	15	15	15	15	15	15	15
5 Hydrogenation degree (%)	15	15	15	15	15	15	15
6 Molecular weight (g/mol)	15	15	15	15	15	15	15
7 Melt flow rate (g/10 min)	15	15	15	15	15	15	15
8 Nature of polymerization	15	15	15	15	15	15	15
9 Tensile strength of the polymer	15	15	15	15	15	15	15

89

27
EXAMPLES 21-26 AND COMPARATIVE EXAMPLES 9-11

(Preparation of compositions of hydrogenated diamine copolymer and polyurethane)

A hydrogenated diamine copolymer, a polyurethane, in some cases a crosslinking agent such as shown in Table 5 were melt-blended by a twin-screw extruder. The resulting melt-blended products were subjected to a further extrusion and then subjected to injection molding to produce test pieces for measurement of physical properties. The results of measurement of physical properties are shown in Table 5.

The compositions of Examples 21-26 are superior in impact resistance and surface appearance of molded article. However, the compositions of Comparative Examples 9-11 are insufficient in impact resistance.

28
blend copolymer (hereinafter referred to as Copolymer P-9). The amount of maleic anhydride grafted in Copolymer P-9 was 0.55%.

(C) Preparation of composition with crosslinking polyurethane (spicy resin)

A crosslinking resin composition (a spicy resin composition) was obtained according to the following procedure.

Component	Parts
Copolymer P-9	100
Maleic anhydride grafted polyurethane	10
Diisocyanate (MDI)	10
Diisocyanate (MDI)	10
Diisocyanate (MDI)	10

TABLE 5

Component	Example 21	Example 22	Example 23	Example 24	Example 25	Example 26	Comparative Example 9	Comparative Example 10	Comparative Example 11
Copolymer P-9	100	100	100	100	100	100	100	100	100
Maleic anhydride grafted polyurethane	0	0	0	0	0	0	0	0	0
Diisocyanate (MDI)	0	0	0	0	0	0	0	0	0
Diisocyanate (MDI)	0	0	0	0	0	0	0	0	0
Diisocyanate (MDI)	0	0	0	0	0	0	0	0	0
Diisocyanate (MDI)	0	0	0	0	0	0	0	0	0
Diisocyanate (MDI)	0	0	0	0	0	0	0	0	0
Diisocyanate (MDI)	0	0	0	0	0	0	0	0	0
Diisocyanate (MDI)	0	0	0	0	0	0	0	0	0
Diisocyanate (MDI)	0	0	0	0	0	0	0	0	0

EXAMPLE 27

(Preparation of composition of hydrogenated diamine copolymer and crosslinking polyurethane)

The hydrogenated diamine copolymer (Copolymer P-9) obtained in Example 1 was grafted with maleic anhydride to produce a grafted product (a modified hydrogenated diamine copolymer), and the product was blended with a crosslinking polyurethane to obtain a composition.

(1) Preparation of modified hydrogenated diamine copolymer

100 parts by weight of the hydrogenated diamine copolymer (Copolymer P-9) obtained in Example 1 was subjected to 150° C. and placed in a reactor (KAKIHO REACTOR SYSTEM 40 KIKOKU MOORE 50) manufactured by KAKIHO KIKOKU CO., Ltd. After 2 minutes, 2.5 parts of maleic anhydride was added and mixing was continued. Then, 0.15 part of an organic peroxide (2,2'-azobis(2-amidinopropane) dihydrochloride) was added, and mixing was continued for a further 2 minutes to obtain a hydrogenated diamine

The above materials of the above mixture were blended using a dual type mixer at about 150° C. The blended product was pre-molded at 150° C. The resulting plate was processed with a milling cutter to prepare test samples for measurement of physical properties.

The results of measurement are shown in Table 6.

EXAMPLES 28-30

Two spicy resin compositions were obtained in the same manner as in Example 27, except that the amount of the modified hydrogenated diamine copolymer (Copolymer P-9) used was changed to 5 or 10 parts.

The results of measurement of physical properties of the spicy resin compositions are shown in Table 6.

COMPARATIVE EXAMPLE 12

An spicy resin composition was obtained in the same manner as in Example 27, except that Copolymer P-9 was changed to 10 parts of a liquid aromatic polyurethane (Rytec 1000) manufactured by BP Chemical Co., Ltd. which was used for modification of spicy resin.

29
The results of measurement of physical properties of the spicy resin compositions are shown in Table 6.

COMPARATIVE EXAMPLE 13

An spicy resin composition was obtained in the same manner as in Example 27, except that an hydrogenated diamine copolymer (Copolymer P-9) was used. The results of measurement of physical properties of the spicy resin compositions are shown in Table 6.

EXAMPLE 30

A spicy resin composition was prepared according to the following procedure, using the modified hydrogenated diamine copolymer (Copolymer P-9) obtained in the same manner as in Example 27.

Component	Parts
Copolymer P-9	100
Maleic anhydride grafted polyurethane	10
Diisocyanate (MDI)	10

30
30 was replaced by 10 parts of the same liquid aromatic polyurethane as used in Comparative Example 12. The plates were prepared from the composition in the same manner as in Example 30, and measured for physical properties. The results of measurement are shown in Table 6.

COMPARATIVE EXAMPLE 15

A spicy resin composition was prepared in the same manner as in Example 30, except that the modified hydrogenated diamine copolymer (Copolymer P-9) was not used. The plates were prepared from the composition in the same manner as in Example 30, and measured for physical properties. The results of measurement are shown in Table 6.

As is clear from Table 6, the compositions of Examples 27-30 using the modified hydrogenated diamine copolymer of this invention are superior in both heat impact resistance and thermal stability.

Meanwhile, the compositions or resin of Comparative Examples 12-15 are inferior in heat impact resistance, thermal stability, etc. and show no sufficient resin-modification effect.

TABLE 6

Component	Example 27	Example 28	Example 29	Example 30	Comparative Example 12	Comparative Example 13	Comparative Example 15
Copolymer P-9	100	100	100	100	100	100	100
Maleic anhydride grafted polyurethane	0	0	0	0	0	0	0
Diisocyanate (MDI)	0	0	0	0	0	0	0
Diisocyanate (MDI)	0	0	0	0	0	0	0
Diisocyanate (MDI)	0	0	0	0	0	0	0
Diisocyanate (MDI)	0	0	0	0	0	0	0
Diisocyanate (MDI)	0	0	0	0	0	0	0
Diisocyanate (MDI)	0	0	0	0	0	0	0
Diisocyanate (MDI)	0	0	0	0	0	0	0
Diisocyanate (MDI)	0	0	0	0	0	0	0

EXAMPLES 31-35

(Preparation of modified hydrogenated diamine copolymer)

One of the hydrogenated diamine copolymers (Copolymer Q-1 to Q-5) obtained in Examples 2-4 was subjected to the same graft polymerization as in Example 27 to obtain modified hydrogenated diamine copolymers (hereinafter referred to, respectively, as Copolymers Q-12 to Q-16). The properties of Copolymers Q-12 to Q-16 are shown in Table 7.

TABLE 7

Component	Example 31	Example 32	Example 33	Example 34	Example 35
Modified hydrogenated diamine copolymer	Copolymer Q-12	Copolymer Q-13	Copolymer Q-14	Copolymer Q-15	Copolymer Q-16

50. The polymer blank formed in the first-stage polymerization is referred to as Blank (A).
Successive samples indicated that the second-stage polymerization proceeded as that the reaction product at each sampling stage had a constant styrene/1,3-butadiene ratio. Measurement by GPC indicated that with the proceeding of the reaction the molecular weight of polymer became gradually without parallel formation of low-molecular polymer and the living reaction proceeded as desired. The vinyl content of this 1,3-butadiene portion was found to be 43% by analysis. The polymer composition formed in this second-stage polymerization is referred to as Blank (B).
In the third-stage polymerization, it was confirmed that the styrene content increased gradually with the proceeding of polymerization.
The gradual increase of styrene content exhibits a behavior of almost quadratic function. According to the calculation based on the analytical results, the amount of formed styrene was about 30% at the beginning of the third-stage polymerization and about 80% at the end of the third-stage polymerization. The polymer blank formed in the third-stage polymerization is referred to as Tapered Blank (C).
The total of the total styrene contents in Blank (A) and Tapered Blank (C) was found to be 15% based on the total copolymer based on the analytical values and the conversion.
By analyzing the amount of the radical double bond in the copolymerized chain portion in the hydrogenated diene block copolymer (Copolymer G-1), the hydrogenation degree of Copolymer G-1 was found to be 98%.

The hydrogenated diene block copolymer had a molecular weight of 145,000 and a melt flow rate of 25 g/10 min at 200°C under a load of 2 kg.
The above hydrogenated diene block copolymer caused no blocking of pellets.
EXAMPLE 21
Preparation of hydrogenated diene block copolymer (G-3)
A hydrogenated diene block copolymer (hereinafter referred to as Copolymer G-3) was obtained in the same manner as in Example 21, except that the following polymerization recipe was used.
First-stage polymerization
Styrene 30 g
Tetrahydrofuran 1.2 g
Second-stage polymerization
Styrene 40 g
1,3-Butadiene 410 g
Third-stage polymerization
Styrene 13 g
1,3-Butadiene 13 g
The properties of Copolymer G-3 are shown in Table 11.

EXAMPLE 22
Preparation of hydrogenated diene block copolymer (G-4)
A hydrogenated diene block copolymer (hereinafter referred to as Copolymer G-4) was obtained in the same manner as in Example 21, except that the following polymerization recipe was used.
First-stage polymerization
Styrene 30 g
Tetrahydrofuran 1.2 g
Second-stage polymerization
Styrene 40 g
1,3-Butadiene 410 g
Third-stage polymerization
Styrene 13 g
1,3-Butadiene 13 g
The properties of Copolymer G-4 are shown in Table 11.

EXAMPLE 23
Preparation of hydrogenated diene block copolymer (G-5)
A hydrogenated diene block copolymer (hereinafter referred to as Copolymer G-5) was obtained in the same manner as in Example 21, except that the following polymerization recipe was used.
First-stage polymerization
Styrene 30 g
Tetrahydrofuran 3 g

Second-stage polymerization
Styrene 7 g
1,3-Butadiene 200 g
Third-stage polymerization
Styrene 13 g
1,3-Butadiene 13 g
The properties of Copolymer G-5 are shown in Table 11.

EXAMPLE 24
Preparation of hydrogenated diene block copolymer (G-6)
A hydrogenated diene block copolymer (hereinafter referred to as Copolymer G-6) was obtained in the same manner as in Example 21, except that the following polymerization recipe was used.
First-stage polymerization
Styrene 30 g
Tetrahydrofuran 6 g
Second-stage polymerization
Styrene 70 g
1,3-Butadiene 200 g
Third-stage polymerization
Styrene 70 g
1,3-Butadiene 70 g
The properties of Copolymer G-6 are shown in Table 11.

COMPARATIVE EXAMPLE 25
Preparation of hydrogenated diene block copolymer (G-7)
A hydrogenated diene block copolymer (hereinafter referred to as Copolymer G-7) was obtained in the same manner as in Example 21, except that the following polymerization recipe was used.
First-stage polymerization
Styrene 20 g
Tetrahydrofuran 100 g
Second-stage polymerization
Styrene 70 g
1,3-Butadiene 200 g
Third-stage polymerization
Styrene 30 g
1,3-Butadiene 30 g
The properties of Copolymer G-7 are shown in Table 11.

COMPARATIVE EXAMPLE 26
Preparation of hydrogenated diene block copolymer (G-8)
A hydrogenated diene block copolymer (hereinafter referred to as Copolymer G-8) was obtained in the same manner as in Example 21, except that the following polymerization recipe was used.
First-stage polymerization
Styrene 70 g
Tetrahydrofuran 10 g
Second-stage polymerization
1,3-Butadiene 200 g
Third-stage polymerization
Styrene 70 g
1,3-Butadiene 70 g
The properties of Copolymer G-8 are shown in Table 11.

COMPARATIVE EXAMPLE 27
Preparation of hydrogenated diene block copolymer (G-9)
A hydrogenated diene block copolymer (hereinafter referred to as Copolymer G-9) was obtained in the same manner as in Example 21, except that the following polymerization recipe was used.
First-stage polymerization
Styrene 70 g
Tetrahydrofuran 10 g
Second-stage polymerization
1,3-Butadiene 200 g
Third-stage polymerization
Styrene 70 g
1,3-Butadiene 70 g
The properties of Copolymer G-9 are shown in Table 11.

The copolymers obtained in Examples 21-24 which are the hydrogenated diene block copolymers of this invention, caused no blocking during pellets in polymerization, and exhibited good fusion characteristics which is the

object of this invention. When blended with other resins as shown in Example 29 or so.
Meanwhile, the copolymer obtained in Comparative Example 26, as compared with those obtained in Examples 21-24, exhibited inferior modification effect when

Example 27 caused blocking of pellets, the copolymers obtained in Comparative Examples 23, 28 and 7 had insufficient impact resistance and the composition of Comparative Example 29 further had low surface gloss.

TABLE 12

Characteristics	Example				Comparative Example			
	21	22	23	24	25	26	27	7
Composition ratio								
Styrene/1,3-Butadiene	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8
Type	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8
Block length (mm)	10	10	10	10	10	10	10	10
Block density (g/cm ³)	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Melt flow rate (g/10 min) (200°C, 2.1 kg)	25	25	25	25	25	25	25	25
Initial impact strength (kJ/m ²) (23°C)	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Impact strength (kJ/m ²) (23°C)	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Surface gloss	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Blocking ratio (%)	0	0	0	0	0	0	0	0

Note: 1. Hydrogenation ratio of diene copolymer of styrene and 1,3-butadiene.
2. Hydrogenation ratio of diene copolymer of styrene and 1,3-butadiene.

Blended with other resins.

TABLE 11

Characteristics	Example				Comparative Example			
	21	22	23	24	25	26	27	7
Hydrogenated diene block copolymer								
Styrene/1,3-Butadiene	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8
Type	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8
Block length (mm)	10	10	10	10	10	10	10	10
Block density (g/cm ³)	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Melt flow rate (g/10 min) (200°C, 2.1 kg)	25	25	25	25	25	25	25	25
Initial impact strength (kJ/m ²) (23°C)	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Impact strength (kJ/m ²) (23°C)	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Surface gloss	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Blocking ratio (%)	0	0	0	0	0	0	0	0

Note: 1. Hydrogenation ratio of diene copolymer of styrene and 1,3-butadiene.
2. Hydrogenation ratio of diene copolymer of styrene and 1,3-butadiene.

EXAMPLES 25-28 AND COMPARATIVE EXAMPLES 29-32

(Preparation of composition of hydrogenated diene block copolymer and other resins)

Composition of a hydrogenated diene block copolymer and a resinous resin was obtained in the same manner as in Example 12 using each of the copolymers obtained in Examples 21-24. The results of measurement of physical properties of the compositions are shown in Table 12.

The compositions obtained in Examples 25-28 had good flow property, excellent impact resistance and rigidity, and good appearance. Meanwhile, as shown in Table 12, the compositions obtained in Comparative

EXAMPLES 29-32 AND COMPARATIVE EXAMPLES 33-35

(Preparation of composition of hydrogenated diene block copolymer and other resins)

A hydrogenated diene block copolymer, a resinous resin, in some cases, a compatibilizing agent all shown in Table 13 were melt blended using a twin-screw extruder, pelletized, dried thoroughly, and subjected to injection molding to prepare test pieces for measurement of physical properties. The results of measurement are shown in Table 13.

The compositions obtained in Examples 29-32 are superior in impact resistance and surface appearance, while the compositions obtained in Comparative Examples 33-35 have insufficient impact resistance.

28

TABLE 20

	Component			Substrate groups		
	Type and amount	Type and amount	Type and amount	Acid groups (A) - defined	Base functional groups (B) - defined	Approximate of total units
Sample 10	2.4 10	2.4 10	2.4 10	1	1	1
Sample 11	2.4 10	2.4 10	2.4 10	1	1	1

As is clear from Tables 19-20, the composition of Component Examples 34-36 are, in the component (A), a hydrogenated diene block copolymer of low hydrogenation degree deviating from the range of the invention and are inferior in impact resistance and appearance of finished articles.

What is claimed is:

1. A hydrogenated diene block copolymer having a polystyrene-*tert*-butyl-oxymethylene molecular weight of 100,000-400,000 which is a hydrogenation product of an (A)-(B) block copolymer consisting of (A) an allyl aromatic compound copolymer block and (B) an allyl aromatic compound-hydrogenated diene random copolymer block, or an (A)-(B)-(C) block copolymer consisting of the block (A), the block (B) and (C) an allyl aromatic compound-hydrogenated diene copolymer tapered block wherein the proportion of the allyl aromatic compound increases gradually, or an (A)-(B)-(A) block copolymer consisting of the block (A), the block (B) and the block (A) in which block copolymer:

(1) the weight proportion of the allyl aromatic compound/the hydrogenated diene is 3-40/55-65,

(2) the total of the bound allyl aromatic compound moieties in the block (A) and the block (C) or the

two block (A)'s is 3-35% by weight based on the total moieties and the content of the bound allyl aromatic compound is at least one block (A) is at least 2% by weight, and

(3) the vinyl content in the hydrogenated diene portion in the block (B) is more than 60%, and in which hydrogenation copolymer at least 50% of the double bonds of the hydrogenated diene portion is saturated.

2. The hydrogenated diene block copolymer according to claim 1, wherein the block copolymer is a block copolymer represented by the general formula [A]_n-[B]_m-[C]_p-X or [A]_n-[B]_m-[A]_n-X wherein (A), (B) and (C) are as defined in claim 1, n is an integer of 1-4 and X is a coupling agent moiety.

3. A modified hydrogenated diene block copolymer obtained by modifying 100 parts by weight of a hydrogenated diene block copolymer according to claim 1 with 5-25 parts by weight of an unsaturated compound having at least one functional group selected from the group consisting of acid anhydride group, carboxyl group, hydroxyl group, amino group and epoxy group.

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10

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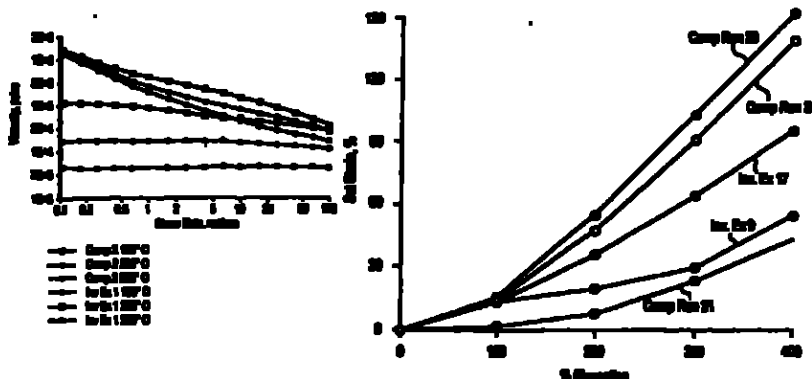
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(54) Title: HYDROGENATED BLOCK POLYMERS HAVING ELASTICITY AND ARTICLES MADE THEREFROM



(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 sulfonated ethylene/vinyl aromatic interpolymers, an elastomeric ethylene/C₃-C₂₀ α -olefin interpolymers, a C₇-C₂₀ α -olefin/conjugated diene interpolymers, 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 polyetheramine), a styrene/conjugated diene interpolymers, 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. Inventive 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.

WO 01/09239 A1



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(54) Sealant compositions

(57) The present invention relates to a sealant composition which comprises:

(a) 100 parts by weight of a hydrogenated vinyl aromatic hydrocarbon butadiene-vinyl aromatic hydrocarbon block copolymer which has an overall weight average molecular weight of from 50,000 to 300,000, a vinyl aromatic hydrocarbon block weight

average molecular weight of from 4000 to 50,000, and wherein the butadiene block has a vinyl content of at least 45% by weight, and
(b) 20-400 parts by weight of an extender permitting resin

The present invention further relates to a sealant solution containing a solvent and at least 95 % by weight of the sealant composition according to the invention.

EP 0 863 193 A1

Description

This invention relates to sealant compositions for use as sealants against air and moisture, sound-dampening, and other functions in construction, automotive, and consumer applications. More particularly, the invention relates to such compositions containing one high vinyl content hydrogenated vinyl aromatic hydrocarbon-butadiene-vinyl aromatic hydrocarbon (HEBH) block copolymer.

There are at least two major criteria in formulating a sealant composition. The sealant must possess some degree of slump resistance at high service temperatures. Additionally, the sealant should have a good working viscosity in the melt so it can be easily coated on to various substrates, and/or the sealant should have a low solution viscosity in solutions containing a high amount (250 %wt, preferably 240 %wt) of solids.

Styrene-butadiene-styrene block copolymers are known to be useful for sealants because of their combination of strength and elastomeric properties. Hydrogenated versions of these polymers (HEBH) are especially useful because of their enhanced resistance to oxidation and chemical attack. These polymers give the compositions in which they are used excellent high temperature resistance properties but they tend to be high in molecular weight and thus too high in viscosity that it is difficult to coat the sealants easily with them.

Other adequate sealant compositions have been made using some of the lower molecular weight polymers of this type but sections in terms of high temperature properties must be accepted. The large styrene endblocks in the higher molecular weight EHBH polymers are resistant to flow but give excellent high service temperature performance. Examples of sealant compositions are the use of a lower molecular weight polymer and blending in a relatively low molecular diblock polymer of this type. Thus it can be seen that it would be advantageous to be able to make an easily sealable sealant composition and which or enhance the high temperature properties obtainable with the higher molecular weight EHBH polymers.

This invention provides the advantages of both low molecular weight polymers and higher molecular weight polymers while obtaining their disadvantages. Using the high vinyl content polymers of the present invention in an sealant application allows sealants with high service temperature properties which have a sufficiently low viscosity to be easily sealable. The present invention is directed towards high service temperatures and a reduction of application viscosity may be mutually exclusive for sealants. This invention provides a novel way to produce compositions which exhibit both of these characteristics.

This invention provides sealant compositions which comprise a hydrogenated vinyl aromatic hydrocarbon-butadiene-vinyl aromatic hydrocarbon (HEBH) block copolymer which has an overall weight average molecular weight of from 20,000 to 300,000, a vinyl aromatic hydrocarbon block weight average molecular weight of from 4,000 to 50,000, and a vinyl content of at least 45% by weight (%wt), preferably 45 to 65%, and extender-permitting resins such as hardening resins. For every 100 parts by weight of block copolymer, there should be 20-400, and preferably 60 to 280 parts by weight of extender-permitting resin. Optionally, the sealant composition may further comprise polyvinyl aromatic hydrocarbon block releasing resins, flow permitting resins, oils, polyethers, fillers, waxes, or other solvents.

The preferred structure for the block copolymers used herein is linear, i.e., H-EBH-B. However, block copolymers having branched, radial, and star structures may also be used in this invention. Such structures may be generally represented by the formula



where A is a polymer block of a vinyl aromatic hydrocarbon, preferably styrene, B is a polymer block of hydrogenated butadiene, and Y is a coupling agent.

The endblocks of the block copolymers to be used in the sealant composition according to the invention are preferably polymer blocks of styrene. Other vinyl aromatic hydrocarbons could be used, including ethynylstyrene, styrene, C₆-C₂ ethyl-substituted styrenes, C₆-C₂ alkyl-substituted styrenes, vinyl cyclohexane, and vinyl toluene.

The butadiene used herein must produce a polymer block with a high vinyl content. In other words, the percent of 1,2 addition of the butadiene should be at least 45%wt, preferably 45 to 65%wt. Below 45 %wt, polymer viscosity is similar to conventional polymers and there is no advantage. Above 65%wt, the viscosity decreases has resulted a plateau and no longer drops with higher 1,2 content. Therefore, there is no further advantage. The 1,2-vinyl content is more preferably at least 50 %wt; even more preferably at least 60 %wt; yet even more preferably at least 70 %wt; most preferably at least 75 %wt. The 1,2-vinyl content is even more preferably at most 80 %wt, even more preferably at most 85 %wt.

Artificial polymerization of conjugated diene hydrocarbons with lithium initiators is well known as described in U.S. Patents Nos. 4,538,882 and No. 27,140 which disclosures are incorporated herein by reference. Polymerization compositions with a novolac resin, diluents, or polyethers initiators which enable a living polymer butadiene at each lithium site. Typical living polymer structures containing polyfunctional conjugated diene hydrocarbons are:

EP 0 863 193 A1

97

10

EP 0 885 103 A1

X-B-U

X-A-B-U

X-A-B-A-U

U-B-Y-B-U

U-A-B-Y-B-A-U

wherein U represents polymerized units of one or more vinyl aromatic hydrocarbon compounds such as styrene, X is the residue of a monofunctional initiator such as an azobisisobutyronitrile, and Y is the residue of a difunctional initiator such as the diadduct of sec-butyldithiol and m-dichloroquinodimethane, these structures, including those pertaining to polythiourethanes or carbon units of styrene and a conjugated chain, generally have limited practical utility although known in the art. The anionic polymerization of the conjugated diene hydrocarbons is typically associated with aromatic nucleophilic such as dialkyl ether or alkyl glycols (1,3-dithiopyranes) to obtain the desired amount of 1,2-addition. As described in Pls 82,148 which is incorporated by reference herein, the level of 1,2-addition of a butadiene polymer or copolymer can greatly affect chemically properties after hydrogenation. The 1,2-addition of butadiene polymers significantly and completely substantially influences the polymer as described above. A 1,2-addition of about 40% is achieved during polymerization at 80°C with about 6% by volume of dialkyl ether or about 300 ppm of alkyl glycols in the final solution. A 1,2 addition of about 40% (within the scope of this invention) is achieved during polymerization by the presence of about 300 ppm of ortho-dichlorophenylene (OCDE) in the final solution. A 1,2 addition of 70% (within the scope of this invention) is achieved during polymerization by the presence of about 300 ppm of 1,3-dithiopyran (DTP) in the final solution.

In general, the polymers could in this invention may be prepared by contacting the monomer or monomers with an organometal metal compound in a suitable solvent at a temperature within the range from -180°C to 350°C, preferably at a temperature within the range from 0°C to 100°C. Particularly effective polymerization reactions are organolithium compounds having the general formula:

RLi

wherein R is an aliphatic, cycloaliphatic, allyl-substituted cycloaliphatic, aromatic or allyl-substituted aromatic hydrocarbon radical having from 1 to 30 carbon atoms.

Suitable solvents include those useful in the cationic polymerization of the polymer and include aliphatic, cycloaliphatic, allyl-substituted cycloaliphatic, aromatic and allyl-substituted aromatic hydrocarbons, ethers and esters thereof. Suitable solvents, then, include aliphatic hydrocarbons such as butane, pentane, hexane, and heptane, cycloaliphatic hydrocarbons such as cyclohexane, and cyclopentane, allyl-substituted cycloaliphatic hydrocarbons such as allylcyclohexane, and allylcyclopentane, aromatic hydrocarbons such as benzene and the allyl-substituted aromatic hydrocarbons such as toluene, and xylene and others such as tetralin, naphthalene, diethyl ether, and di-n-butyl ether.

The hydrogenation of these polymers may be carried out by a variety of well established processes including hydrogenation in the presence of such catalysts as Raney Nickel, noble metals such as platinum, and palladium and soluble transition metal catalysts. Suitable hydrogenation processes which can be used are ones wherein the chloroconjugating polymer or copolymer is dissolved in an inert hydrogenation solvent such as cyclohexane and hydrogenated by reaction with hydrogen in the presence of a suitable hydrogenation catalyst. Such processes are disclosed in U.S. Patent Nos. 3,113,888, 4,038,888 and Patents 87,148, the disclosures of which are herein incorporated by reference. The polymers are hydrogenated in such a manner as to produce hydrogenated polymers having a residual unsaturation content in polythiurethanes of less than 5 percent by weight, preferably less than 1 % and more preferably as close to 0 percent as possible, of their original unsaturation content prior to hydrogenation. A thienic catalyst such as disclosed in U.S. Patent 3,038,788, which is herein incorporated by reference, may also be used in the hydrogenation process.

EP 0 885 103 A1

The molecular weights of linear polymers or unassociated linear segments of polymers such as linear, di-, tri-, tetra-, etc., or the arms of star polymers before coupling are essentially measured by Gel Permeation Chromatography (GPC), where the GPC system has been appropriately calibrated, typically with polystyrene standards of known molecular weight. For substantially polydisperse linear polymers, the polymer is essentially monodisperse (weight average molecular weight/polymer average molecular weight ratio approaches unity), and it is both unassociated and sufficiently disperse to report the "peak" molecular weight of the linear 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. The materials used in the columns of the GPC are styrene-divinyl benzene gels or silica gels. The solvent is tetrahydrofuran and the detector is a refractive index detector.

Measurement of the true molecular weight of the final coupled radial or star polymer is not as straightforward or as easy to make using GPC. This is because the radial or 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 method to test for a radial or 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 ppm of sample per 100 milliliters of solvent and allowed 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. The following references relate to the subject of measuring molecular weight.

1. *Modern Size-Exclusion Liquid Chromatography*, W. W. Yee, J. J. Kirkland, D. D. By, John Wiley & Sons, New York, NY, 1978.
2. *Light Scattering from Polymer Solutions*, M. R. Huggins, ed., Academic Press, New York, NY, 1972.
3. W. Ruge and A. J. Hawk, *Journal of Polymer Science*, 33, 541 (1979).
4. M. L. McCormick, *Journal of Polymer Science*, 65, 1049, 1978.

The hydrogenated vinyl aromatic hydrocarbon-butadiene-vinyl aromatic hydrocarbon (HBDB) block copolymer preferably has an overall weight average molecular weight of from 48,000 to 385,000. The vinyl aromatic hydrocarbon block weight average molecular weight is preferably 8,000 to 32,000.

The poly(vinyl aromatic hydrocarbon) content, typically the polymers content, is preferably in the range from 18 to 48 % by weight on the basis of the total polymer; more preferably from 30 to 40 % and, more preferably from 30 to 38 %.

In certain applications, it is common practice to add an additive preventing resin such as a hardening resin that is compatible with the polymer, generally from 50 to 400 parts per hundred parts of polymer by weight (pphr), preferably 80 to 350 pphr. For every 100 parts by weight (pphr) of copolymer, there should be at least 50 pphr of resin to achieve the low viscosity and nonreactivity required for certain applications. No more than 400 pphr additive preventing resin per 100 parts polymer can be used or the solvent will not have the rheo-elastic properties required to make flow after application.

A common hardening resin is a diene-styrene copolymer of pterylene and 2-methyl-2-butene having a softening point of about 80°C. This resin is available commercially under the trademark Wapacel® 88 and is prepared by the cationic polymerization of 60% pterylene, 10% isoprene, 8% cyclo-pentadiene, 10% 2-methyl-2-butene and about 10% diene, as taught in U.S. Patent No. 3,877,388. Other hardening resins may be employed wherein the monomer/copolymer comprises 50-80 weight percent of pterylene and 50-50 weight percent of 2-methyl-2-butene.

Other substances preventing resin which are also useful in the composition of this invention include hydrogenated steric, esters of carbon, polyurethanes, isopropylalcohol resins and polymerized related esters, lower alcohols, polyols and ester resins. An example of a liquid resin is Araldite® LV resin from Huls. To obtain good rheo-elastic and color stability, it is preferred that the hardening resin be a saturated resin, e.g., a hydrogenated diene/tertiarybutylene resin such as Escorex® 6500 resin made by Ebecor or a hydrogenated polyurethane or polyether/tertiarybutylene resin such as Pagedent® resin made by Huls. Pig and ball coloring pigments of solid resins may be from 40°C to 140°C, preferably 80 to 110°C, as determined by ASTM E88. Liquid resins, i.e., softening points less than room temperature, may be used as well as combinations of solid and liquid resins. The selection of the particular hardening agent is, in large part, dependent upon the specific polymer employed in the respective solvent composition.

A comparison of the known literature may further exhibit plasticizers, such as rubber containing plasticizers, or softening oils or esters or isoprene polymers and glycols. Plasticizers are well-known in the art and include both high molecular weight and low molecular weight. Preferred plasticizers are highly saturated oils, e.g. Tuflex® 6500 and 6504 of made by Amco and neopentyl glycol, e.g. Shellflex® SP1 oil made by Shell. The amounts of plasticizer

88

EP 0 883 183 A1

Example 2

Block copolymers PP 8888 and B described in Example 1 were used to prepare emulsion formulations containing 40 % by weight of solids as shown in table 2. The solution viscosity was determined at 25°C using a Brookfield viscometer. The emulsion formulation containing polymer B (not according to the invention) had a solution viscosity of 82.2 centipoise, whereas the emulsion formulation containing polymer PP 8888 according to the invention had a solution viscosity of 22.8 centipoise. A low solution viscosity at 40 % solids content is advantageous as the emulsion can then be easily applied, or alternatively, the solids content can then be increased to e.g. 45-48 % by weight, preferably 48 to 49% by weight.

Table 2

	Emulsion formulation	
	1	2
A	100 g	-
PP 8888	-	10.0 g
Plagelita R 101	44.0 g	0.5 g
Croton 60	18.4 g	10.4 g
n-butyl acetate	82.0 g	82.0 g
toluene	48.0 g	48.0 g

Croton 60 is a hydrogenated pentaerythritol processing oil (polyethylene)

Kaloblen FY30 is an aromatic releasing resin

Plagelita R101 is a hydrogenated hydrocarbon tackifying resin

Claims

1. Emulsion composition which comprises:

- (a) 100 parts by weight of a hydrogenated vinyl aromatic hydrocarbon butadiene-vinyl aromatic hydrocarbon block copolymer which has an overall weight average molecular weight of from 20,000 to 300,000, a vinyl aromatic hydrocarbon block weight average molecular weight of from 4000 to 20,000, and wherein the butadiene block has a vinyl content of at least 40% by weight, and
- (b) 20-400 parts by weight of an adhesion promoting resin.

2. Emulsion composition according to claim 1 wherein the vinyl content is from 40 to 80% by weight

3. Emulsion composition according to claim 1 or 2 wherein the overall weight average molecular weight is from 40,000 to 800,000.

4. Emulsion composition according to any one of claims 1-3 wherein the vinyl aromatic hydrocarbon block molecular weight is from 5,000 to 20,000.

5. Emulsion composition according to any one of the preceding claims further comprising a filler.

6. Emulsion composition according to any one of the preceding claims, further comprising a plasticizer.

7. Emulsion composition according to any one of the preceding claims, further comprising a releasing resin.

8. Emulsion solutions containing a solvent and at least 30 % by weight on the basis of the total solution of a emulsion composition as claimed in any one of the preceding claims.

that provides a packaging film which has well-balanced film-to-film adhesion (favorable easy-tearing), inter-etc, balance between softening and peeling while drawing the rolled film from a film box. Another object of the second invention is to provide a stretched packaging film made of the resin composition.

1. Disclosure of the Invention

[0007] On the basis of the aforementioned Japanese Patent Application Laid-Open (kokai) No. 6-082164, the present inventors have conducted further studies on as to provide novel ethylene-free film endowed with a good balance between such properties as heat resistance, adhesion, transparency, and ease-of-cutting which are required for wrap film. The inventors have found that a film made of a specific resin composition prepared by incorporating a hydrogenated product of an aromatic vinyl compound-conjugated diethers copolymer, polyesters, a tackifier, and an optional tackifier aid into a polypropylene resin composition having excellent heat resistance and water-vapor-barrier properties exhibits improved heat resistance, adhesion, and transparency, and allows the film to be stretched facilitating ease of cutting. The first invention has been accomplished on the basis of these findings. The inventors have also found that a resin composition comprising a polypropylene resin, an optionally added hydrogenated product of an aromatic vinyl compound-conjugated diethers copolymer, polyesters, a tackifier, and a tackifier aid, each component being incorporated in the composition in an amount falling within a specific range, particularly imparts an excellent easy-tearing property to a film made of the resin composition. The second invention has been accomplished on the basis of this finding.

[0008] Accordingly, in the first invention, there is provided a polypropylene resin composition which comprises 60-90 parts by weight of a polypropylene resin (A) having a crystalline melting point of 130°C or higher; 1-40 parts by weight of a hydrogenated copolymer (B) of an aromatic vinyl compound and a conjugated diethers (which hereinafter may be referred to as simply "hydrogenated copolymer"); 0.1-50 parts by weight of polyesters (C) having a kinematic viscosity as measured at 37.8°C in accordance with JIS K2253 of 10-2,000,000 cSt; 0.1-50 parts by weight of a tackifier (D); and 0-5 parts by weight of a tackifier aid (E), the amounts of components (B), (C), and (E) being on the basis of 100 parts by weight of the sum of components (A) and (B).

[0009] In the first invention, there are also provided:

- a stretched film for packaging which is made of the aforementioned polypropylene resin composition;
- a laminated stretched film for packaging in which at least one outer surface is formed of the aforementioned stretched film for packaging;
- a laminated stretched film for packaging in which an inner layer is formed of a layer made of a polypropylene resin or resin composition comprising 70-100 parts by weight of a polypropylene resin (A) and 0-30 parts by weight of the aforementioned hydrogenated copolymer (B) and at least one outer surface is formed of the aforementioned stretched film for packaging; and
- the aforementioned laminated stretched film for packaging having an Elmendorf tear resistance in the TD direction of 10 gf or less.

[0010] In the second invention, there is provided a polypropylene resin composition which comprises 65-100 parts by weight of a polypropylene resin (A) having a crystalline melting point of 130°C or higher; 0-5 parts by weight of a hydrogenated copolymer (B) of an aromatic vinyl compound and a conjugated diethers; 0-50 parts by weight of polyesters (C) having a kinematic viscosity of 10-2,000,000 cSt as measured at 37.8°C in accordance with JIS K2253; 0.1-50 parts by weight of a tackifier (D); and 0.01-1 part 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).

[0011] In the second invention, there are also provided:

- the aforementioned polypropylene composition, wherein the polyesters (C) comprise 0.1-10 parts by weight of a low-molecular-weight polyesters having a kinematic viscosity of 10-20,000 cSt as measured at 37.8°C and the balance being a high-molecular-weight polyesters having a kinematic viscosity of 50,000-2,000,000 cSt, the total amount of the two polyesters being 0-50 parts by weight;
- the aforementioned polypropylene composition, wherein the tackifier (D) is at least one species selected from petroleum rubber; and
- the aforementioned polypropylene composition, wherein the tackifier aid (E) is at least one species selected from carbonic acid.

[0012] In addition, the second invention provides

- a stretched film for packaging made of any one of the polypropylene resin compositions as recited in the second

invention;

the stretched film for packaging which is biaxially stretched; and

a laminated stretched film for packaging in which at least one outer surface is formed of the aforementioned stretched film for packaging.

Best Modes for Carrying Out the Invention

[0013] Hereinafter, the first invention will be described in detail.

[0014] The polypropylene resin (A) which is employed as a base material of the polypropylene resin composition of the first invention may be a propylene homopolymer or a copolymer predominantly containing propylene with an α -olefin other than propylene such as ethylene or butylene. Of these, ethylene-propylene copolymers are preferred. The copolymers may be a random copolymer or a block copolymer, with a random copolymer being preferably employed. Physical properties of the polypropylene resin of the present invention are not particularly limited. However, the resin has a melt index (MFI) suitable for forming film at 0.5-50 g/10 min (in accordance with JIS K6720, 230°C, 0.10 kg load), particularly preferably 0.5-10 g/10 min. The resin preferably has a density of 0.89-0.91 g/cm³. Although required heat resistance depends on the type of load to be packaged or the mode of use of the thus-obtained stretched film for packaging (hereinafter may be referred to as "wrap film"), the crystalline melting point is typically 130°C or higher, preferably 140°C or higher, more preferably 150°C or higher. The term "crystalline melting point" as used herein refers to the maximum of the heat absorption peak in a melting curve for crystalline material as measured using a differential scanning calorimeter (DSC-Y, product of Perkin-Elmer) at a temperature scanning rate of 10°C/min.

[0015] The hydrogenated copolymer (B) of an aromatic vinyl compound and a conjugated diethers employed in the first invention is a type of thermoplastic elastomer. In the wrap film provided by the present invention, the hydrogenated copolymer (B) serves as an excellent compatibilizer for blending out polyesters (C) in the resin and/or as an excellent toughening agent, thereby possibly imparting excellent adhesion to wrap film enriched with polyesters (C) and the tackifier (D). In addition, the above-referenced hydrogenated copolymer (B) and the tackifier (D) have high compatibility with the polypropylene resin (A), and are considered to play an important role in obtaining the transparency of the obtained wrap film.

[0016] The aforementioned hydrogenated copolymer (B) is a hydrogenated product of a copolymer consisting at least one aromatic vinyl compound and a conjugated diethers having an ester/anhydride unit. Among such hydrogenated copolymers, a copolymer consisting exclusively one aromatic vinyl compound and a conjugated diethers is preferably used. The copolymer may be a block polymer or a random polymer, with a block polymer being preferred.

[0017] Examples of aromatic vinyl compounds include styrenes, α -methylstyrenes, vinyltoluenes, p -tert-butylstyrenes, vinylacetates, ethylvinylketones, and vinylpyridines. Examples of conjugated diethers include butadienes, isoprenes, 1,3-pentadienes, and 1,3-dienylbutadienes.

[0018] Among these hydrogenated copolymers, a hydrogenated product of a styrene-butadiene-styrene (SBS) block copolymer is particularly preferred. A hydrogenated product of a styrene-isoprene-styrene (SIS) block copolymer is relatively preferred.

[0019] In the SBS block copolymers, the styrene component may be partially substituted by an aromatic vinyl compound such as α -methylstyrene, vinyltoluene, p -tert-butylstyrene, vinylphenyl, ethylvinylphenyl, or vinylpyridylstyrene. Similarly, the butadiene component may be partially substituted by a diene such as isoprene, 1,3-pentadiene, or 1,3-dienylbutadiene. Although the block copolymer may have a variety of structures, no one block is preferably an aromatic vinyl compound having. The block copolymer preferably has a number-average molecular weight of approximately 10,000 to approximately 100,000, particularly preferably 20,000 to approximately 500,000.

[0020] Aliphatic diethers bonds in the hydrogenated copolymer (B) are preferably hydrogenated in an amount of 60% or more, particularly preferably 90% or more. As disclosed in Japanese Patent Application Laid-Open (kokai) No. 65-105407, such a hydrogenated copolymer has a structure similar to a copolymer block of ethylene and 1-butene (1-butylene) (EB) or a similar structure, since a certain ratio of butadiene residues in a butadiene polymer block takes the 1,3-configuration. Thus, the hydrogenated copolymer is generally called "a styrene-ethylene-butylene-styrene block copolymer" (SEBS block copolymer) and is commercially available under various trade names, such as Elastomer AR (Aristar Co., Ltd.) and Kraton G (Shion Kasei K.K.).

[0021] Into the resin composition of the first invention, the propylene resin (A) is incorporated in an amount of 60-90 parts by weight, preferably 70-80 parts by weight, more preferably 80-90 parts by weight. Similarly, the hydrogenated copolymer (B) is incorporated in an amount of 1-40 parts by weight, preferably 0-30 parts by weight, more preferably 10-30 parts by weight. When the amount of the hydrogenated copolymer is in excess of 40 parts by weight, the resin composition has poor film formability and the produced film has poor transparency, whereas when the amount is less than 1 part by weight, adhesion of the produced film deteriorates. Hence, the total amount of components (A) and (B) is 100 parts by weight.

[0022] The polyesters (C) used in the first invention serve as a tackifier for a packaging film of the present inven-

2-1. Adhesion

[0097]

- ☒: the two adhesion property test can be pushed off
- ☐: the ability to itself when the film is applied to the glass and is difficult to peel off.
- A: adhesive agent is transferred onto hands but adhesive agent transferred to the glass cannot be observed visually.
- X: adhesive agent is transferred onto hands and adhesive agent transferred to the glass can be observed visually.

2-2. Adhesion to glass cup

[0098]

- ☒: very good adhesion
- ☐: good adhesion
- A: slight adhesion
- X: no adhesion

3. Ease-of-peeling with a V-shape serrated cutter

- [0099] Wrap films were manufactured as an experimental basis. Each of the films was rolled onto a cardboard core roll and the thus-obtained rolled film was put into a box (in film case of New Kurem; product of Kuraray Chemical Industry Co., Ltd.). Thereafter, an end of the rolled wrap film was drawn from the box and then the film was cut using a V-shape serrated cutter, which is attached to the box, and ease-of-peeling of the film was evaluated. Evaluation standards were as follows. Example rated "◎" or "○" are suitable for practical use.

- ☒: film can be cut with ease
- ☐: film can be cut
- A: film is difficult to cut
- X: film stretches and cannot be cut

3. Stretched tear resistance test

- [0100] The tear resistance of each sample was measured in accordance with JIS K7180 using an Charadaf tear resistance-measuring instrument (product of Toyo Rumi Co., Ltd.).

3. Oxygen permeability

- [0101] Oxygen permeability of each test film was measured using an oxygen permeability measuring instrument (O2-TRANSMIC; product of Mochida Chemical) at 25°C and 65%RH. The measured values are expressed in units of $\text{cm}^3/\text{m}^2 \cdot \text{day} \cdot \text{atm}$.

7. Heat resistance test

- [0102] The heat resistance of each sample film was tested in accordance with the heat resistance testing method for food-wrapping films prescribed by Tokyo Metropolitan Ind. Inc. The testing method was as follows. Sample film of 5 cm in width and 14 cm in length was prepared. Margins of 2.5 cm in length from both ends of each sample film were fixed and then a load of 10 g was applied to the film. The thus-obtained sample was put into a glass case and then heated at a predetermined temperature. Tests were performed at intervals of 5°C. If the sample film broke within 1 hour of initiation of heat application, a temperature 5°C lower than the temperature at which the sample film broke is referred to as a "heat resistant temperature."

8. Easy-drawing

- [0103] Wrap films were manufactured as an experimental basis. Each of the films was rolled onto a cardboard core roll and the thus-obtained rolled film was put into a box (in film case of New Kurem; product of Kuraray Chemical Industry Co., Ltd.). Thereafter, the end of the rolled wrap film was drawn from the box and the easy-drawing property of the

film was evaluated. Evaluation standards are as follows. Examples rated "◎" or "○" are suitable for practical use.

- ☒: film can be drawn from the box with ease while the cardboard core roll remains in the box
- ☐: film can be drawn from box if the cardboard core roll is retained in position by exerting slight pressure on the lid of the box
- A: it is difficult to draw film from the box even when the cardboard core roll is retained in position by exerting slight pressure on the lid of the box
- X: entire rolled film and the cardboard core roll come out of the box

9. Measurement of 0.5% Break Modulus

- [0104] The 0.5% Break Modulus of each sample film (30 mm in width and 100 mm in length) was measured by use of a measuring instrument (Instron 1130-10; product of Oriental) at a pulling speed of 10 mm/min.

10. (Examples 1-6 and Comparative Examples 1-4)

- [0105] Resin compositions containing the resins shown in Table 1 were prepared using the following materials: a maleic copolymer of propylene and ethylene (MOLEEN FL30; product of Sumitomo Chemical Co., Ltd.; MFR = 0.9 g/10 min, melting point = 145°C) serving as the polypropylene resin (A); a 6666 block copolymer (ELASTOMER AF0402; product of Asahi Kasei Co., Ltd.) serving as the hydrogenated copolymer (B), or an ethylene- α -olefin copolymer as a substitute for the hydrogenated copolymer (B) in Comparative Examples (DAKASEN P0100, product of Mitsui Chemicals, Inc.); Nucleol polycarbonate HV300 (characteristic viscosity = 32,000 cSt, number-average molecular weight = 1,500) serving as the polycarbonate (C); an alkylene substituted hydrocarbon resin of formula (1) (AFRICAL P-140; product of Asahi Chemical Industries, Ltd.) serving as a modifier (D); and a glycerol fatty acid ester (GEMAL AC-070; product of Fina Viscosa Co., Ltd.) serving as a lubricant (E). Each of the resultant resin compositions was rolled through extrusion.

- [0106] Specifically, the above-described additives and a portion of polypropylene resin (A) were blended and then extruded at 250°C to obtain master pellets using a double-screw extruder. Thereafter, the thus-obtained master pellets and the remaining portion of the polypropylene resin (A) were blended as so to obtain the resin composition shown in Table 1. The resultant resin composition was melted into a film through extrusion at 250°C by use of a single-screw extruder (by extruding pressure 107; product of Nissei Engineering Co., Ltd.). Then the thus-obtained film was stretched at 120°C into a film having the same length and the same the width of the original film. The temperature of 120°C is slightly lower than the melting point of a polypropylene resin (namely polypropylene MOLEEN FL30; melting point = 145°C). The thickness of the packaging stretched film (may be referred to as "wrap film") thus obtained is 10 μm .
- [0107] Concerning each of the wrap films, adhesion to a glass cup was evaluated and "tear" (transparency) and "glare" (surface smoothness) were measured. The results are shown in Table 2.

(Detailed Examples)

- [0108] For reference purposes, commercial wrap films made from various resin materials were subjected to the above-described evaluation and measurements. The results are shown in Table 2. The commercial wrap films used were as follows. "New Kurem" (product of Kuraray Chemical Industry Co., Ltd.) made from ethylene chloride copolymer; thickness = 10 μm ; "Coronal" film A" made from low-density polyethylene, thickness = 11 μm ; "Coronal" film B" made from poly-4-methylpentene, thickness = 10 μm ; "Coronal" film C" laminated film of polypropylene/polypropylene, thickness = 9 μm .

Table 1

	Film Composition (parts by weight)					
	Propylene resin (A)	Block Copolymer (B)		Polyethylene (C)	Tackifier (D)	Tackifier oil (E)
		SEBS	E=oil ¹			
Example 1	90	10	0	5	5	0
Example 2	90	10	0	5	5	0.1
Example 3	90	10	0	10	5	0.1
Example 4	90	10	0	10	5	0
Example 6	90	10	0	5	5	0
Comp. Ex. 1	90	10	0	5	0	0.1
Comp. Ex. 2	90	10	0	10	0	0
Comp. Ex. 3	90	10	0	5	0	0
Comp. Ex. 4	90	0	10	5	0	0
Ref. Ex. 1	¹ New Kresap [®] produced by Kuraray Chemical Industry Co., Ltd.; made from vinylidene chloride copolymer, 10 µm.					
Ref. Ex. 2	Commercial product Acrista from low-density polyethylene, 11 µm.					
Ref. Ex. 3	Commercial product Bionolle from poly- <i>n</i> -butylacrylate-1, 10 µm.					
Ref. Ex. 4	Commercial product Copolypropylene/ethylene/terephthalate film, 8 µm.					

Seal¹: "Adesol PMSF", styrene-*n*-butyl copolymer

Table 2

	Transparency		Gloss		Adhesion to glass cup
	Evaluation	Haze (%)	Evaluation	GL (D50%) ¹	
Example 1	●	0.28	●	149/147	●
Example 2	●	0.29	●	150/150	●
Example 3	●	0.73	●	144/144	●
Example 4	●	0.28	●	149/147	●
Example 6	●	0.28	●	149/149	●
Comp. Ex. 1	●	0.68	●	149/142	○
Comp. Ex. 2	○	1.19	○	127/121	●
Comp. Ex. 3	●	0.88	○	139/129	○
Comp. Ex. 4	○	3.3	-	-	△
Ref. Ex. 1	●	0.72	●	151/154	●
Ref. Ex. 2	○	1.28	●	149/142	●
Ref. Ex. 3	●	0.45	●	149/138	●
Ref. Ex. 4	○	1.12	○	139/133	△

GL (D50%)¹: indicated as HAZE, MD values in the evaluation chapter during production of film. YD is a direction named in MD.

[0098] As shown in Table 2, the films in Examples of the present invention exhibit excellent "hard" and "glare" values. The addition of olefin saturated hydrocarbon resin confers excellent optical properties on a film. Olefin saturated hydrocarbon resin serving as a tackifier (D) improves the transparency and glare of a wrap film. This is because the olefin saturated hydrocarbon resin smoothens the film surface to thereby reduce irregular reflection.

[0099] Moreover, as shown in Table 2, films of Examples of the present invention exhibit excellent adhesion to a glass cup and exhibit low shrinkage. Conventionally, in order to obtain adhesion to a glass cup, the incorporated amount of polyethylene is increased or the incorporated amount of the SEBS block copolymer, which acts as a blocking promoter of polyethylene, is increased. Although such a composition reduces the shrinkage of a film in a glass cup possible, the composition also reduces the film tensile strength. Such film is not suitable for practical use. On the contrary, through the addition of the olefin saturated hydrocarbon resin, sufficient adhesion to a glass cup can be obtained while excessive shrinkage and excessive reduction in tensile strength when the film is rolled can be avoided.

[0100] The adhesion promoting effect of olefin saturated hydrocarbon resin on wrap film is strongly related to the above-described surface smoothing effect on wrap film. That is, if the surface of the wrap film is smooth, the contact area of the contact substance increases, which results in an apparent increase in adhesive strength. Therefore, increasing the contact area gives rise to the desired adhesion property even when the adhesive strength is low.

(Examples 9-10 and Comparative Examples 5-6)

[0101] Laminated films were produced through extrusion using a triple-layered die and an extruder (dry spinning process SGM) product of Yamaguchi Chemical Co., Ltd. The above-described polypropylene resin (A) in Example 1 was employed for lower layers of the laminated film. The compositions described in Examples 1-6 and Comparative Examples 5-6 were employed for outer layers attached to both sides of the lower layers of Examples 9-10 and Comparative Examples 5-6 respectively. Each layer was extruded at 230°C. Then each of the thus-obtained laminated films was stretched at 120°C into a film having the three times the length and the three times the width of the original film. The thickness of the wrap film thus obtained was 10 µm and the thickness of each layer constituting the laminated film was 3.333 µm.

[0102] The thus-obtained film and above-described reference film were evaluated for adhesion to a glass cup and ease-of-cutting using a V-shape serrated cutter. These films were also subjected to chemical tear resistance testing (quantitative evaluation of ease-of-cutting) and heat resistance testing. The results are shown in Table 3.

(Examples 15-17 and Comparative Examples 6-10)

[0071] The same polypropylene resin (A) as employed in Example 1 was formed into an inner layer, which was combined with a layer made of the same polypropylene resin composition as shown in Table 4. The prepared laminate was subjected to a reverse draw to that employed in Example 1. The thus-obtained film and reference samples were subjected for adhesion to a glass cup, easy drawing, oiliness, transparency, gloss, ease-of-cutting, and heat resistance. The results are shown in Tables 5 and 6.

Table 3

	Construction	Adhesion to glass cup	Easy cutting	El. Strength ¹ g	Heat resistance ² °C
Example 1	Single layer	●	●	49	120
Example 6	The surface layer is of the same material as in Ex. 1	●	●	49	120
Example 7	The surface layer is of the same material as in Ex. 2	●	●	49	120
Example 8	The surface layer is of the same material as in Ex. 3	●	●	39	120
Example 9	The surface layer is of the same material as in Ex. 4	●	●	40	120
Example 10	The surface layer is of the same material as in Ex. 5	●	●	49	120
Example 11	The inner layer contains 6555	●	●	39	120
Comp. Ex. 1	The surface layer is of the same material as in Comp. Ex. 1	○	●	49	140
Comp. Ex. 2	The surface layer is of the same material as in Comp. Ex. 2	●	●	49	140
Comp. Ex. 3	The surface layer is of the same material as in Comp. Ex. 3	○	●	49	140
Comp. Ex. 4	The surface layer is of the same material as in Comp. Ex. 4	△	●	49	140
Ref. Ex. 1	Metallene-olefinic polymer	●	●	60	140
Ref. Ex. 2	Low-density polyethylene	●	X	49700	110
Ref. Ex. 3	Poly- <i>n</i> -butylacrylate-1	●	X	394	120
Ref. Ex. 4	Polypropylene/polypropylene terephthalate film	●	△	7121	120

El. Strength¹: Elongation tear resistance, MPa/10

Example 11

[0080] The procedure used in Example 10 was repeated, except that the composition comprising 80 parts by weight of the polypropylene resin (A) in Example 1 and 10 parts by weight of the 6555 in Example 1 was employed for the inner layer. The results are shown in Table 5.

[0081] As shown in Table 3 sample film having a low Elongation tear resistance TD value (longitudinal strength) exhibits the property of easy-cutting. It was also confirmed that the TD value of Elongation tear resistance serves as a good index of the strength of a wrap film against tearing in the TD direction, which is initiated by the film being placed. In consideration of the Elongation tear resistance TD value and its relationship to ease-of-cutting, the TD value is preferably not greater than 10 g, more preferably not greater than 8 g, and yet more preferably not greater than 5 g.

[0082] As shown in Table 3, it was also confirmed that the addition of hydrogenated copolymer (B) and tackifier and stabilizer did to polypropylene resin for the purpose of adhesion improvement does not affect the heat resistance of the polypropylene resin when compared to a single layer film. Moreover, the heat resistant temperature of the film is nearly equal to the melting point of the matrix resin. The heat resistant temperatures of the films of the Examples of the present invention are higher than those of conventional polypropylene wrap films, and are comparable to those of the polyolefin-olefin films. The heat resistant temperatures of wrap films in which inner layers of polypropylene resin are combined between layers of the adhesive polypropylene resin composition are the same as the heat resistant temperatures of single-layered wrap films of polypropylene resin.

Industrial Applicability

[0072] The chlorine-free wrap film obtained from the polypropylene resin composition of the present invention has heat resistance equivalent to that of a wrap film made of only polypropylene resin. In addition, the wrap film of the present invention is non-sticky but is excellent with favorable adhesion. The film is stretched to thereby exhibiting wrap-
ing properties and has excellent transparency. Particularly, the film having an elongated tear substance of 10 gf or less exhibits remarkably favorable wrap-casting properties. Thus, a wrap film having an "wrap-casting property" which is an important property when a wrap film is used for a cardboard case and built in a film box, can be produced.

Claims

1. A polypropylene resin composition which comprises 80-99 parts by weight of a polypropylene resin (A) having a crystalline melting point of 135°C or higher; 1-10 parts by weight of a hydrogenated copolymer (B) of an aromatic vinyl compound and a conjugated diolefin; 0.1-50 parts by weight of polybutene (C) having a Maviscite viscosity of 10-5,000,000 cSt as measured at 57.8°C in accordance with JIS K8202; 0.1-50 parts by weight of a tackifier (D); and 0-4 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).
2. A polypropylene resin composition according to claim 1, wherein the hydrogenated copolymer (B) of the aromatic vinyl compound and the conjugated diolefin is a styrene-ethylene-butylene-styrene (SEBS) block copolymer.
3. A polypropylene resin composition according to claim 1 or 2, wherein the tackifier (D) is an olefinic substituted hydrocarbon resin.
4. A stretched film for packaging which is made of a polypropylene resin composition as recited in any one of claims 1 through 3.
5. A stretched film for packaging according to claim 4, which is biaxially stretched.
6. A horizontal stretched film for packaging comprising at least one outer surface layer formed of a stretched film for packaging as recited in claim 4.
7. A horizontal stretched film for packaging according to claim 6, wherein the inner layer is formed of a layer made of a polypropylene resin or resin composition comprising 70-100 parts by weight of a polypropylene resin (A) and 0-30 parts by weight of a hydrogenated copolymer (B) of an aromatic vinyl compound and a conjugated diolefin.
8. A stretched film for packaging according to any one of claims 4 through 7, which has an elongated tear substance in the TD direction of 10 gf or less.
9. A stretched film for packaging according to any one of claims 4 through 8, wherein the hydrogenated copolymer (B) of the aromatic vinyl compound and the conjugated diolefin is a styrene-ethylene-butylene-styrene (SEBS) block copolymer.
10. A polypropylene resin composition which comprises 80-100 parts by weight of a polypropylene resin (A) having a crystalline melting point of 135°C or higher; 0-8 parts by weight of a hydrogenated copolymer (B) of an aromatic vinyl compound and a conjugated diolefin; 0-50 parts by weight of polybutene (C) having a Maviscite viscosity of 10-5,000,000 cSt as measured at 57.8°C in accordance with JIS K8202; 0.1-50 parts by weight of a tackifier (D); and 0.01-1 part 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).
11. A polypropylene resin composition according to claim 10, wherein the polypropylene resin (A) is contained in an amount higher than 90 parts by weight up to 100 parts by weight, and the hydrogenated copolymer (B) of an aromatic vinyl compound and a conjugated diolefin is contained in an amount greater than 0 parts by weight but less than 1 part by weight (provided that the sum of the components (A) and (B) reaches 100 parts by weight).
12. A polypropylene resin composition according to claim 10 or 11, wherein the polybutene (C) comprises 0.1-10 parts by weight of a low-molecular-weight polybutene having a Maviscite viscosity of 10-50,000 cSt as measured at 57.8°C and the balance being a high-molecular-weight polybutene having a Maviscite viscosity of 50,000-

5,000,000 cSt, the total amount of the two polybutenes being 0-50 parts by weight.

13. A polypropylene resin composition according to claim 10 or 11, wherein the tackifier (D) is at least one species selected from petroleum resins.
14. A polypropylene resin composition according to claim 10 or 11, wherein the tackifier aid (E) is at least one species selected from waxes.
15. A stretched film for packaging made of a polypropylene resin composition as recited in any one of claims 10 through 14.
16. A stretched film for packaging according to claim 15, which is biaxially stretched.
17. A horizontal stretched film for packaging comprising at least one outer surface layer formed of a stretched film for packaging as recited in claim 15.

(54) CONSTRUCTION OF MULTILAYER FILM FOR CONTAINER SLERVE LABELS

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(73) Assignee: American Pulp Seal, Inc., Buckhannon, KY (US)

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

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(57) ABSTRACT

A multilayer sheet, which is particularly well adapted for use as a label above and below beverage containers, includes first and second substantially uniform layers of polymer compositions each comprising essentially of polyethylene, polypropylene and a compatibilizer agent. The polyethylene and polypropylene are in a weight ratio in the range of about 20/80 to 70/30, and the compatibilizer agent is in the amount of about 5% to 10% by total weight. A pigment is included in one or both of the substantially uniform layers. The polyethylene preferably is selected from the group consisting of polyethylene, polypropylene and mixtures thereof, and the compatibilizer agent preferably comprises a styrene-butadiene-glycidyl ether block copolymer. One of the substantially uniform layers is thicker and of higher strength than the other layer, while the other layer has a smooth uniform convex surface.

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Related U.S. Application Data

(62) Division of application No. 08/943,771, filed on Aug. 28, 1997, now Pat. No. 4,943,802.

(51) Int. Cl.⁷ B29C 47/00; B29C 47/02

(52) U.S. Cl. 264/146; 264/202.2; 264/202; 264/173.16; 264/173.18; 264/174.1; 264/211.12; 264/437

(53) Field of Search 264/146, 159, 264/173.16, 173.18, 174.1, 211.12, 211.12, 234, 237, 280.1, 282; 425/133.1, 380, 386.1

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25 Claims, 3 Drawing Sheets

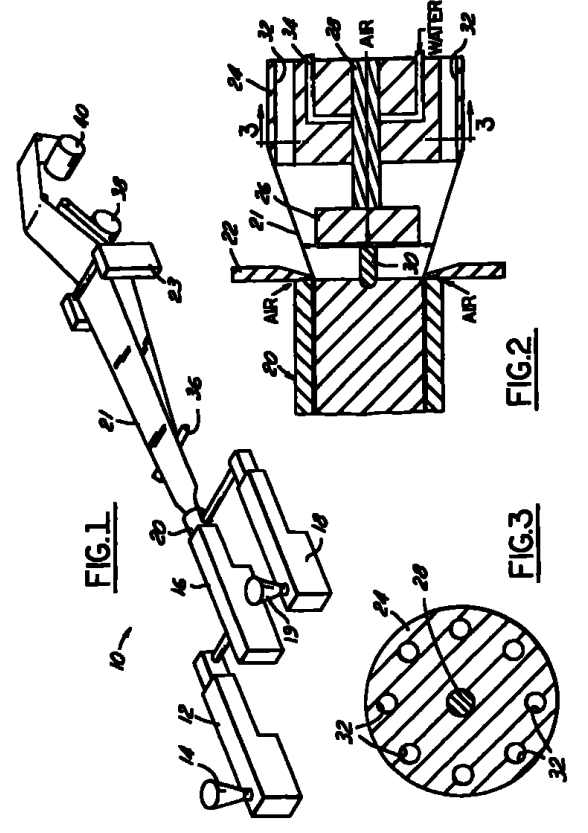
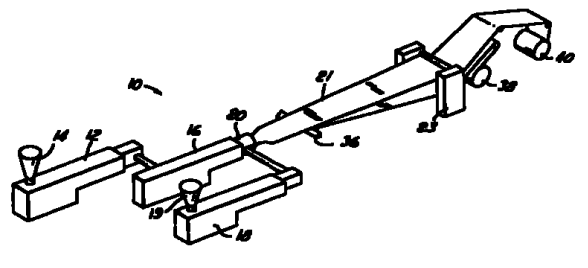
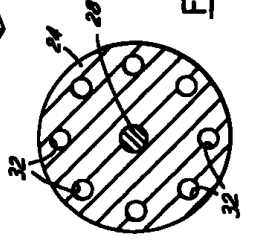
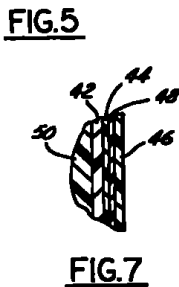
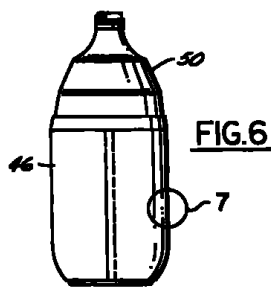
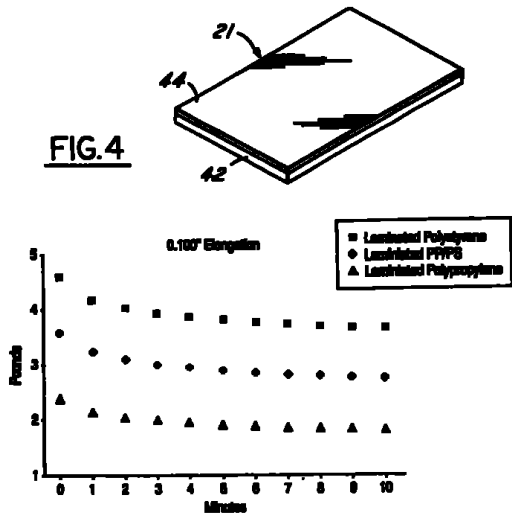


FIG. 2

FIG. 1

FIG. 3





CORRECTION OF MULTILAYER FILM FOR CONTAINER SLEEVE LABELS

This application is a division of application No. 08/919,771 filed Aug. 20, 1997, now U.S. Pat. No. 6,042, 987.

The present invention is directed to sleeve labels for beverage containers, and more particularly to a method and system for constructing an improved multilayer sheet for such sleeve labels.

BACKGROUND AND OBJECTS OF THE INVENTION

U.S. Pat. No. 5,303,664 assigned to the assignee hereof, discloses a method and apparatus for making a clear single-layer multilayer polypropylene film for use as a sleeve label. A sheet of extruded polypropylene containing an internal oil and a black pigments is extruded through an annular orifice and then stretched over a cooling mandrel. The film is stretched in both the machine direction and cross direction. The film may be formed into sheets with the machine stretch direction oriented circumferentially, and then sheeted into beverage containers.

It is well known that polyethylene, such as polyethylene and polypropylene, have better toughness and strength characteristics than polystyrene. However, polystyrene films exhibit superior to polyethylene in terms of stiffness and moduli. Efforts to overcome some of the limitations in properties of polyethylene, polypropylene in particular, have been to produce films or sheets with high levels of orientation in both machine and cross directions (biaxially oriented). Such techniques require substantial equipment investment and high capacity requirements.

Polypropylene is an amorphous material with excellent stiffness, cutting and stretching qualities. It can be biaxially or polyaxially with lamellae or other various-type modifying materials to increase its toughness and strength characteristics. It can also be oriented with a much lower equipment investment than biaxial orientation equipment for polypropylene. However, even by using intermediate amounts of liquid plasticizers or very expensive copolymers, the best film memory to make polypropylene stretch towards values for polypropylene and values required in some market applications. One example where stretch under a low force is desirable is with label stock for PET oriented beverage containers. Conventional beverages are bottled at low temperatures, around 50° F. Labels are applied to the containers after before or after filling with the beverage. These labels are wrapped around the containers in the machine direction such of the sheet, with the ends being overlapped and bonded by a hot melt adhesive. As the pressure created by carbonation makes the container expand, exerting a circumferential force on the container label. For example, a two liter bottle with carbonated content at typical carbonation levels can increase in diameter sufficiently to increase the circumferential diameter of the container 0.10 inches or more. The hot melt adhesives used in the beverage labeling industry are formulated for ease of processing, and typically do not possess high shear strength at room temperature. It is therefore necessary that the label be such as to stretch at a lower force level than the shear strength of the adhesives in order to accommodate expansion of the container without fracture at the label seam. This force level is typically less than five pounds. Label stocks of high impact polypropylene typically require in excess of five pounds to stretch the required 0.10 inches.

Polyethylene and polypropylene, usually incompatible, can be made compatible by use of a compatibilizer agent, such as a styrene-ethylene-butylene-styrene block copolymer. However, processing problems created by the nature of the blends of amorphous polypropylene and crystalline polypropylene have reduced commercial application of this technology. With a significant amount of polypropylene (above 60%) combined with polypropylene, the blend has a low melt strength that creates problems in extruding a sheet, particularly one that has a low caliper and is commercially unacceptably visible. The presence of the polypropylene also makes the extruded sheet sensitive to a condition known as swelling (similar to fish scales), which is an appearance that is undesirable as a beverage pattern with variable opacity.

It is therefore an object of the present invention to provide a multilayer sheet and method of manufacture adapted for use as a label sheet on containers that contains the desirable properties of polyethylene in terms of toughness and strength, and the desirable properties of polypropylene in terms of stiffness and moduli. Another object of the present invention is to provide a system and method for constructing a sheet film of polyethylene and polypropylene composition that are combined in a particular way that provides sheet labels having the desirable properties described above. A further object of the present invention is to provide a container for carbonated beverages having a sleeve label in accordance with the present invention as described above.

SUMMARY OF THE INVENTION

A multilayer sheet in accordance with a presently preferred embodiment of the invention, which is particularly well adapted for use as a label sheet on carbonated beverage containers, includes first and second substantially oriented layers of polymer composition containing essentially polyethylene, polypropylene and a compatibilizer agent. The polyethylene and polypropylene are in a weight ratio in the range of about 30/70 to 70/30, and the compatibilizer agent is in the amount of about 5% to 10% by total weight. A pigment is in the amount of about 10% to 15% by total weight may be included in one or both of the oriented layers. The polyethylene is selected from the group consisting of polyethylene, propylene/adipylene copolymers, propylene/adipylene copolymers, propylene/adipylene copolymers and mixtures thereof, and the compatibilizer agent preferably comprises a styrene-ethylene-butylene-styrene block copolymer or a styrene-isobutylene-styrene block copolymer. One of the oriented layers preferably is thicker and of higher strength than the other layer, while the other layer has a smooth surface exterior surface.

The constructed multilayer sheet preferably is fabricated by directing polymer material from first and second extrusion devices to an extension die in such a way that the polymer materials from the first and second extrusion devices exit the die as respective constructed first and second layers of a composite sheet. Strength and appearance properties of the constructed sheet are obtained by controlling temperature of the polymer materials as they enter the extension die such that the polymer materials from one extrusion device enter the die at a different temperature than that entering the extension die from the other extrusion device. In particular, the polymer material is cooled at one extrusion device so as to enter the die at a lower temperature than the material from the other extrusion device. This lower temperature greatly enhances the strength characteristics of the resulting sheet. To obtain desirable appearance qualities in the resulting sheet, the constructed first and second layers

are coated at different rates downstream of the extruder die. In particular, the layer of material that was coated prior to extrusion through the die is further coated downstream of the die at a slower rate than the other layer.

In the preferred embodiment of the invention, the sheet is extruded through an annular extruder die from which the layers exit as a composite coated film. Cooling air is directed onto the outer layer as the composite film exits the die, while cooling air is directed onto the inner layer at a position spaced downstream from the die in the direction of extrusion through the die. This delayed cooling of the inner layer after extrusion has been found to eliminate cooling in the inner layer. The extrusion process of the present invention preferably also includes stretching the film axially and circumferentially by pulling the film over a mandrel having a diameter greater than that of the extruder die while cooling the material to extract heat from the film. The film is cut circumferentially downstream of the cooling mandrel and wound into rolls of sheet material for further processing.

BRIEF DESCRIPTION OF THE DRAWINGS

The invention, together with additional objects, features and advantages thereof, will be best understood from the following description, the appended claims and the accompanying drawings in which:

FIG. 1 is a schematic diagram of a system for controlling a multilayer sheet in accordance with a presently preferred embodiment of the invention;

FIG. 2 is a cross-sectional view of an enlarged scale of a portion of the system illustrated in FIG. 1;

FIG. 3 is a cross-sectional view taken substantially along the line 3-3 in FIG. 2;

FIG. 4 is a perspective view of a multilayer sheet formed in accordance with the present invention;

FIG. 5 is a graph that illustrates a characteristic of the present invention;

FIG. 6 is an elevational view of a multilayer beverage container in accordance with a presently preferred embodiment of the invention; and

FIG. 7 is a fragmentary view on an enlarged scale of the portion of FIG. 6 within the circle 7.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

FIG. 1 illustrates a system 10 for forming a multilayer sheet adapted for use as a label shown on a container in accordance with a presently preferred embodiment of the invention. A first extruder extruder 12 extrudes material from a hopper 14 for making and adding the material, and directing the material at elevated temperature to a cooling extruder 16. A second or satellite extruder 18 has a hopper 19 for supplying raw material to be extruded, and feeds extruder 16 at elevated temperature to an annular extruder die 20. The extruder streams are directed through die 20 in such a way that the material from extruder 12, 16 forms an inner layer and the material from extruder 18 forms an outer layer of the extrudate 21 that flows through die 20.

An air ring 22 (FIG. 2) is disposed at the outlet of extruder die 20 for directing cooling air onto the outer layer of the extrudate 21 as the film exits die 20. The film is pulled by a nip roll 24 from die 20 over a cooling mandrel 26 (FIGS. 2 and 3) in such a way that the film is stretched both axially in a machine direction and circumferentially in a cross direction as the film flows from die 20 to mandrel 26. An inner air ring 28 is mounted on a shaft 30 that extends from

mandrel 26, and is spaced from the end of die 20 by a spacer 32. Ring 28 rotates cooling air, and directs the cooling air axially outwardly against the inner layer of film 21 as it passes, determined by spacer 32, downstream from die 20 and over ring 22. A circumferential array of passages 34 extend radially through mandrel 26 for passage of the air from ring 28 so that film 21 does not expand or inflate from air pressure. A passage 34 in mandrel 26 also provides for water-cooling of the mandrel. Downstream from mandrel 26, there is a nip roll 36 for cutting film 21 circumferentially across the film. From roll 36, the separated film edges extend to nip rolls 38, and thence to rollers 40, 42 for cutting the separated sheet into separate rolls.

The material components of the desired polymer formulation are mixed and fed to extruder 12, 16 by means of hoppers 14, 19. The rate of flow at extruder 12, 16 and at extruder 18 are related so as to provide the desired layer thicknesses at film 21 (FIGS. 1, 2 and 3). As noted above, the extruder from extruder 12, 16 forms the inner layer 48 of the multilayer film 21, while the material from extruder 18 forms the outer layer 44. Film 21 flows in a downstream direction as it emerges from extruder die 20 and is drawn over the mandrel. Another ring 22 closely adjacent to the extruder die provides laminar cooling air flow to the outer layer of the extrudate as it emerges from the die. Suitable controls for volume and temperature are used for the forced air cooling. Inner ring 22 applies controlled volume and temperature forced air cooling downstream from the die from mandrel 26 is placed with axial clearance and is highly polished. This axial smooth surface improves the surface of the film produced and contributes to control of web tension between the mandrel and pull nip rolls 38. In one implementation of the present invention, extruder 12 comprises a 418 inch (10.6 m) extruder, while extruder 16 comprises a 6 inch (15.2 cm) extruder. Extruder 18 is a 104 inch (2.6 m) extruder. Die 20 is a 104 inch extruder, also two-layer extruder die, while mandrel 26 is a 200 inch (5.08 m) cooling mandrel with a high finish smooth axial/draw surface. Inner ring 22 is located 36 inches (91.4 cm) downstream from the film of die 20, and the cooling water applied to mandrel 26 is maintained at 160° F. The mandrel and die are used to provide a stretch ratio (die diameter to mandrel diameter) of 1.75.

Extruder 18 is employed strictly to cool the melt from extruder 12, which will become too viscous. In one implementation of the invention, the melt from extruder 12 is at about 425° F., and is cooled to about 325° F. during passage through extruder 16 to die 20. While this cooling increases melt strength, it also has some negative effects on microstructure and appearance of the formed sheet. The second layer from extruder 18 is extruded on the outside of the inner film, and has a melt temperature of about 400° F. as it exits extruder 18 to die 20. This preferred temperature differential was achieved by trial and error employing the specific materials hereinafter described. Other temperature differentials may be suitable for other materials. The cooled inner layer with increased melt strength provides support for the hot outer layer. By extending the outer layer at elevated temperature, it develops the desired properties of glass and microstructure with uniform appearance over the surface of the processed inner layer.

It has also been found that further cooling of the processed inner layer must be accomplished at a slower rate after exit from extruder die 20, as compared with rapid cooling of the outer layer by ring 22. This lower cooling rate for the inner layer helps prevent cooling at the inner layer. Air ring 28 and mandrel 26 are closely axially aligned with extruder die 20.

In this way, air ring 28 is centered and equidistant from web 21 to total circumference. This also compensates the objective of providing a slower cooling rate for the inner layer due to being further away from the material than if air ring 28 was mounted on the opposing film of die 20, as is typical in the prior art. The leading or nose portion of mandrel 26 has a slight taper so that film 21 contracts the mandrel at a smaller diameter than the body of the mandrel. This helps ensure that the material will make better contact over the outer diameter of the mandrel, which then causes the tension needed between the mandrel and the pull nip rolls for achieving the desired amount of stretch in the web or multilayer direction. Changes in the temperature of the mandrel, by means of controlling temperature of water flowing through cooling passages 34, can be used to increase or decrease this web tension. Lower temperatures increase tension while higher temperatures decrease tension.

A number of tests have been run in implementation of the invention. In these tests, the rate of flow through extruder 12, 16, 18 was such as to provide a total material thickness of about 1.5 to 2.5 mils. It is preferred that the thickness of the inner layer be two to eight times the thickness of the outer layer. It is considered preferable to maintain layer 44 at a thickness of about 0.3 to 0.5 mil. A currently preferred composition has an inner layer 48 of about 1.2 mils thickness and outer layer 44 of about 0.3 mils thickness. The following materials were used: (1) Shell Chemical Co. 330000—A polypropylene copolymer having a melt flow rate of 7.0 g/10 min. and a melting point (by DSC) of 130° C.; (2) Hercules Chemical Co. 200—a general purpose polypropylene having a melt flow rate of 8.0 (condition G); (3) Shell Chemical Co. Krasen 1657—a linear styrene-ethylene-butylene copolymer block copolymer having a styrene-to-butylene ratio of 13 to 87 (Krasen D1102 would be a suitable block copolymer); (4) O'Neil TPO, which comprises containing 60% TPO, and 40% polypropylene. Formulations have been extended varying the weight ratio of polypropylene to polypropylene/copolymer from 30/70 through 40/60, 50/50, 60/40 to 70/30. To these blends, the Krasen copolymer and a kinetically selected polypropylene sheet. These sheets are low pump film-like materials suitable for use as substrates in laminated structures with clear polypropylene film for the embossed beverage market.

TABLE I

Material Properties, Extruded Sheet			
	Polypropylene	PP/PP Blend	Polypropylene
Color (bulk)	1.4	1.7	1.3
Shore D (DIN)	62	60	57
100° Yield (psi)	670	600	570
100° Elongation (%)	300	40	100
100° Modulus (psi)	200	200	200
100° Modulus (psi)	2.4	1.4	0.3
100° Modulus (psi)	4.4	1.4	2.4
100° Modulus (psi)	200	100	100
100° Modulus (psi)	20	10	20

TABLE I—continued

Material Properties, Extruded Sheet			
	Polypropylene	PP/PP Blend	Polypropylene
100° Modulus (psi)	2.4	1.4	0.3
100° Modulus (psi)	2.4	1.4	0.3
100° Modulus (psi)	2.4	1.4	0.3

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SEALANT FORMULATIONS CONTAINING HIGH VINYL CONTENT HYDROGENATED STYRENE-BUTADIENE-STYRENE BLOCK COPOLYMERS

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Int. Cl. C08C 26/02

U.S. Cl. 524/500; 524/501; 524/502

Field of Search: 524/500, 524/501, 524/502

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5,303,124 1997 Shaw et al. 5,600,000

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Shaffer, U.S. Pat. No. 5,777,043

Primary Examiner—Melissa L. Mearns
Assistant Examiner—D. Aylward
Attorney, Agent, or Firm—Donald W. Shaw

ABSTRACT

This invention provides sealant compositions which comprise a hydrogenated styrene-butadiene-styrene (SBS) block copolymer which has an overall weight average molecular weight of from 20,000 to 200,000, a styrene block weight average molecular weight of from 4,000 to 20,000, and a vinyl content of at least 40% by weight (% wt), preferably 45 to 60%, and an adhesion promoting resin. For every 100 parts by weight of copolymer, there should be at least 20 parts of adhesion promoting resin.

3 Claims, No Drawings

5,777,043

SEALANT FORMULATIONS CONTAINING HIGH VINYL CONTENT HYDROGENATED STYRENE-BUTADIENE-STYRENE BLOCK COPOLYMERS

FIELD OF THE INVENTION

This invention relates to sealant compositions for use as sealants against air and moisture, solvent-leaking, and other functions in construction, automotive, and consumer applications. More particularly, this invention relates to such compositions containing high vinyl content hydrogenated styrene-butadiene-styrene (SBS) block copolymers.

BACKGROUND OF THE INVENTION

There are at least two major classes in formulating a sealant composition. The sealant must possess some degree of shear resistance at high service temperatures. Additionally, the sealant should have a good wetting ability in the past so it can be easily coated on to various substrates.

Styrene-butadiene-styrene block copolymers are known to be useful for sealants because of their combination of strength and elastic properties. Hydrogenated versions of these polymers (HSBS) are especially useful because of their enhanced resistance to oxidation and chemical attack. These polymers give the compositions in which they are used excellent high temperature and chemical properties but they tend to be high in molecular weight and thus on high in viscosity that it is difficult to coat the sealant onto with them.

Other adequate sealant compositions have been made using some of the lower molecular weight polymers of this type but sealants in terms of high temperature properties must be accepted. The high styrene content in the higher molecular weight HSBS polymers are known to flow but give excellent high service temperature performance. Examples of copolymer sealants are the use of a lower molecular weight polymer and blending in a relatively low molecular weight polymer of this type. Thus it can be seen that it would be advantageous to be able to make an easily curable sealant composition and make or enhance the high temperature properties achievable with the higher molecular weight HSBS polymers.

This invention provides the advantages of both low molecular weight polymers and higher molecular weight polymers while maintaining their disadvantages. Using the high vinyl content polymers of the present invention in an adhesion application allows sealants with high service temperature properties which have a sufficiently low viscosity to be easily curable. The present invention in this art requires that high service temperatures and a modulus of application viscosity may be mutually exclusive for sealants. This invention provides a novel way to produce compositions which exhibit both of these characteristics.

SUMMARY OF THE INVENTION

This invention provides sealant compositions which comprise a hydrogenated styrene-butadiene-styrene (HSBS) block copolymer which has an overall weight average molecular weight of from 20,000 to 200,000, a styrene block weight average molecular weight of from 4,000 to 20,000, and a vinyl content of at least 45% by weight (% wt), preferably 45 to 60%, and an adhesion promoting resin such as tackifying resin, and, optionally, polyisoprene block reinforcing resin, flow promoting resin, and oil, polyethylene,

silicon, wax, and solvent. For every 100 parts by weight of copolymer, there should be at least 20 and preferably 25 to 50 parts by weight of resin.

The preferred structure for the block copolymers used herein is linear, i.e., B- α -B. However, block copolymers having branched, radial, and star structures may also be used in this invention. Such structures may be generally represented by the formula

B- α -B-Y

wherein B is a polymer block of styrene, B is a polymer block of hydrogenated butadiene, and Y is a coupling agent.

DETAILED DESCRIPTION OF THE INVENTION

The copolymers of these sealant compositions are polymer blocks of styrene. Other vinyl aromatic hydrocarbons could be used, including alpha-methyl styrene, various styryl-substituted styrenes, allyl-substituted styrenes, vinyl copolymers, vinyl monomers and the like.

The butadiene used herein must produce a polymer block with a high vinyl content. In other words, the percent of 1,3 addition of the butadiene should be at least 40% wt, preferably 45 to 60% wt. Below 40% wt, polymer viscosity is higher to commercial polymers and there is no advantage. Above 60% wt, the viscosity decreases but not a great amount and no longer drops with higher 1,3 content. Therefore, there is no further advantage.

As olefinic polymerization of conjugated diene hydrocarbons with various initiators is well known as described in U.S. Pat. Nos. 4,639,000 and No. 5,774,000 which disclose an improved method by which a polymerization composition with a composition, initiator, or polyfunctional initiator which initiates a living polymer backbone at each initiation site. Typical living polymer systems including polyfunctional conjugated diene hydrocarbons are

X-B-A-I

X-A-B-A-I

X-A-B-A-A-I

I-A-B-X-B-A-I

wherein B represents polyfunctional units of one or more conjugated diene hydrocarbons such as butadiene or isoprene. A represents polyfunctional units of one or more vinyl aromatic compounds such as styrene, X is the residue of a monofunctional initiator such as α -bromoisobutyrate, and Y is the residue of a difunctional initiator such as the diethylene of α -bromoisobutyrate and α -chloroisobutyrate. Such structures, including those providing to polyfunctional initiator or monofunctional initiator and a conjugated diene, generally have limited practical utility although known in the art.

The olefinic polymerization of the conjugated diene hydrocarbons is typically controlled with various methods such as olefinic or vinyl groups (1,3-diene) or olefinic or vinyl groups (1,3-diene) to obtain the desired amount of 1,3-addition. As described in U.S. Pat. No. 5,774,000 which is incorporated by reference herein, the level of 1,3-addition of a butadiene polymer or copolymer can greatly affect elastomeric properties after hydrogenation. The 1,3-addition of butadiene polymers significantly and completely influences the polymer as described above. A 1,3-addition of about 40% is obtained during polymerization at 50° C. with about 6% by volume of diisobutyl or about 200 parts of vinyl groups to the final mixture. A 1,3 addition of about 40% yields the

5.777.043

7
EXAMPLES

PP2220 is an HDPE block copolymer with a high vinyl content. Its molecular characteristics are compared with those of Polymer A, a commercial polymer whose viscosity is considered too high for most. If not all, commercial random copolymer, and others in Table 1 below. It can be seen that PP2220 and Polymer A are very similar except for the vinyl content: 30% of the random block of PP2220 is in a 1:3 alternation compared to 20% for Polymer A. The flow properties of PP2220 are drastically better than Polymer A as indicated by melt viscosity (more than an order of magnitude lower). Polymer B is the block copolymer of this type that is currently used to make random homopolymers commercially. The melt viscosity of the homopolymers of this invention, made with PP2220, is one-fifth of that of the homopolymers made with Polymer B while the SAFT and slump temperatures are the same. Similarly, PP2220 (70% 1:3 adding exhibits much lower melt viscosity than other Polymer A or B. PP2220 has an immediate level of 1:3 structure (47%), but is still mostly better (more) in melt viscosity than Polymer A or B. The last column clearly shows that the random copolymer can be added, prepared, and applied more easily than random with higher viscosity.

TABLE 1

Random Homopolymers				
Polymer	SAFT (sec)	HDPE Block Structure	1:3 Ratio	100%
A	25,000	10-20-10	20%	20,000
PP2220	25,000	10-20-10	30%	20,000
B	25,000	1:3-20-1:3	20%	20,000
PP2220	25,000	1:3-20-1:3	30%	20,000
PP2220	25,000	1:3-20-1:3	30%	20,000

TABLE 2

Random Homopolymers			
Polymer	SAFT (sec)	HDPE Block Structure	1:3 Ratio
A	25,000	10-20-10	20%
PP2220	25,000	10-20-10	30%

TABLE 2-continued

Random Homopolymers			
Polymer	SAFT (sec)	HDPE Block Structure	1:3 Ratio
A	25,000	10-20-10	20%
PP2220	25,000	10-20-10	30%

Temperature dependent properties, such as those obtained from temperature (SAFT) and slump temperature, and melt viscosity were measured. A Brookfield Viscometer model RVTD and spindle 20 was used to measure the viscosity at 177° C. To measure the slump temperature, the random homopolymers were prepared and allowed to solidify in steel channels with the following dimensions: 2.5 cm wide, by 2.5 cm high, and 1.25 cm deep. The channels were placed vertically in an oven and the temperature was raised to 5°C increments, allowing the sample to equilibrate for 20 minutes at each temperature before measuring the temperature again. The slump temperature was the temperature at which the sample sagged more than 1/4 inch in the channel. SAFT was determined on a top-down load of 2.5 g/cm² on an aluminum surface under a load of 100 g. The temperature was raised up from 40° C. to 5° C. increments every 10 minutes until bond failure occurred.

No claim

1. A high service temperature random copolymer which comprises:

(a) 100 parts by weight of a hydrogenated symmetrical random copolymer block copolymer which has an overall weight average molecular weight of from 20,000 to 200,000, a symmetrical block weight average molecular weight of from 4000 to 20,000, and wherein the glass block has a vinyl content of 40% to 90% by weight, and

(b) at least 20 parts by weight of an ethylene propylene resin.

2. The random copolymer of claim 1 wherein the ethylene propylene resin is present in an amount of from 20 to 400 parts by weight per 100 parts of copolymer.

3. The random copolymer of claim 1 wherein the overall weight average molecular weight is from 40,000 to 200,000 and the symmetrical block molecular weight is from 5,000 to 20,000.

116

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02004008.0 24 October 2002 (24.10.2002) EP

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valls-la-Merle (FR).

(82) Designated States (optional) AR, AU, AT, AM, AZ, AX, AZ, BA, BB, BG, BR, BY, BE, CA, CH, CN, CO, CR, CU, CY, CZ, DE, DK, DM, DO, EC, EE, EG, ES, FI, FR, GB, GR, GT, HK, HU, IL, IN, JP, KE, KG, KH, KR, KZ, LA, LB, LI, LU, LV, LY, MA, MD, MG, MK, MN, MW, MY, NZ, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, RO, RU, SA, SD, SE, SG, SI, SK, SL, SV, TH, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(83) Designated States (optional) ARIPO patent (CH, CN, DE, ES, FR, GB, GR, HU, IL, IN, JP, KE, KG, KR, KZ, LA, LB, LI, LU, LV, LY, MA, MD, MG, MK, MN, MW, MY, NZ, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, RO, RU, SA, SD, SE, SG, SI, SK, SL, SV, TH, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW).

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13 April 2004

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.

(58) Title BLOCKCOPOLYMER COMPOSITIONS, HAVING IMPROVED MECHANICAL PROPERTIES AND PROCESSABILITY

(57) Abstract A composition to be used for the manufacture of films, sheets, melt blown or spun bond non-wovens or cast or blown films, comprising at least 50 wt% of a styrene block copolymer; a polyethylene in an amount of from 10 to 30 wt% with a melt which is compatible with the polyethylene block in the styrene block copolymer in an amount of at least 5 wt%, and a male which is compatible with the hydrogenated polyethylene block in the styrene block copolymer in an amount of at least 3 wt%, wherein all weight percentages are relative to the weight of the complete composition; styrene block copolymer to be used thereby, and films, melt blown or spun bond non-wovens or cast or blown films prepared from it.

INTERNATIONAL SEARCH REPORT

Int. Application No.
PCT/EP 02/00277

IPC 7th Class. C08F 297/04 B32B 3/00

According to International Patent Classification (IPC) or to both national classification and IPC

5. FIELDS OF CLASSIFICATION

Classifications searched (Mandatory system indicated by classification symbol)
IPC 7th Class. C08F 297/04 B32B 3/00

Documentation examined other than abstracts (indicate in the column that each document was included in the table searched)

Documents that have been examined during the international search phase of this process, where practical, must be cited

EPO-Internal, MPI Data, PAJ

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7. Further documents are listed in the classification of item 5.

8. Patent family members are listed in annex.

9. Special categories of cited documents:

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- * Document relating to an oral disclosure, use, exhibition or other activity
- * Document published only in the international language but not in the national language

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Date of the cited completion of the international search

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Hammann, A

Form PCT/ISA (Form dated 1 July 2003)

INTERNATIONAL SEARCH REPORT		
PCT Application No. PCT/EP 03/08277		
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Form PCT/ISA/210 (Continuation of Form 1) (July 1993)

INTERNATIONAL SEARCH REPORT	
PCT Application No. PCT/EP 03/08277	
Section I: Observations where certain claims were found unsearchable (Continuation of Form 1 of first sheet)	
This International Search Report has not been established in respect of certain claims under Article 17(2)(b) for the following reasons:	
1. ☐ Claims Nos.:	
because they relate to subject matter not required to be searched by this Authority, namely:	
2. ☐ Claims 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. ☐ Claims Nos.:	
because they are dependent claims and are not drafted in accordance with the manual and third editions of Rule 8.4 App.	
Section II: Observations where unity of invention is lacking (Continuation of Form 2 of first sheet)	
This International Searching Authority found multiple inventions in this International Application, as follows:	
see additions? 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 available claims could be searched without effect 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.:	
1-6	
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is submitted in the form in which it was received in the International Application, it is covered by claims Nos.:	
Remarks on Patent	
☐ 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 Form 1) (July 1993)

INTERNATIONAL SEARCH REPORT

International application No. PCT/EP 03/00277

International application No. PCT/EP 03/00277

FURTHER INFORMATION CONTAINED FROM PCT/DA/ 210

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

1. Claims: 1-5

A composition suitable for the manufacture of fibres, filaments, melt blown or spun bond non-wovens or cast or blown films. The said composition comprising at least 60 wt.% of a styrenic block copolymer of either molecular structure S-EB-S ... (1), or of molecular structure (S-EB)MI ... (2) as described in the application claim 1; 10-30 wt.% of a polyolefin; at least 5 wt.% of a resin which is compatible with the polystyrene blocks; at least 3 wt.% of a resin which is compatible with the hydrogenated polybutadiene blocks.

2. Claim: 6

Fibres, filaments, melt blown or spun bond non-wovens or cast or blown films, derived from a composition according to any one of the claims 1 to 5.

3. Claims: 7-10

A styrenic block copolymer product as described in application claims 7-10.

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	IN EP/PCOM European Patent Office P.O. Box 3700 1000 BR Amsterdam PAYS-BAS	European Patent Office Description I Claims I Drawings I	European Patent Office Description II Claims II Drawings II
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Applicant No. 03 701 508 8 - 1000	Ref. L000485F42	Date 08.12.2005
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Communication pursuant to Article 86(2) EPC

The examination of the above-identified application has revealed that it does not meet the requirements of the European Patent Convention for the reasons indicated hereafter. If the deficiencies indicated are not rectified the application may be refused pursuant to Article 87(1) EPC.

You are invited to file your observations and counter as the deficiencies are such as to be ascertainable, to correct the indicated deficiencies within a period

of 4 months

from the notification of this communication, this period being computed in accordance with Rules 79(2) and 80(2) and (4) EPC.

One set of amendments to the description, claims and drawings is to be filed within the said period on separate sheets (Rule 36(1) EPC).

Failure to comply with this invitation in due time will result in the application being deemed to be withdrawn (Article 86(2) EPC).



Harmann, A
Primary Examiner
for the Examining Division

Enclosure(s): 3 page(s) reasons (Form 8908)

Registered Letter
no further action

	Revised/Updated (Antep) Date 08.12.2005	Communication/Notice (Form) Ref. 1	Notification/Notice-sent (Form) Applicant No. 03 701 508 8
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The examination is being carried out on the following application documents:

Description, Pages

1-13 as originally filed

Claims, Numbers

1-8 as originally filed

1. The following documents are referred to in this communication ; the numbering will be adhered to in the rest of the procedure :

- D1 WO/2000/02237
- D2 US/5,333,533
- D3 EP/1,081,089
- D4 US/6,429,077
- D5 WO/2001/08239
- D6 US/6,408,853

US 5,777,043
US 5,364,964

Article 87(1) EPC

2. The present application does not appear to meet the requirements of Article 87(1) EPC because the present application is considered to describe the same invention as disclosed in D1. D1, also assigned to the same applicant as the present application, claims the priority of 60/237,533 US of 4/10/2000. Thus the present application does not have the right to claim the priority date of 31/1/02, because it is not the first application for the claimed subject-matter. Therefore the valid date for the present application appears to be its date of filing, that is 13/1/03. This consideration means that the document D1, published on 11/4/02, forms part of the state of the art pursuant to Articles 54(2) and 56

EPC Form 8908 of 02/00

	Examined/Notexamined (Language)	Communicated/Notcommunicated (Form)	Notified/Notnotified (Form)
	Examination Date 08.12.2005	Examination Result 2	Notification No.: 03 701 508.0 Date of Notification

EPC against all of the present claims that are the same invention as that disclosed in D1. This situation is also considered to be valid for D8.

Article 52 EPC

3. As previously communicated with the invitation to pay additional fees attached to the original search report for the present subject-matter, the present application claims contain several inventions (claims 1-3 ; claim 4 ; claims 5-6) for the reasons as previously outlined in the said invitation and lack of unity extra sheet(s), and consequently the applicant was invited to choose which of the further said inventions he wished to pursue. The applicant decided to pay the additional fees for the further invention relating to application claim 4, and consequently the application claims 1-4 are examined herein.

Article 54 EPC

4. The present application does not meet the requirements of Article 52(1) EPC because the subject-matter of claims 1-4 is not considered to be novel in the sense of Article 54(1) and (2) EPC.

(a) D1 is considered to disclose a composition comprising a styrenic block copolymer as described in the application claim 1.
The disclosures of D1 (page 2, line 30 - page 3, line 2 ; claims 1-8 ; page 5, line 16-32 ; page 4, line 29 - page 5, line 16 ; examples ; page 10, line 22-23 ; page 6, line 22 - page 8, line 5 ; claim 6) are considered to be novelty-attacking for the subject-matter of present claims 1-4.
The disclosures of D2 (column 7, line 30, particularly "films, sheets" ; column 1, line 81 - column 2, line 1 ; column 2, line 31-38 ; column 3, line 8-12, 40-44 ; column 3, line 66 - column 4, line 6 ; abstract ; column 7, line 44-48,51-58) are considered to be novelty-attacking for the subject-matter of present claims 1-4.
The disclosures of D3 (claims 1,2,4,3-17, particularly films and laminated films ; page 4, line 9-31, 42-57 ; page 2, line 1-3 ; abstract) are considered to be novelty-attacking for the subject-matter of present claims 1-4.
The disclosures of D4 (abstract ; claims 1-5 ; column 5, line 41-43) ; D5 (abstract, particularly elastic films ; claims 1,3 ; page 2, line 11,12) ; D6 (abstract ; claims 7,8,10 ;

	Examined/Notexamined (Language)	Communicated/Notcommunicated (Form)	Notified/Notnotified (Form)
	Examination Date 08.12.2005	Examination Result 3	Notification No.: 03 701 508.0 Date of Notification

column 5, line 43-45) are considered to be novelty-attacking for the subject-matter of present claims 1-4.

5. To meet the requirements of Rule 27(1)(b) EPC, the documents D1-D6 should be identified in the description and the relevant background art disclosed therein should be briefly discussed.

6. In order to facilitate the examination of the conformity of the amended application with the requirements of Article 123(2) EPC, the applicant should clearly identify the amendments carried out, irrespective of whether they concern amendments by addition, replacement or deletion, and to indicate the passages of the application as filed on which these amendments are based (see Guidelines E-4, 1).

If the applicant regards it as appropriate these indications could be submitted in handwritten form on a copy of the relevant parts of the application as filed.

Revised/Revised (Page)		Comments/Comments (Page)		Revised/Revised (Page)	
	18.04.2006	2	2	18.04.2006	3
	18.04.2006				

3. The present application does not meet the requirements of Article 57(1) EPC because the present application appears to describe the same invention as disclosed in D1. D1, also assigned to the same applicant as the present application, claims the priority of 04.10.2000. Thus the present application does not have the right to claim the priority date of 31.01.02, because it is not the first application for the claimed subject-matter. Therefore the valid date for the present application appears to be its date of filing, that is 13.01.03. This consideration means that the document D1, published on 11.04.02, forms part of the state of the art pursuant to Articles 54(2) and 56 EPC against all of the present application claims that are the same invention as that disclosed in D1.

Article 54 EPC

4. The present application does not meet the requirements of Article 52(1) EPC because the subject-matter of application claims 1-8 is not considered to be novel in the sense of Article 54(1) and (2) EPC.

(a) D1 is considered to disclose a composition as described in the application claim 1. The disclosure of D1 (page 2, line 16-25; page 6, line 22; page 8, line 10 - page 8, line 5; page 8, line 11 - page 10, line 25; claims 1-8; examples; page 1, line 8-20; page 6, line 26-32; claim 8) are considered to be novelty-attacking for the subject-matter of the present application claims 1-4. The disclosure of D2 (column 7, line 30; column 1, line 61 - column 2, line 1; column 2, line 31-38; column 3, line 9-12, 40-44; column 8, line 22-33; column 10, line 61 - column 12, line 20; column 3, line 55 - column 4, line 8; column 7, line 44-60) are considered to be novelty-attacking for the subject-matter of the present application claims 1-8. The disclosure of D3 (page 2, line 11-12; claims 1-7; abstract; page 33, line 32; page 1, line 21-22; page 34, line 19 - page 36, line 24) are considered to be novelty-attacking for the subject-matter of the present application claims 1-8. The disclosure of D4 (page 6, line 2-5; page 2, line 28-54; page 3, line 64-68; page 4, line 29-34; page 4, line 41 - page 6, line 58) are considered to be novelty-attacking for the subject-matter of the present application claims 1-5.

5. To meet the requirements of Rule 27(1)(b) EPC, the documents D1-D4 should be identified in the description and the relevant background art disclosed therein should be

Revised/Revised (Page)		Comments/Comments (Page)		Revised/Revised (Page)	
	18.04.2006	3	3	18.04.2006	3
	18.04.2006				

briefly discussed.

6. In order to facilitate the examination of the conformity of the amended application with the requirements of Article 123(2) EPC, the applicant should clearly identify the amendments carried out, irrespective of whether they concern amendments by addition, replacement or deletion, and to indicate the passages of the application as filed on which these amendments are based (see Guidelines E-4, 1).

If the applicant regards it as appropriate these indications could be submitted in handwritten form on a copy of the relevant parts of the application as filed.

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

(19) World Intellectual Property
Organization
International Bureau



1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100
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(43) International Publication Date
7 August 2003 (17.08.2003)

PCT

(14) International Publication Number
WO 2003/064527 A3

(11) International Patent Classification
C07C 21/04, B01J 23/04

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(74) Agents: KRATON POLYMERS COMPANY, INC.,
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Durham, N.C. 27701. (75) Agents: KRATON POLYMERS COMPANY, INC.,
DURHAM, N.C.; Legal Department, 100
Durham, N.C. 27701.

(21) International Application Number:

1571-2002-00017

(22) International Filing Date: 13 January 2023 (13.01.2023)

(20) Family Language

Keywords: *Self-esteem, self-worth, self-esteem threat, self-esteem threat response, self-esteem threat response strategies, self-esteem threat response strategies, self-esteem threat response strategies*

000 Publication Language:

[illegible]

Case	Priority Date	31 January 2022 (31.01.2022)	31 October 2022 (31.10.2022)
80973463.6		EP	
82028678.8		EP	

2

ALA, LA, MW, MX, MD, ME, MI, TN, UT, VM, SW,
 Kansas point (AM, AZ, WY, SD, ND, MO, IL, TX, TN),
 Missouri point (AT, AR, NC, CH, CY, CL, DE, DR, SE,
 MS, FL, HI, OR, OH, NJ, NY, VT, LI, MA, RI, PT, ME, N.
 SK, TH, GA) point (BP, BI, CP, OL, CI, CM, GN, ON,
 OJ, OV, MT, MR, NE, NW, TO, TD).

References

- with international search report
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

(10) Date of publication of the international trends reports
15 April 2004

For two-letter codes and other abbreviations, refer to the "Child-care Notes on Codes and Abbreviations" appearing at the beginning of each number issue of the NCT Gazette.

**194 Thin BLOCKCOPOLYMER COMPOSITES, HAVING IMPROVED MECHANICAL PROPERTIES AND PROCESS-
ABILITY**

(377) *Aluminis*. A composition to be used for the manufacture of films, elements, melt blown or spun head non-wovens or wet or blown films, comprising at least 50 parts by weight of a styrenic block copolymer; a polyolefin in an amount of from 10 to 30 parts by weight which is compatible with the polyolefin(s) blocks in the styrenic block copolymer in an amount of at least 5 parts, and a resin which is compatible with the hydrocarbon polybutadiene blocks in the styrenic block copolymer in an amount of at least 3 parts, wherein all weight percentages are relative to the weight of the complete composition; styrenic block copolymer(s) to be used flexible and linear, melt blown or spun head non-wovens or wet or blown films. (See paragraph 369.)

INTERNATIONAL SEARCH REPORT

PCT/EP 03/00277

6. CLASSIFICATION OF SUBJECT MATTER
 TYPE 7 CODE 13/02 CITE 297/04 R33827/31

According to International Patent Classification (IPC) codes, both national applications and PCT

Medium	domesticated	reared	Identification	Specimen	Collected by	domesticated	reared
IPC 7	COAL	COOD	COOJ	COOE	COOK	BLVD	0001

Before the 1990s, the only way to get a copy of a document was to go to the National Archives and Records Administration (NARA) and request it. This was often a tedious process, and the cost of obtaining a copy could be high. The 1990s brought a revolution in the way we access information. The Internet became a powerful tool for research, and the National Archives and Records Administration (NARA) began to make its collections available online. This was a significant step forward, but it was not until the 2000s that the process became truly accessible to the general public. The National Archives and Records Administration (NARA) began to digitize its collections, and the cost of obtaining a copy dropped significantly. This was a major breakthrough, and it allowed millions of people to access the documents of our nation's history. The 2000s also brought a new wave of interest in the documents of our nation's history. The 9/11 attacks, the Iraq War, and the financial crisis of 2008 all led to a renewed interest in the documents of our nation's history. This was a good thing, as it allowed us to learn from the mistakes of the past and to better understand the events that shaped our nation. The 2010s brought a new wave of interest in the documents of our nation's history. The 2012 election, the 2013-2014 government shutdown, and the 2015-2016 election all led to a renewed interest in the documents of our nation's history. This was a good thing, as it allowed us to learn from the mistakes of the past and to better understand the events that shaped our nation. The 2020s brought a new wave of interest in the documents of our nation's history. The 2020 election, the 2021-2022 government shutdown, and the 2023-2024 election all led to a renewed interest in the documents of our nation's history. This was a good thing, as it allowed us to learn from the mistakes of the past and to better understand the events that shaped our nation.

Remember this: **no smoking** during the interview! **no use of cell phones** and, when possible, **avoid heavy use**

EPP-Internal, MPI Data, PA

5. DOCUMENTS CONTAINED TO BE RELEASED:

Category	Details of document, citation, abstract, where appropriate, of the relevant passages	Relevant to claims 1-6
P, X	WD 02 28065 A (KRAYON POLYMERS RES B V HUBBARD DALE INC (US); KRAYON LYE KRON) 11 Apr 11 2002 (2002-04-11) * (same applicant, same invention - invalid application priority date); pg.2, line 10-25; pg.6, line 22; pg.6, line 10- pg.8, line 5; pg.8, line 11-pg.10, line 25; claims 1-6; examples; pg.1, line 9-20 * page 6, line 28-32; claim 8	1-6
X	US 5 346 984 A (SHIBATA TOGURU ET AL) 13 September 1994 (1994-09-13) * column 7, line 30; column 1, line 61-column 2, line 1; column 2, line 31-38; column 3, line 9-12, 40-44; column 9, line 22-33; column 10, line 61-column 12, line 80; column 3, line 65-column 4, line 50 column 7, line 44-50	1-6

-/-

7 Further discuss the role of the state in the construction of law.

FIGURE 1 Present study's conclusions are linked to common

• **Specialized training of staff**

- | | |
|--|---|
| <p>"1 document relating to the personal data of the individual in question</p> <p>"2 other document not published on or after the International Day of the Girl</p> <p>"3 document which may have caused an offence against the person in question or which may have caused an offence against the person in question</p> <p>"4 document relating to an offence, a crime, a violation or other crime</p> <p>"5 document relating to the International Day of the Girl</p> <p>"6 document relating to the International Day of the Girl</p> | <p>"7 document relating to the personal data of the individual in question</p> <p>"8 other document not published on or after the International Day of the Girl</p> <p>"9 document which may have caused an offence against the person in question or which may have caused an offence against the person in question</p> <p>"10 document relating to an offence, a crime, a violation or other crime</p> <p>"11 document relating to the International Day of the Girl</p> <p>"12 document relating to the International Day of the Girl</p> |
|--|---|

Rate of the actual production of the finished goods

2 February 2004

1202 04

Name and mailing address of the RIA
 Hampton Police Chief, P.O. Box 10000
 JR - 2000 HW Road
 Tel. (410) 386-0000, Tel. 01 000 0000,
 Fax 01 01 000 0000

Hammond, A.

INTERNATIONAL SEARCH REPORT		
I (International Application No. PCT/EP 03/06277)		
A (Classification) International Classification to the extent possible		
Category	Number of documents, with indication of the nature of the documents	Relevant to classification
X	WO 01 08239 A (ESREALLY CALVIN P; PHARMAS REFFORD A (US); HO THOI H (US); PATEL R) 8 February 2001 (2001-02-08) * page 2, line 11-12; claim 1-7; abstract; page 33, line 32; page 1, line 21-22; page 34, line 19 - page 35, line 24	1-6
X	EP 0 863 183 A (SHELL INT RESEARCH) 9 September 1998 (1998-09-09) * page 6, line 2-5; page 2, line 29-54; page 3, line 54-56; page 4, line 29-34; page 4, line 41 - page 5, line 38 *	1-6
Y	US 4 970 259 A (MITCHELL NEIL F ET AL) 13 November 1990 (1990-11-13) * claim 1-15; column 3, line 1-9; column 4, line 29-38; 42-46; examples *	1-6
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A	EP 0 854 340 A (SHELL INT RESEARCH) 27 January 1998 (1998-01-27) * claims 1-10; abstract *	1-6
A	US 6 042 907 A (BLACKWELDER MAURICE W ET AL) 28 March 2000 (2000-03-28) * abstract; claims 1-5; column 5, line 41-43	1-6
A	EP 0 413 262 A (KIMURA CO) 20 February 1991 (1991-02-20) * abstract; page 3, line 1-50	1-6
A	EP 0 822 227 A (SHELL INT RESEARCH) 4 February 1998 (1998-02-04) * page 2, line 46-56; page 3, line 1-6; table 1 *	1-6
A	US 5 627 236 A (HINES GLENN R) 6 May 1997 (1997-05-06) * column 1, line 10-13; column 1, line 60 - column 2, line 5; column 2, line 68-69; abstract; table 1	1-6

Form PCT/ISA/210 (pre-2000) (July 1999)

INTERNATIONAL SEARCH REPORT	
I (International Application No. PCT/EP 03/06277)	
Section I: Observations relevant to certain claims which are 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)(b) for the following reasons:	
1. ☐ Claims Nos.:	because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims 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. ☐ Claims Nos.:	because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).
Section 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 claimable claims.	
2. ☐ As all available 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.:	1-6
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention that recited in the claims; it is covered by claims Nos.:	
Presented as Prior Art	☐ The additional search fees were accompanied by the applicant's protest. ☒ No protest accompanied the payment of additional search fees.

Form PCT/ISA/210 (pre-2000) (July 1999)

International Application No. PCT/EP 03/20277

FURTHER INFORMATION CONTAINED FROM PCT/EP 210

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

1. Claims: 1-5

A composition suitable for the manufacture of fibres, filaments, melt blown or spun bond non-wovens or cast or blown films. The said composition comprising at least 50 wt.% of a styrenic block copolymer of either molecular structure S-EB-S ... (1), or of molecular structure (S-EB)nI ... (2) as described in the application claim 1; 10-30 wt.% of a polyolefin; at least 5 wt.% of a resin which is compatible with the polystyrene blocks; at least 3 wt.% of a resin which is compatible with the hydrogenated polybutadiene blocks.

2. Claim: 6

Fibres, filaments, melt blown or spun bond non-wovens or cast or blown films, derived from a composition according to any one of the claims 1 to 5.

3. Claims: 7-10

A styrenic block copolymer product as described in application claims 7-10.

INTERNATIONAL SEARCH REPORT

1. Inventor's Name
PL/1/EP 03/20277

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From PCT/EP 03/20277 (patent family name) (only 1000)

INTERNATIONAL SEARCH REPORT				Patent Application No. PCT/EP 03/00277	
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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 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 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.

133



WO 02/28965 A1