EXHIBIT V

PART 2

2

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE 08/544497 A

"Express Mail" mailing label number TB192922488US
Date of Deposit October 18, 1995
I hereby certify that this paper or fee is being deposited with the United States Postal Service with sufficient postage "Express Mail Post Office to Addressee" service under 37 CFR 1.10 on the date indicated above and is addressed to the Commissioner of Patents and Trademarks, Washington, D.C. 20231
Stephen P. Krupp
(Typed or printed name of person mailing paper or fee)
(Signature of person mailing paper or fee)

#2/Pre A 01/23/96 JCJ

Docket No. C-40,121-AU
Anticipated Classification of this Application:
Class 526 Subclass ___
Prior Application:
Examiner David Wu
Unit 1505

MAIL ROOM OCT 18 25 1995 PAT. & TRADEMARK OFFICE

Commissioner of Patents and Trademarks
Washington, D.C. 20231

This is a request for filing a ☒ continuation) divisional)
application under 37 CFR 1.60 and claiming benefit under 35 USC 120
of pending prior application Serial No. 08378,998
filed on January 27, 1995 of Pak-Wing Steve Chum; Ronald P. Markovich; George W. Knight, Shih-Yaw Lai
for FABRICATED ARTICLES MADE FROM ETHYLENE POLYMER BLENDS

1. ☒ Enclosed is a copy of the prior application, including the oath or declaration as originally filed
2. ☐ Cancel in this application original claims _____ of the prior application before calculating the filing fee.
3. ☒ The filing fee is calculated below

For	Number Filed		Number Extra		Rate	Basic Fee $750.00
Total Claims	30	- 20 =	10	x	$ 22.00 =	220
Independent Claims	4	- 3 =	1	x	$ 78.00 =	78
Multiple Dependent Claims Presented					$250.00 =	
Total Filing Fee					=	$ 1,048

4. ☒ The Commissioner is hereby authorized to charge any fees which may be required, or credit any overpayment, to Account No. 04 1512. This sheet is enclosed in duplicate

5. ☒ Amend the specification by inserting after Title of the Invention | Cross Reference to Related Application | This is a ☒ continuation divisional of application Serial No. 08378,998 filed January 27, 1995 now abandoned which is

A1

1/30/96

6. ☐ Transfer the drawings from the prior application to this application and abandon said prior application as of the filing date accorded this application. A duplicate copy of this sheet is enclosed for filing in the prior application file. (May only be used if signed by person authorized in Rule 138 and before payment of base issue fee.)

7. ☒ New drawings are enclosed

8. ☒ The prior application is assigned to The Dow Chemical Company by virtue of an unrecorded assignment
☐ The prior application is assigned of record to _____ and is recorded at Reel No _____ Frame No _____

9. ☒ The inventorship of this application is the same as that of the prior copending U.S. application
Fewer inventors are to be named in this application than in the prior copending U.S. application. Delete _____ as inventor(s) in this application

10. ☒ The Power of Attorney in the prior application is to STEPHEN P. KRUPP, Reg. No. 34,366, L. Wayne White, Reg. No. 25,415, Glenn H. Korfhage, Reg. No. 27,204, Richard G. Waterman, Reg. No. 20,128
Please address all communications to Osborne K. McKinney, 2301 Brazosport Blvd., B-1211; Freeport, Texas 77541
a. ☒ The power appears in the original papers in the prior application
b. ☐ The power does not appear in the original papers. A copy of the power in the prior application is enclosed
c. ☒ Recognize as Associate Attorney Osborne K. McKinney whose Registration No. is P-40,084 and whose phone number is (409) 238-7889

11. ☐ A Preliminary Amendment is enclosed. (Claims added by this amendment have been properly numbered consecutively beginning with the number next following the highest numbered original claim in the prior application.)

12. ☐ A new Disclosure Statement is enclosed
☐ Applicant(s)' Disclosure Statement is as filed with the parent application (copy attached)

13. ☒ I hereby verify that the attached papers are a true copy of prior application Serial No. 08/378,998 as originally filed on January 27, 1995, with the exception that the attorney's docket number in the lower left-hand corner of each page has been adjusted to reflect the instant application.

The undersigned declares further that all statements made herein of his/her own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements may jeopardize the validity of the application or any patent issuing thereon

10-18-95

Stephen P. Krupp
Registration No. 34,366
Phone 409-238-7889

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PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

GROUP 1500 FEB 14 1996

Applicants: Pak-Wing Steve Chum, et al.

Serial No.: 08/544,497
Filed: October 18, 1995
Attorney Docket No.: C-40,121-AU

Art Unit: 1505
Previous Examiner: D. Wu

For: FABRICATED ARTICLES MADE FROM ETHYLENE POLYMER BLENDS

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HEREBY CERTIFY THAT THIS CORRESPONDENCE IS BEING DEPOSITED WITH THE UNITED STATES POSTAL SERVICE AS FIRST CLASS MAIL WITH SUFFICIENT POSTAGE IN AN ENVELOPE ADDRESSED TO: COMMISSIONER OF PATENTS AND TRADEMARKS, WASHINGTON, D.C. 20231, on February 2, 1996
DATE OF DEPOSIT

Jan Alverson
PRINT OR TYPE NAME OF PERSON SIGNING CERTIFICATE

Jan Alverson
SIGNATURE OF PERSON SIGNING CERTIFICATE

2-2-96
DATE OF SIGNATURE

Hon. Commissioner of Patents & Trademarks
Washington, D.C. 20231

Sir:

FIRST PRE-EXAMINATION AMENDMENT

Prior to examination of the above-identified continuation application, Applicants respectfully request entry and consideration of the following:

In the Specification:

Page 1, line 3, after the words "number 07/776,130," please insert the words -- now USP 5,272,236, -- ;

Page 1, line 4, after the words "number 07/939,281," please insert the words -- now USP 5,278,272, -- ;

Page 3, line 2, please delete the word "temperture" and insert therefore the word -- temperature --;

Page 3, line 14, please the letters "e.g," and insert therefore the letters -- e.g., --;

Page 3, line 15, after the words "The compositions comprise" please insert the letter -- (A) --;

Page 3, line 17, please delete the symbol " : ";

Page 3, line 18, please delete the letter "(A)";

Page 5, line 9, please delete the word "homogeniety" and insert therefore the word -- homogeneity --;

Page 5, line 28, please delete the word "homogeneouslt" and insert therefore the word -- homogeneously --;

Page 8, line 4, please delete the word "substantialy" and insert therefore the word -- substantially --;

Page 10, lines 11 and 16, please delete the word "intial" and insert therefore the word -- initial --;

Page 11, line 2, please delete the word "heterogenously" and insert therefore the word -- heterogeneously --;

Page 14, line 5, please delete the word "tempertaures" and insert therefore the word -- temperatures --;

Page 14, line 9, please delete the word "concommitantly" and insert therefore the word -- concomitantly --;

Page 17, line 23, please delete the word "decribed" and insert therefore the word -- described --;

Page 17, line 27, please delete the word "dicusses" and insert therefore the word -- discusses --;

Page 18, line 11, please delete the word "terepthalate" and insert therefore the word -- terephthalate --;

Page 22, line 5, please delete the word "coplymer" and insert therefore the word -- copolymer --;

Page 22, line 10, please delete the word "recator" and insert therefore the word -- reactor

Page 23, line 4, please delete the word "baout" and insert therefore the word -- about --;

Page 23, line 5, please delete the word "distrubution" and insert therefore the word -- distribution --;

Page 26, line 11, please delete the word "ipact" and insert therefore the word -- impact --;

Page 26, line 12, please delete the words "DC ppt tear" and insert therefore the words -- CD ppt tear --.

In the Claims

Please cancel Claims 9-16 and 24-30 (originally filed April 28, 1993 under USSN 08/054,379) as drawn to matter being examined under a related application. Please amend the remaining claims as follows:

1. (Amended) A film made from an ethylene polymer composition, wherein the composition comprises

(A) from about 10 percent (by weight of the total composition) to about 95 percent (by weight of the total composition) of [:]

[(A)] at least one homogeneously branched substantially linear ethylene/α-olefin interpolymer having:

(i) a density from about 0.89 grams/cubic centimeter (g/cm^3) to about 0.92 g/cm^3,

(ii) a molecular weight distribution (M_W/M_n) from about 1.8 to about 2.8,

(iii) a melt index (I_2) from about 0.001 grams/10 minutes (g/10 min.) to about 10 g/10 min.,

(iv) no linear polymer fraction, and

(v) a single melting peak as measured using differential scanning calorimetry; and

(B) from about 5 percent (by weight of the total composition) to about 90 percent (by weight of the total composition) of at least one heterogeneously branched ethylene polymer having a density from about 0.93 g/cm^3 to about 0.965 g/cm^3 and wherein the heterogeneously branched ethylene polymer has no more than about 10 percent (by weight of the polymer) of a polymer fraction having a slope of strain hardening coefficient (SHC) greater than or equal to about 1.3.

2. (Amended) The film of claim 1 wherein the homogeneously branched substantially linear ethylene/α-olefin interpolymer has a slope of strain hardening coefficient greater than or equal to about 1.3 and up to about 2.3.

17. (Amended) In a composition comprising at least one homogeneously branched ethylene/α-olefin interpolymer and at least one heterogeneously branched ethylene/α-olefin interpolymer, the improvement comprising incorporating into the composition from about 10 percent (by weight of the total composition) to about 95 percent (by weight of the total composition) of at least one homogeneously branched substantially linear ethylene/α-olefin interpolymer having:

(i) a density from about 0.89 grams/cubic centimeter (g/cm^3) to about 0.92 g/cm^3,

(ii) a molecular weight distribution (M_W/M_n) from about 1.8 to about 2.8,

(iii) a melt index (I_2) from about 0.001 grams/10 minutes (g/10 min.) to about 10 g/10 min.,

(iv) no linear polymer fraction, and

(v) a single melting peak as measured using differential scanning calorimetry,

wherein the heterogeneously branched ethylene polymer has no more than about 10 percent (by weight of the polymer) of a polymer fraction having a slope of strain hardening coefficient (SHC) greater than or equal to about 1.3.

18. (Amended) The improvement of claim 17 wherein the homogeneously branched substantially linear ethylene/α-olefin interpolymer has a slope of strain hardening coefficient greater than or equal to about 1.3 and up to about 2.3.

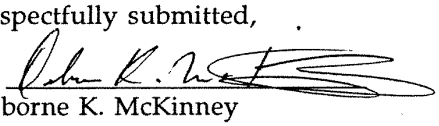
REMARKS

The amendments to the specification and the claims are intended to bring the present application to the status of parent application USSN 08/054,379 (now abandoned) immediately before the parent application was abandoned. Continuity of prosecution as to parent application USSN 08/054,379 was maintained through patent application USSN 08/378,998, now abandoned.

The amendments to the specification update the priority application data and correct typographical and/or transcription errors.

The amendments to independent Claims 1 and 17 describing the heterogeneously branched ethylene polymer are supported in the specification on page 14, lines 22-23. There are also amendments to Claims 1 and 17 to correct transcription errors. The other amendment to independent Claim 1 clarifies the composition used to make the film as comprising components (A) and (B). The amendments to dependent Claims 2 and 18 are supported in Table 1, page 12, in Polymer Q. Applicants believe none of the amendments add any new matter and accurately reflect the status of the parent application before abandonment. Entry of the amendments is respectfully requested.

Respectfully submitted,

By 

Osborne K. McKinney
Registration No. P-40,084
Phone: (409) 238-7889

Dated: February 2, 1996

The Dow Chemical Company
Patent Department
Building B-1211
Freeport, Texas 77541
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PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants: Pak-Wing Steve Chum, et al.

Serial No.: 08/544,497
Filed: October 18, 1995
Attorney Docket No.: C-40,121-AU

Art Unit: 1505
Previous Examiner: D. Wu

4C

For: FABRICATED ARTICLES MADE FROM ETHYLENE POLYMER BLENDS

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Jan Alverson
SIGNATURE OF PERSON SIGNING CERTIFICATE

2-2-96
DATE OF SIGNATURE

Hon. Commissioner of Patents & Trademarks
Washington, D.C. 20231

Sir:

SECOND PRE-EXAMINATION AMENDMENT

Prior to examination of the above-identified continuation application and after entry of amendments requested in the First Pre-Examination Amendment filed herewith, Applicants respectfully request consideration of the Third Markovich Declaration being submitted herewith as well as entry and consideration of the following:

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26074 102 156.00CH

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In the Specification:

On page 1, line 2, please delete "pending" .

On page 1, line 4, please delete "related to pending" and insert therefor -- continuation-in-part of -- .

On page 9, before the heading "Determination of Slope of Strain Hardening", please insert the following:

-- Determination of Critical Shear Stress and Critical Shear Rate

Gas extrusion rheometry (GER) is described by M. Shida, R.N. Shroff and L.V. Cancio in Polymer Engineering Science, Vol. 17, no. 11, p. 770 (1977), and in "Rheometers for Molten Plastics" by John Dealy, published by Van Nostrand Reinhold Co. (1982) on page 97, both publications of which are incorporated by reference herein in their entirety. All GER experiments are performed at a temperature of 190°C, at nitrogen pressures between 5250 to 500 psig using a 0.0296 inch diameter, 20:1 L/D die. An apparent shear stress vs. apparent shear rate plot is used to identify the melt fracture phenomena. According to Ramamurthy in Journal of Rheology, 30(2), 337-357 1986, above a certain critical flow rate, the observed extrudate irregularities may be broadly classified into two main types: surface melt fracture and gross melt fracture.

Surface melt fracture occurs under apparently steady flow conditions and ranges in detail from loss of specular gloss to the more severe form of "sharkskin." In this disclosure, the onset of surface melt fracture is characterized at the beginning of losing extrudate gloss at which the surface roughness of extrudate can only be detected by 40x magnification. The critical shear rate at onset of surface melt fracture for the substantially linear olefin polymers is at least 50 percent greater than the critical shear at the onset of surface melt fracture of a linear olefin polymer having about the same I_2 and M_w/M_n.

Gross melt fracture occurs at unsteady flow conditions and ranges in detail from regular (alternating rough and smooth, helical, etc.) to random distortions. For commercial acceptability, (e.g., in blown film products), surface defects should be minimal, if not absent. The critical shear rate at onset of surface melt fracture (OSMF) and onset of gross melt fracture (OGMF) will be used herein based on the changes of surface roughness and configurations of the extrudates extruded by a GER. Preferably,

the critical shear stress at the OGMF and the critical shear stress at the OSMF for the substantially linear ethylene polymers [described] used herein is greater than about 4 x 10^6 dyne/cm^2 and greater than about 2.8 x 10^6 dyne/cm^2, respectively. --

In the Claims

Please cancel Claims 2 and 18 as the slope of strain hardening limitation is to be incorporated into remaining the claims by the amendments that follow.

Please amend the claims as follows:

1. (Twice amended) A film made from an ethylene polymer composition, wherein the composition comprises

(A) from about 10 percent (by weight of the total composition) to about 95 percent (by weight of the total composition) of at least one homogeneously branched substantially linear ethylene/α-olefin interpolymer having:

(i) a density from about 0.89 grams/cubic centimeter (g/cm^3) to about 0.92 g/cm^3,

(ii) a molecular weight distribution (M_W/M_n) from about 1.8 to about 2.8,

(iii) a melt index (I_2) from about 0.001 grams/10 minutes (g/10 min.) to about 10 g/10 min.,

(iv) no [linear] high density fraction, [and]

(v) a single melting peak as measured using differential scanning calorimetry[;], [and]

(vi) a critical shear stress at onset of gross melt fracture of greater than about 4 x 10^6 dyne/cm^2, and

(vii) a slope of strain hardening coefficient greater than or equal to about 1.3 and up to about 2.3; and

(B) from about 5 percent (by weight of the total composition) to about 90 percent (by weight of the total composition) of at least one heterogeneously branched ethylene polymer having a density from about 0.93 g/cm^3 to about 0.965 g/cm^3 and wherein the heterogeneously branched ethylene polymer has no more than about 10 percent (by weight of the polymer) of a polymer fraction having a slope of strain hardening coefficient (SHC) greater than or equal to about 1.3.

17. (Twice amended) In a composition comprising at least one homogeneously branched ethylene/α-olefin interpolymer and at least one heterogeneously branched ethylene/α-olefin interpolymer, the improvement comprising incorporating into the composition from about 10 percent (by weight of the total composition) to about 95 percent (by weight of the total composition) of at least one homogeneously branched substantially linear ethylene/α-olefin interpolymer having:

(i) a density from about 0.89 grams/cubic centimeter (g/cm^3) to about 0.92 g/cm^3,

(ii) a molecular weight distribution (M_w/M_n) from about 1.8 to about 2.8,

(iii) a melt index (I_2) from about 0.001 grams/10 minutes (g/10 min.) to about 10 g/10 min.,

(iv) no [linear polymer] high density fraction, [and]

(v) a single melting peak as measured using differential scanning calorimetry, [and]

(vi) a critical shear stress at onset of gross melt fracture of greater than about 4×10^6 dyne/cm^2, and

(vii) a slope of strain hardening coefficient greater than or equal to about 1.3 and up to about 2.3; and

from about 5 percent (by weight of the total composition) to about 90 percent (by weight of the total composition) of at least one heterogeneously branched ethylene polymer having a density from about 0.93 g/cm^3 to about 0.965 g/cm^3 wherein the heterogeneously branched ethylene polymer has no more than about 10 percent (by weight of the polymer) of a polymer fraction having a slope of strain hardening coefficient (SHC) greater than or equal to about 1.3.

Please add the following new claims:

-- 31. A film made from an ethylene polymer composition, wherein the composition comprises

(A) from about 10 percent (by weight of the total composition) to about 95 percent (by weight of the total composition) of

at least one homogeneously branched substantially linear ethylene/α-olefin interpolymer having:

(i) a density from about 0.89 grams/cubic centimeter (g/cm³) to about 0.92 g/cm³,

(ii) a molecular weight distribution (M_w/M_n) from about 1.8 to about 2.8,

(iii) a melt index (I_2) from about 0.001 grams/10 minutes (g/10 min.) to about 10 g/min.,

(iv) no high density fraction,

(v) a single melting peak as measured using differential scanning calorimetry,

(vi) a critical shear stress at onset of gross melt fracture of greater than about 4 x 10^6 dyne/cm², and

(vii) a slope of strain hardening coefficient greater than or equal to about 1.3 and up to about 2.3; and

(B) from about 5 percent (by weight of the total composition) to about 90 percent (by weight of the total composition) of at least one heterogeneously branched ethylene polymer.

32. An ethylene polymer composition comprising

(A) from about 10 percent (by weight of the total composition) to about 95 percent (by weight of the total composition) of

at least one homogeneously branched substantially linear ethylene/α-olefin interpolymer having:

(i) a density from about 0.89 grams/cubic centimeter (g/cm³) to about 0.92 g/cm³,

(ii) a molecular weight distribution (M_w/M_n) from about 1.8 to about 2.8,

(iii) a melt index (I_2) from about 0.001 grams/10 minutes (g/10 min.) to about 10 g/min.,

(iv) no high density fraction,

(v) a single melting peak as measured using differential scanning calorimetry,

(vi) a critical shear stress at onset of gross melt fracture of greater than about 4 x 10^6 dyne/cm², and

(vii) a slope of strain hardening coefficient greater than or equal to about 1.3 and up to about 2.3; and

(B) from about 5 percent (by weight of the total composition) to about 90 percent (by weight of the total composition) of at least one heterogeneously branched ethylene polymer.

33. A film made from an ethylene polymer composition, wherein the composition comprises

(A) from about 10 percent (by weight of the total composition) to about 95 percent (by weight of the total composition) of at least one homogeneously branched substantially linear ethylene/α-olefin interpolymer having:

(i) a density from about 0.89 grams/cubic centimeter (g/cm^3) to about 0.92 g/cm^3,

(ii) a molecular weight distribution (M_W/M_n) from about 1.8 to about 2.8,

(iii) a melt index (I_2) from about 0.001 grams/10 minutes (g/10 min.) to about 10 g/10 min.,

(iv) no high density fraction,

(v) a single melting peak as measured using differential scanning calorimetry,

(vi) a critical shear rate at onset of surface melt fracture for the substantially linear olefin polymers is at least 50 percent greater than the critical shear at the onset of surface melt fracture of a linear olefin polymer having about the same I_2 and M_w/M_n, and

(vii) a slope of strain hardening coefficient greater than or equal to about 1.3 and up to about 2.3; and

(B) from about 5 percent (by weight of the total composition) to about 90 percent (by weight of the total composition) of at least one heterogeneously branched ethylene polymer.

34. An ethylene polymer composition comprising

(A) from about 10 percent (by weight of the total composition) to about 95 percent (by weight of the total composition) of at least one homogeneously branched substantially linear ethylene/α-olefin interpolymer having:

(i) a density from about 0.89 grams/cubic centimeter (g/cm^3) to about 0.92 g/cm^3,

(ii) a molecular weight distribution (M_W/M_n) from about 1.8 to about 2.8,

(iii) a melt index (I_2) from about 0.001 grams/10 minutes (g/10 min.) to about 10 g/10 min.,

(iv) no high density fraction,

(v) a single melting peak as measured using differential scanning calorimetry,

(vi) a critical shear rate at onset of surface melt fracture for the substantially linear olefin polymers is at least 50 percent greater than the critical shear at the onset of surface melt fracture of a linear olefin polymer having about the same I_2 and M_w/M_n, and

(vii) a slope of strain hardening coefficient greater than or equal to about 1.3 and up to about 2.3; and

(B) from about 5 percent (by weight of the total composition) to about 90 percent (by weight of the total composition) of at least one heterogeneously branched ethylene polymer.

18 ~~35~~. The film of Claims ~~31~~ 14 or ~~33~~ 16, or the composition of Claims ~~32~~ 15 or ~~34~~ 17, wherein the composition comprises more than about 40 percent (by weight of the total composition) of at least one homogeneously branched substantially linear ethylene/α-olefin interpolymer. --

REMARKS

Amendment to the Cross-Reference section updates the status of parent applications. A Supplement Oath, pursuant to 37 CFR § 1.67(a), will be filed forthwith declaring the present application is a continuation-in-part application of USSN 07/939,281.

The amendment to the specification pertaining to critical shear stress and critical shear rate is provided to more distinctly set forth the present invention as directed to substantially linear ethylene polymers. Support for the amendment can be found in parent application USSN 07/776,130 (now USP 5,272,236) at page 7, lines 27-34

bridging to page 8, lines 1-27 and in parent application USSN 07/939,281 (now USP 5,278,272) at page 13, lines 4-15. The parent applications were explicitly incorporated in to the present application by reference at page 1, lines 2-8 of the present specification. The amendment to the otherwise verbatim text of the parent application directs the incorporated description to the use of substantially linear ethylene polymers rather than a description referring to the novelty of such polymers.

Support for the amendments to Claims 1 and 17 respecting the critical shear stress limitation can be found in the parent application specifically at page 8, lines 23-27. Claim 17 was also amended to incorporate the weight percent and density requirements for the at least one heterogeneously branched ethylene polymer component of the inventive composition. This amendment provides conformity with Claim 1 and corrects an inadvertent transcription error.

Claims 1 and 17 were also amended as to the "no linear fraction" parameter to correct a transcription error. The substituted term "no high density fraction" refers to substantially linear ethylene polymers and to other homogeneously branched ethylene polymers while the term "linear fraction" or "linear polymer fraction" (at least as used in the present application) refers to heterogeneously branched ethylene polymers. See, specification at page 5, lines 23-27; compare, page 14, lines 6-10.

Support of the slope of strain hardening coefficient amendment to Claims 1 and 17 can be found in Claims 2 and 18, now canceled.

New Claim 31 is supported by the description at page 13, lines 3-6 in the specification, original Claim 1, Claim 2 and parent application 07/776,130 at page 8, lines 23-27. New Claim 32 is supported by the description at page 13, lines 3-6 in the specification, original Claim 17, Claim 18 and parent application 07/776,130 at page 8, lines 23-27. New Claim 33 is supported by the description at page 13, lines 3-6 in the specification, original Claim 1, Claim 2 and parent application 07/939,281 at page 13, lines 4-15. New Claim 34 is supported by the description at page 13, lines 3-6 in the specification, original Claim 17, Claim 18 and parent application 07/939,281 at page 13, lines 4-15. New Claim 35 is supported by Example 6 at page 22 in the specification..

Applicants do not believe that the amendments to the specification or claims add any new matter. Entry of the amendments is respectfully requested and consideration of the Third Markovich Declaration and amendments is also respectfully requested.

Respectfully submitted,

By _____
Osborne K. McKinney
Registration No. P-40,084
Phone: (409) 238-7889

Dated: February 2, 1996

The Dow Chemical Company
Patent Department
Building B-1211
Freeport, Texas 77541
OKM/okm

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PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants: Pak-Wing Steve Chum, et al.

Serial No.: 08/544,497
Filed: October 18, 1995
Attorney Docket No.: C-40,121-AU

Art Unit: 1505
Previous Examiner: D. Wu

For: FABRICATED ARTICLES MADE FROM ETHYLENE POLYMER BLENDS

HEREBY CERTIFY THAT THIS CORRESPONDENCE IS BEING DEPOSITED WITH THE UNITED STATES POSTAL SERVICE AS FIRST CLASS MAIL WITH SUFFICIENT POSTAGE IN AN ENVELOPE ADDRESSED TO: COMMISSIONER OF PATENTS AND TRADEMARKS, WASHINGTON, D.C. 20231, on February 2, 1996
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Jan Alverson
PRINT OR TYPE NAME OF PERSON SIGNING CERTIFICATE

Jan Alverson
SIGNATURE OF PERSON SIGNING CERTIFICATE

2-2-96
DATE OF SIGNATURE

Hon. Commissioner of Patents & Trademarks
Washington, D.C. 20231

Sir:

THIRD MARKOVICH DECLARATION UNDER 37 CFR § 1.132

Ronald P. Markovich declares and states:

THAT, he obtained a Bachelor of Science degree in Chemistry from Wayne State University (Detroit, Michigan) in 1983;

THAT, he joined The Dow Chemical Company (Midland, Michigan) in 1983 as a Chemist in the Research Assignments Program (RAP), and was promoted to Senior Research Chemist in 1989 and to his present position as Project Leader in 1993;

THAT, his first two RAP assignments pertained to analytical test method development, his RAP third assignment was in the Polyolefins Research and Development department and his fourth (and last) RAP assignment in the Polyolefins Technical Service and Development department;

THAT, after his last RAP assignment, he joined the Polyolefins Research and Development department full time and for the last ten and half years, he has focused his research and development efforts in the area of polyolefin product properties and analytical test method procedures and development;

THAT, his current responsibilities pertain to polyolefin product development as related to the interrelationships between fundamental polymer structure, process requirements and product performance properties;

THAT, he is an inventor as to the above-identified patent application and is therefore familiar with the patent application, the Examiner's rejections of the claims and the WO '414 reference on which the Examiner relies;

THAT, as a follow up to the incomplete impact performance results reported in the Second Markovich Declaration, he had the Dynatup impact properties for Inventive Examples and Comparative Examples re-measured and also had the slope of strain hardening coefficient measured for the component polymers used to prepare the various Inventive and Comparative Examples;

THAT, a full report of important component properties, including slope of strain hardening coefficients, is provided in the attached Table 1 and a report of the performance results for Inventive Examples and Comparative Example are provided in Table 2, and that Tables 3, 4 and 5 provide the specific performance results (Dynatup impact strength, Intrinsic tear and Tensile break strength, respectively) for the various Examples at an equivalent Molecular Weight of 71,6000;

THAT, in addition to having very different component polymers, performance results and data conclusively show that Inventive (Blend) Examples as defined by specific component properties, including a slope of strain hardening coefficient greater than or equal to about 1.3 and up to about 2.3, exhibit superior to dramatically superior impact resistance and intrinsic tear resistance relative to WO '414 compositions when directly compared at equivalent weight percentages through the range of 38%/62%, 50%/50% and 72%/28% Component A/Component B;

THAT, the impact properties of the Inventive Examples are particularly unexpected and surprising in that they show substantially higher impact resistance even at slightly higher densities relative to blend compositions representative of WO '414, whereas one skilled in the art would ordinarily expect compositions having higher densities to show inferior impact properties relative to comparative compositions having lower densities; and

THAT, with respect to tensile break strength, although superior or dramatically superior results are easily obtained with Inventive compositions, this property appears to be more sensitive to component polymer concentrations than impact resistance and/or tear resistance, and as such, compositions containing more than 40 weight percent of a substantially linear ethylene interpolymer are considered to be preferred compositions.

The undersigned declares further that all statements made herein of his own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under §1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Date 2/2/96

Ronald P. Markovich

Ronald P. Markovich

Table 1

Sample Designation	A Component Example A	B Component Example B	C Component Example C	D Component Example D	AB1 Comparative Component AB1	AB2 Comparative Component AB2	AB3 Comparative Component AB3	Exact 3027 Comparative Resin	Exact 3022 Comparative Resin
Polymer Type	Substantially Linear Ethylene/ Octene Copolymer	Substantially Linear Ethylene/ Butene Copolymer	Substantially Linear Ethylene/ Octene Copolymer	Substantially Linear Ethylene/ Octene Copolymer	Homogeneously Branched Linear Ethylene/Butene Copolymer	Homogeneously Branched Linear Ethylene/Butene Copolymer	Homogeneously Branched Linear Ethylene/Butene Copolymer	Homogeneously Branched Linear Ethylene/Butene Copolymer	Homogeneously Branched Linear Ethylene/Butene Copolymer
Density (g/cc)	0.906	0.9052	0.90575	0.9032	0.9031	0.9033	0.9034	0.9015	0.9065
I2	4.01	4.23	3.99	2.7	3.83	3.93	4.19	3.26	8.48
I10 / I2	8.22	7.88	5.82	7.80	5.90	5.69	5.64	5.65	5.49
I10	32.96	33.32	23.21	21.05	22.6	22.38	23.64	18.42	46.57
Mw by GPC	68200	67100	77400	72300	79100	80700	77500	85800	65100
Mw/Mn by GPC	2.23	2.12	1.89	2.15	2.15	2.17	2.06	2.00	2.00
Slope of Strain Hardening Coefficient	1.5	1.0	1.7	1.3	1.2	1.0	1.1	1.2	1.0
>Shear Stress @ OSGMF (dyn/cm^2)	> 3.88 x 10^6	> 4.31 x 10^6	> 4.31 x 10^6	gross melt fracture not observed up to 4.41 x 10^6	> 3.45 x 10^6	> 3.45 x 10^6	> 3.45 x 10^6	> 3.45 x 10^6	> 3.23 x 10^6
<Shear Stress @ OSGMF (dyn/cm^2)	< 4.09 x 10^6	< 4.48 x 10^6	< 4.48 x 10^6	gross melt fracture not observed	< 3.66 x 10^6	< 3.66 x 10^6	< 3.66 x 10^6	< 3.66 x 10^6	< 3.45 x 10^6

Note 1: Comparative Resin AB1 is a blend containing of 75.87% Exact 3027 and 24.13% Exact 3022.
Note 2: Comparative Resin AB2 is a blend containing of 74.44% Exact 3027 and 25.56% Exact 3022.
Note 3: Comparative Resin AB3 is a blend containing of 73.75% Exact 3027 and 26.25% Exact 3022.

Table 2

Sample Designation	AD1 Inventive Blend Example	BD1 Comparative Example	CD1 Inventive Blend Example	X1 Comparative Example	AD2 Inventive Blend Example	BD2 Comparative Example	CD2 Inventive Blend Example	X2 Comparative Example	AD3 Inventive Blend Example	BD3 Comparative Example	CD3 Inventive Blend Example	X3 Comparative Example	ED3 Inventive Blend Example	X4 Comparative Example
Blend Component														
A	38.46%				72.35%				50.00%					
B		38.14%				71.75%				50.00%				
C			38.46%				72.35%				50.00%			
PL 1850													50.00%	
EXACT 3027				28.95%				53.90%				36.88%		50.00%
EXACT 3022				9.21%				18.50%				13.13%		
HDPE 04352N	61.54%	61.86%	61.54%	61.84%	27.65%	28.25%	27.65%	27.60%	50.00%	50.00%	50.00%	50.00%	50.00%	50.00%
I2	4.11	4.25	4.18	4.13	4.08	4.10	4.04	4.09	4.04	5.02	4.07	4.17	3.43	3.74
I10 / I2	7.31	6.96	6.29	6.19	7.67	7.64	5.98	5.84	7.42	8.22	6.20	5.58	7.33	6.09
I10	30.06	29.59	26.29	25.57	31.29	31.34	24.15	23.87	29.96	41.24	25.23	23.27	25.13	22.76
Mw by GPC	74900	74800	77200	83400	71700	73800	77200	80500	71600	75000	78700	80600	76100	79700
Mw/Mn by GPC	2.56	2.53	2.58	2.52	2.47	2.33	2.20	2.27	2.46	ND	2.44	2.54	2.46	2.42
Strain @ Yield	15.0	15.0	14.9	15.0	14.9	15.0	14.8	15.0	15.0	15.0	15.1	14.9	15.0	15.0
Break Strength	1835	2070	1921	1801	3187	2253	3268	2729	2188	1646	3655	1652	3050	1539
Break Energy	385	57	509	108	1130	781	991	990	981	144	1329	249	1168	214
Intrinsic Tear	160	102	221	110	279	107	377	142	224	112	264	116	269	34
Dynatup (30 Mil Plaque) Total Energy	2.84	2.08	2.84	2.59	3.66	2.39	5.67	2.78	3.44	2.63	4.23	2.63	3.81	2.91

ND = not determined

Dynatup Total Energy Impact Strength (Corrected)*

Table 3

Weight Percent of Polymer Representative of '013	38%	50%	72%
Inventive Examples			
A	**2.71** (AD1)	**3.44** (AD3)	**3.65** (AD2)
C	**2.63** (CD1)	**3.85** (CD3)	**5.26** (CD2)
E	**NA**	**3.58** (ED3)	**NA**
Comparative Examples			
B	**1.99** (BD1)	**2.51** (BD3)	**2.32** (BD2)
1	**2.22** (X1)	**2.34** (X3)	**2.47** (X2)
2	**NA**	**2.61** (X4)	**NA**
Calculations	Percent Relative Performance of Inventive Examples (Relative to Comp Ex 1) **18-22% higher** (Relative to Comp Ex B) **32-36% higher**	Percent Relative Performance of Inventive Examples (Relative to Comp Ex. B) **37-53% higher** (Relative to Comp Ex 1) **47-65% higher** (Relative to Comp Ex 2) **32-48% higher**	Percent Relative Performance of Inventive Examples (Relative to Comp Ex 1) **48-113% higher** (Relative to Comp Ex B) **57-127% higher**
Performance Conclusions - *Inventive Examples are:*	superior	superior	dramatically superior

NA = not available.
( ) provides the Example designation as set forth in Table 2.
* Impact strength values were corrected to 71,600 equivalent Molecular Weight for each Example.

Intrinsic Tear (Corrected)*

Table 4

Weight Percent of Polymer Representative of '013	38%	50%	72%
Inventive Examples			
A	**153** (AD1)	**224** (AD3)	**279** (AD2)
C	**205** (CD1)	**240** (CD3)	**350** (CD2)
E	**NA**	**253** (ED3)	**NA**
Comparative Examples			
B	**98** (BD1)	**107** (BD3)	**104** (BD2)
1	**94** (X1)	**103** (X3)	**126** (X2)
2	**NA**	**31** (X4)	**NA**
Calculations	Percent Relative Performance of Inventive Examples (Relative to Comp Ex B) **56-109% higher** (Relative to Comp Ex 1) **63-118% higher**	Percent Relative Performance of Inventive Examples (Relative to Comp Ex B) **109-136 % higher** (Relative to Comp Ex 1) **117-147 % higher** (Relative to Comp Ex 2) **623-716% higher**	Percent Relative Performance of Inventive Examples (Relative to Comp Ex B) **168-237% higher** (Relative to Comp Ex 1) **121-178% higher**
Performance Conclusions - *Inventive Examples are:*	dramatically superior	dramatically superior	dramatically superior

NA = not available.
( ) provides the Example designation as set forth in Table 2.
* Intrinsic tear values were corrected to 71,600 equivalent Molecular Weight for each Example.

Tensile Break Strength (Corrected)*

Table 5

Weight Percent of Polymer Representative of '013	**38%**	**50%**	**72%**
Inventive Examples			
A	**1754** (AD1)	**2188** (AD3)	**3183** (AD2)
C	**1781** (CD1)	**3325** (CD3)	**3031** (CD2)
E	**NA**	**2870** (ED3)	**NA**
Comparative Examples			
B	**1981** (BD1)	**1571** (BD3)	**2186** (BD2)
1	**1546** (X1)	**1468** (X3)	**2427** (X2)
2	**NA**	**1383** (X4)	**NA**
Calculations	Percent Relative Performance of Inventive Examples (Relative to Comp Ex B) **10-11% lower** (Relative to Comp Ex 1) **13-15% higher**	Percent Relative Performance of Inventive Examples (Relative to Comp Ex B) **39-112% higher** (Relative to Comp Ex 1) **49-126% higher** (Relative to Comp Ex 2) **58-140% higher**	Percent Relative Performance of Inventive Examples (Relative to Comp Ex B) **39-46% higher** (Relative to Comp Ex 1) **25-31% higher**
Performance Conclusions - *Inventive Examples are:*	similar	dramatically superior	superior

NA = not available.
( ) provides the Example designation as set forth in Table 2.
* Tensile break strength values were corrected to 71,600 equivalent Molecular Weight for each Example.

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PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

MAR 15 1996
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Applicants:	Pak-Wing Steve Chum et al.
Serial No.:	08/544,497
Attorney's Docket No. :	C-40,121AU
Filed:	October 18, 1995
For:	FABRICATED ARTICLES MADE FROM ETHYLENE POLYMER BLENDS

H 5

W 5
030

HEREBY CERTIFY THAT THIS CORRESPONDENCE IS BEING DEPOSITED WITH THE UNITED STATES POSTAL SERVICE AS FIRST CLASS MAIL WITH SUFFICIENT POSTAGE IN AN ENVELOPE ADDRESSED TO: COMMISSIONER OF PATENTS AND TRADEMARKS, WASHINGTON, D.C. 20231, on March 11, 1996
DATE OF DEPOSIT

Margaret Greene
PRINT OR TYPE NAME OF PERSON SIGNING CERTIFICATE

Margaret Greene
SIGNATURE OF PERSON SIGNING CERTIFICATE

March 11, 1996
DATE OF SIGNATURE

Hon. Commissioner of Patents & Trademarks
Washington, D.C. 20231

Sir:

INFORMATION DISCLOSURE STATEMENT UNDER 37 CFR 1.56

Pursuant to Applicant's duty of disclosure under 37 CFR 1.56, listed on the attached PTO-1449 are those patents, publications and other information known to the Applicants which were considered during the drafting of the claims of the above-identified application and/or the Applicants became aware of after the original filing of the above-identified application. One copy of each listed document is attached.

This application is a continuation application of USSN 08/378,998, filed January 27, 1995, now abandoned, which was a continuation application of USSN 08/054,379, now abandoned, and it is also related to the following applications:

USSN	Filing Date
08/327,156	October 21, 1994
08/010,958	January 29, 1993
08/239,495	May 9, 1994
08/239,496	May 9, 1994
07/776,130	October 15, 1991
07/939,281	September 2, 1992
08/289,985	August 12, 1994
08/084,054	March 7, 1995
08/344,262	November 23, 1994
07/945,034	September 15, 1992
08/417,626	April 6, 1995

Copies of Form 1449 for USSN 08/010,958; 08/239,496; 07/776,130; 07/939,281; 08/289,985; 08/084,054; 08/344,262; and 07/945,034 are attached together with copies of supplemental submissions for these related applications. Copies of the references considered relevant by the Applicants, as well as copies of references cited during the examination of the related applications identified above, including USSN 08/054,379 and 08/327,156, are available in their respective files. However, if the Examiner requires an additional copy of any of these related references, the Applicants will provide such upon request.

The Applicants respectfully request that the documents listed on the attached Form 1449 and related references be considered by the Examiner, that the various references be made of record in the present application, and that an initialed copy of the attached Form 1449 be returned to the undersigned in accordance with MPEP 609.

If there is a charge involved in this submission, please charge our account, Account No. 04-1512, accordingly.

Respectfully submitted,

By _____
Osborne K. McKinney
Registration No. 40,084
Phone: (409) 238-7889

Dated: March 8, 1996

The Dow Chemical Company
Patent Department
Building B-1211
Freeport, Texas 77541
OKM/okm

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Sheet 1 of 3

FORM PTO 1449 (modified)	Atty. Docket No. C-40121-AU	Serial No. 08/544,497
LIST OF REFERENCES CITED BY APPLICANT	Applicant: Pak-Wing Steve Chum et al.	
	Filing Date: 10-18-95	Group: 1505

U.S. PATENT DOCUMENTS

Examiner Initial*		Document Number	Date	Name	Class	Sub-class	Filing Date If Appropriate
DW	AA	3,998,914	12-21-76	Lillis et al.	260	897	
	AB	4,405,774	09-20-83	Miwa et al.	526	348.2	
	AC	4,429,079	01-31-84	Shibata et al.	525	240	
	AD	4,438,238	03-20-84	Fukushima et al.	525	240	
	AE	4,981,760	01-01-91	Naito et al.	428	523	
	AF	5,189,106	02-23-93	Morimoto et al.	525	240	
	AG	5,206,075	04-27-93	Hodgson, Jr.	428	216	
	AH	5,218,071	06-08-93	Tsutsui et al.	526	348	
	AI	5,272,236	12-21-93	Lai et al.	526	348.5	
	AJ	5,278,272	01-11-94	Lai et al.	526	348.5	
DW	AK	5,374,700	12-20-94	Tsutsui et al.	526	348.3	

FOREIGN PATENT DOCUMENTS

		Document Number	Date	Country	Class	Sub-class	Translation	
DW	BA	CA 2,008,315	07-24-90	Canada	C08F	4/16		
	BB	EP 0 447 035 A3	09-18-91	EPO	C08F	297/08		
	BC	WO 90/03414 A1	04-05-90	PCT	C08L	23/08		
	BD	WO 93/08221 A2	04-29-93	PCT	C08F	10/00		
DW	BE	WO 94/06857 A1	03-31-94	PCT	C08L	23/04		

OTHER REFERENCES *(Including Author, Title, Date, Pertinent Pages, Etc.)*

DW	C A		Modern Methods of Polymer Characterization, pp. 103-112, (1991) "Measurement of Long-Chain Branch Frequency in Synthetic Polymers", by Alfred Rudin
	C B		The Journal of Chemical Physics, vol. 17, no. 12, December (1949), pp. 1301-1314, "The Dimensions of Chain Molecules Containing Branches and Rings", by Bruno H. Zimm and Walter H. Stockmayer
	C C		Antec 93-Be In That Number, New Orleans, May 9-13, (1993), vol. II, "Dow Constrained Geometry Catalyst Technology (CGCT): New Rules For Ethylene a-Olefins Interpolymers-Controlled Rheology Polyolefins", pp. 1188-1192, by S. Lai and G. W. Knight
	C D		Journal of Rheology, (1986), pp. 340-341, 344-345, 348-349, 352-353, 356-357, "Wall Slip in Viscous Fluids and Influence of Materials of Construction", by A. V. Ramamurthy
	C E		Rheometers for Molten Plastics, (1982), pp. 97-99, by John Dealy
DW	C F		Polymer Engineering and Science, vol. 17, No. 11, November (1977), pp. 769-774, "Correlation of Low Density Polyethylene Rheological Measurements with Optical and Processing Properties", by M. Shida, R. N. Shroff, and L. V. Cancio

EXAMINER	DATE CONSIDERED
David W	8-2-96

*EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609; Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

attch #5

United States Patent [19]

Lillis et al.

[11] 3,998,914

[45] Dec. 21, 1976

[54] **FILM FROM A BLEND OF HIGH DENSITY POLYETHYLENE AND A LOW DENSITY ETHYLENE POLYMER**

[75] Inventors: Rupert Martin Lillis, Mount Chesney; Carmen Van Thomas, Beaconsfield, both of Canada

[73] Assignee: Du Pont of Canada, Ltd., Montreal, Canada

[22] Filed: Sept. 24, 1974

[21] Appl. No.: 508,889

Related U.S. Application Data

[63] Continuation of Ser. No. 324,372, Jan. 17, 1973, abandoned.

[30] Foreign Application Priority Data

Feb. 1, 1972 Canada 133717

[52] U.S. Cl. ..... 260/897 A; 264/289

[51] Int. Cl.² C08L 23/06; C08L 23/08

[58] Field of Search 260/897

[56] References Cited

UNITED STATES PATENTS

2,983,704	5/1961	Roedel	260/897
3,176,051	3/1965	Gregorian et al.	260/897
3,176,052	3/1965	Peticolas	260/897
3,231,686	1/1966	Snyder et al.	260/897
3,299,194	1/1967	Golike	260/897
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Primary Examiner—Carman J. Seccuro

[57] ABSTRACT

High density polyethylene film of improved clarity and stiffness is disclosed. The improved high density polyethylene film may be manufactured from a blend of polymers comprising an ethylene polymer of density in the range about 0.950–0.965 and of melt index less than about 10, and not more than about 30% of an ethylene polymer of melt index in the range of about 0.1 to about 10 and of density in the range about 0.910–0.945.

18 Claims, No Drawings

FILM FROM A BLEND OF HIGH DENSITY POLYETHYLENE AND A LOW DENSITY ETHYLENE POLYMER

This is a continuation of Ser. No. 324,372, filed Jan. 17, 1973, now abandoned.

This invention relates to a process for the manufacture of polyolefin film of improved optical and stiffness properties and in particular, this invention relates to film manufactured from high density polyethylenes, such polyethylenes being of density about 0.950–0.965. Preferably, the polyethylenes are narrow molecular weight distribution high density ethylene polymers blended with a minor amount of either an ethylene homopolymer or a copolymer of ethylene and a higher molecular weight α-olefin.

The manufacture of film from homopolymers and copolymers of ethylene of densities in the range of about 0.910 to 0.940 is well known. These films have a wide variety of end uses such as, for example, in the packaging of food, fertilizers, peat moss, hardware and chemicals and as a barrier in the construction industry and in greenhouses. Films derived from polyethylenes of densities in the range 0.910–0.940 are referred to as low to medium density polyethylene films and such films generally tend to have acceptable optical properties, flexibility and heat sealability.

Polypropylene films, and especially biaxialiy oriented polypropylene films, which are also widely used for packaging purposes, usually have good optical and stiffness properties. For example, oriented polypropylene films may have a haze of about 2% and a stiffness of greater than 400,000 pounds per square inch, the measurement of haze and stiffness being described hereinafter. Polyethylene films exhibiting a similar combination of optical and stiffness properties are not commercially available.

The manufacture of film from linear ethylene polymers has been disclosed, for example, in U.S. Pat. No. 2,862,917, which issued to A. W. Anderson, E. L. Fallwell and J. M. Bruce on December 2, 1958. The linear ethylene polymers described in this Anderson et al. patent typically have densities of about 0.955–0.965. The manufacture of film from polyethylene having a density of at least 0.94 is disclosed in Canadian Patent 685,170 of R. Doyle which issued on April 28, 1964.

Blends of a high density polyethylene (density 0.940–0.970) with 0.1 to 10% of an ethylene homopolymer or of an ethylene-butene-1 copolymer to improve optical clarity have been disclosed in U.S. Pat. No. 3,176,051 to R. S. Gregorian et al. which issued on March 30, 1965. The polymers blended into the high density polyethylenes are characterized in terms of reduced viscosity as the molecular weight of these polymers is so high that melt index measurements above 0.0 are not obtainable. Melt index is a measure of melt viscosity and is obtained using ASTM method D-1238.

It has now been found that film having improved optical and stiffness properties may be obtained from a polymer blend comprising a high density polyethylene blended with a polyethylene of melt index of at least 0.1. In particular, it has been found that a high density polyethylene film of improved optical and stiffness properties may be obtained from a narrow molecular weight distribution high density polyethylene blended with a minor amount of either a broad molecular weight distribution ethylene homopolymer of similar density, a polyethylene of different density, or a narrow or broad molecular weight distribution ethylene-butene-1 copolymer.

Accordingly, the present invention provides high density polyethylene film of improved clarity and stiffness, said polyethylene film being manufactured from a blend of polymers comprising an ethylene polymer of density in the range about 0.950–0.965 and of melt index less than about 10 and not more than about 30% of an ethylene polymer of melt index in the range of about 0.1 to about 10 and of density in the range about 0.910–0.945.

In a preferred embodiment, the present invention provides high density polyethylene film of improved clarity and stiffness, said polyethylene film being manufactured from a blend of ethylene polymers comprising an ethylene polymer of density in the range about 0.950–0.965 and of melt index less than about 10 and 5 to 30% (preferably, 10 to 25%) of an ethylene polymer of melt index in the range of about 10 to about 0.1 selected from the group consisting of an ethylene homopolymer of density in the range about 0.910–0.945 and ethylene-butene-1 copolymer of density about 0.910–0.945.

In a further embodiment, the present invention provides high density polyethylene film of improved clarity and stiffness manufactured from a narrow molecular weight distribution ethylene polymer of density in the range about 0.950–0.965 blended with either an ethylene homopolymer of density about 0.910–0.945 or an ethylene-butene-1 copolymer of density about 0.910–0.945.

In particular, the present invention provides a high density polyethylene film having a haze of less than 15% and especially below 10%, and in a preferred embodiment a haze of less than 5%.

In another embodiment, the high density polyethylene film of improved clarity may be oriented and such oriented films may have a stiffness, as measured by tensile modulus of elasticity, which is described hereinafter, of more than 200,000 pounds per square inch (psi).

The properties of polyolefins and in particular the properties of ethylene polymers may be characterized in a number of ways including melt index, density and molecular weight. While the weight or number average molecular weight is of prime importance in determining polymer properties, the molecular weight distribution of the polyethylene chains may also be a significant factor in determining the polymer properties.

The molecular weight distribution may be defined conveniently in terms of the stress exponent of the polymer. Stress exponent is discussed in U.S. Pat. No. 2,993,882 which issued July 25, 1961 to C. E. Ashby, S. P. Foster and E. T. Pieski and in U.S. Pat. No. 3,380,978 which issued April 30, 1968 to D. J. Ryan and B. J. Starkey. The stress exponent is determined by measuring the throughput of a melt indexer at two stresses (2160 and 6280g loading) using the procedures of the ASTM melt index test method D-1238. The stress exponent is calculated using the formula:

$$\text{Stress exponent} = \frac{1}{0.477}\left(\log \frac{\text{wt. extruded with 6480 g wt.}}{\text{wt. extruded with 2160 g wt.}}\right)$$

The stress exponent of a polymer is a measure of melt viscosity and is not a direct measure of molecular

weight distribution. Stress exponent may be a function of polymer molecular weight and it is preferred that the stress exponent values of different polymers be measured at similar levels of molecular weight or melt index whenever possible. A suitable melt index for the measurement of stress exponent of film grade polymers is 1.0.

Very narrow molecular weight distribution polyethylenes are characterized by low stress exponent values such as about 1.30 or less for polymers of melt index of about 1.0. Similarly, very broad molecular weight distribution polymers are characterized by stress exponent values above about 1.8. In the present application, all polymers of stress exponent less than about 1.4 have been classed as narrow molecular weight distribution polymers and all polymers of stress exponent above about 1.4 have been classed as broad molecular weight distribution polymers. However, it should be noted that the change from narrow to broad molecular weight distributions is not abrupt but rather a continuous spectrum of molecular weight distributions may exist between polymers classed as being of narrow or of broad molecular weight distribution.

The polymer comprising not less than about 70% of the polymer blend is hereinafter referred to as the base polymer. According to the present invention, the base polymer is an ethylene polymer of density about 0.950–0.965. This polymer may be of either broad or narrow molecular weight distribution, although in the preferred embodiment the polymer is of narrow molecular weight distribution. The polymer must be capable of being made into film; suitable polymers have a melt index in the range about 0.1–10.0. The polymer may be a homopolymer of ethylene or the polymer may contain a minor amount of a comonomer such as butene-1, the amount of comonomer not being in excess of the amount required to lower the polymer density below about 0.950.

The polymer blended into the base polymer may be an ethylene polymer of density in the range about 0.910–0.945, preferably 0.930–0.945, and may be of either broad or narrow molecular weight distribution. The melt index of this polymer is preferably in the range 0.1 to 10. In particular, the ethylene polymer may be a homopolymer of ethylene.

Alternatively, the polymer blended into the base polymer may be an ethylene-butene-1 copolymer of density about 0.910–0.945, of melt index in the range 0.1 to 10 and preferably having a narrow molecular weight distribution. In a preferred embodiment, the copolymer may have a density in the range about 0.930–0.945.

Processes for the manufacture of such polymers are known and may include free radical, coordination catalyst or solid catalyst polymerization processes.

Techniques for the blending of the polymers are also known. For example, the polymers may be blended by physically blending the polymers in the form of pellets, or the polymers may be melt blended prior to use or the polymers may be fed separately into the film extruder in the form of pellets or in a molten state, and blended in the extruder.

Film of improved optical properties may be manufactured from the blended polymers by known techniques. These processes include flat sheet extrusion techniques, such as water quench or cold roll quench processes, and blown film processes with or without internal and/or external cooling. Preferred techniques are those disclosed in Canadian Patent 579,650 which issued to G. B. Dyer and W. P. Heinstein on July 14, 1959 and in copending Canadian application 038,315 of M. Bunga and C. V. Thomas filed December 19, 1968. The optical properties of the film may depend on the process used in the manufacture of the film; the preferred techniques employ rapid cooling of the film immediately after extrusion.

The melt index of the base polymer, and of the polymer blended into the base polymer has been stated to be less than about 10 for the process of the present invention. This upper level of melt index for the polymers is not a critical feature of the invention except for the requirement that the blend of polymers must be capable of being made into film. The upper level of melt index is governed primarily by the technique used in the manufacture of film from the blended polymer. For example, flat film extrusion processes may be operable using polymers of higher melt index than may be used in a blown film process. Such melt index requirements are known.

As illustrated in the examples hereinafter, it has been found that high density polyethylene film of improved clarity and higher stiffness may be obtained by the process of the present invention.

A further improvement in the optical clarity and stiffness of the film may be obtained by orientation of the blended film. Such orientation may be uniaxial especially in the machine direction, i.e., the direction of extrusion of the film, or biaxial such as obtained by the use of a tenter frame. In a preferred embodiment, the film may be uniaxially oriented by at least a ratio of about 6:1, or more, in the machine direction. Orientation may not only result in a further improvement in optical clarity but may yield a film having a tensile modulus of elasticity greater than 200,000 psi. In a preferred embodiment the film may be characterized by a tensile modulus of elasticity of greater than 200,000 psi and by a haze of less than 5%.

The invention is further illustrated by the following examples.

To ascertain the film properties of unblended polymers, film was manufactured from the polymers listed in Table I using the process described in Canadian application 038,315 referred to hereinabove. The 3.5 inch extruder was operated at a speed of 100 lb./hour and with a die temperature in the range 245° to 260° C. in all cases. A metering screw was used in the extruder.

The properties of the film obtained are given in Table II. The haze was measured by ASTM method D-1003-59, the gloss by ASTM method D-523-53T and the stiffness as described by the tensile modulus of elasticity by ASTM method D-882-64T.

The film thickness in all cases was 1.0 mil.

EXAMPLE I

SCLAIR* 19×6 polymers in pellet form was physically blended with another polymer also in pellet form and fed to a film extruder. The extruder was operated in the manner outlined above.

* Registered trademark of Du Pont of Canada for its olefin polymers

The polymer blends and properties of the film produced are given in Table III.

EXAMPLE II

To show the effect of orientation, 6 mil film manufactured from blended polymers was monoaxially oriented in the machine direction. Orientation was carried out at

a film wind-up speed of 35 fpm using a hot roll temperature of 135° C., a cold roll temperature of 90° C. and an orientation gap of 0.010 inches.

The properties of the 1 mil film produced are given in Table IV.

TABLE I

Polymer Type*	Polymer Properties Density	Melt Index	Stress Exponent
SCLAIR 19X6	0.955	1.1	1.30
SCLAIR 59C	0.960	0.46	1.76
SCLAIR 14B	0.935	2.0	1.35
ALATHON 4476	0.933	2.0	1.55

*SCLAIR is the registered trademark of Du Pont of Canada Limited for its polyolefin polymers. SCLAIR 14B is an ethylene-butene-1 polymer, all other SCLAIR polymers in Table I are ethylene polymers.
ALATHON is the registered trademark of E.I. du Pont de Nemours Inc. for its ethylene polymers.

butene-1 copolymer containing a minor amount of butene-1.

2. The high density polyethylene film of claim 1 wherein the polymer of density in the range 0.950–0.965 has a melt index of at least 0.1.

3. The high density polyethylene film of claim 2 wherein the ethylene polymer of density in the range 0.950–0.965 is blended with not more than 30% of an ethylene homopolymer of density about 0.910–0.945.

4. The high density polyethylene film of claim 3 wherein the ethylene polymer of density 0.950–0.965 is blended with about 5–30% of an ethylene homopolymer of density about 0.930–0.945.

5. The high density polyethylene film of claim 3 wherein the ethylene polymer of density 0.950–0.965 is blended with about 10–25% of an ethylene homopolymer of density about 0.930–0.945.

TABLE II

Polymer Type	Film Properties Film Density	Haze (%)	Average Gloss (%)	Tensile Modulus of Elasticity* MD	TD	Melt Index	Stress Exponent
SCLAIR 19X6	0.935	5.5	105	87	110	1.0	1.30
SCLAIR 59C	0.943	81	0	110	164	0.46	1.76
SCLAIR 14B	0.925	2.5	140	55	62	1.85	1.30

*Tensile Modulus of Elasticity results are in psi × 10⁻³

TABLE III

Base Polymer*		Added Polymer*		Properties of Film from Blended Polymers Film Density	Haze (%)	Tensile Modulus of Elasticity** MD	TD	Average Gloss (%)
SCLAIR 19X6	(85%)	ALATHON 4476	(15%)	0.935	4.8	82	104	105
SCLAIR 19X6	(75%)	ALATHON 4476	(25%)	0.932	3.3	82	78	110
SCLAIR 19X6	(85%)	SCLAIR 14B	(15%)	0.933	4.7	88	110	96
SCLAIR 19X6	(75%)	SCLAIR 14B	(25%)	0.931	4.0	72	96	100
SCLAIR 59C	(85%)	ALATHON 4476	(15%)	0.944	14.4	98	131	70

*The percentages in brackets are the proportion by weight in the final blend.
**in psi × 10⁻³

TABLE IV

Polymer Type		Film From Blended Polymer/Effect of Orientation Orientation Ratio	Gauge (mil)	Film Density	Haze (%)	Average Gloss (%)	Tensile Modulus of Elasticity* MD	TD
Blend of SCLAIR 19X6 / ALATHON 4476	(85%) / (15%)	6:1	1.0	0.948	3.4	94	263	220

*in psi × 10⁻³

I claim:

1. High density polyethylene film of improved clarity and stiffness exhibiting a haze below about 10 percent, said polyethylene film being manufactured from a blend of polymers comprising (1) a high density ethylene homopolymer of density in the range about 0.950–0.965, of melt index less than about 10, and a stress exponent value less than 1.4, and (2) about 5 to 30% of a low density ethylene polymer of melt index in the range of about 0.1 to about 10 and of density in the range about 0.910–0.945, said low density ethylene polymer being an ethylene homopolymer having a stress exponent value greater than 1.4 or an ethylene-

6. The high density polyethylene film of claim 3 whenever oriented.

7. The high density polyethylene film of claim 3 whenever uniaxially oriented by a ratio of at least about 6:1.

8. The high density polyethylene film of claim 3 whenever oriented such that the tensile modulus of elasticity of the oriented film is greater than about 20,000 pounds per square inch.

9. The high density polyethylene film of claim 3 whenever characterized by a haze of less than 5%.

10. The high density polyethylene film of claim 3 whenever oriented such that the oriented film is characterized by a tensile modulus of elasticity greater than

about 200,000 pounds per square inch and a haze of less than 5%.

11. The high density polyethylene film of claim 2 wherein the low density ethylene polymer is an ethylene-butene-1 copolymer containing a minor amount of butene-1.

12. The high density polyethylene film of claim 11 wherein the ethylene-butene-1 copolymer is of density about 0.930–0.945.

13. The high density polyethylene film of claim 11 wherein the ethylene polymer is blended with 10–25% of the ethylene-butene-1 copolymer of density about 0.930–0.945.

14. The high density polyethylene film of claim 11 whenever oriented.

15. The high density polyethylene film of claim 11 whenever uniaxially oriented by a ratio of at least about 6:1.

16. The high density polyethylene film of claim 11 whenever oriented such that the tensile modulus of elasticity of the oriented film is greater than about 200,000 pounds per square inch.

17. The high density polyethylene film of claim 11 whenever characterized by a haze of less than 5%.

18. The high density polyethylene film of claim 11 whenever oriented such that the oriented film is characterized by a tensile modulus of elasticity of greater than about 200,000 pounds per square inch and a haze of less than 5%.

* * * * *



United States Patent [19]

Miwa et al.

[11] 4,405,774

[45] Sep. 20, 1983

[54] ETHYLENE COPOLYMER

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[52] U.S. Cl. ..... 526/348.2; 252/429 C; 526/119; 526/124; 526/125; 526/348.3; 526/348.4; 526/348.5; 526/348.6

[58] Field of Search 526/348.2, 348.3, 348.4, 526/348.5, 348.6

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[57] ABSTRACT

A copolymer of ethylene and a minor proportion of an α-olefin having 4 to 10 carbon atoms is characterized by having the properties

(1) a melt flow rate (MFR) of 0.1 to 100 g/10 min.;

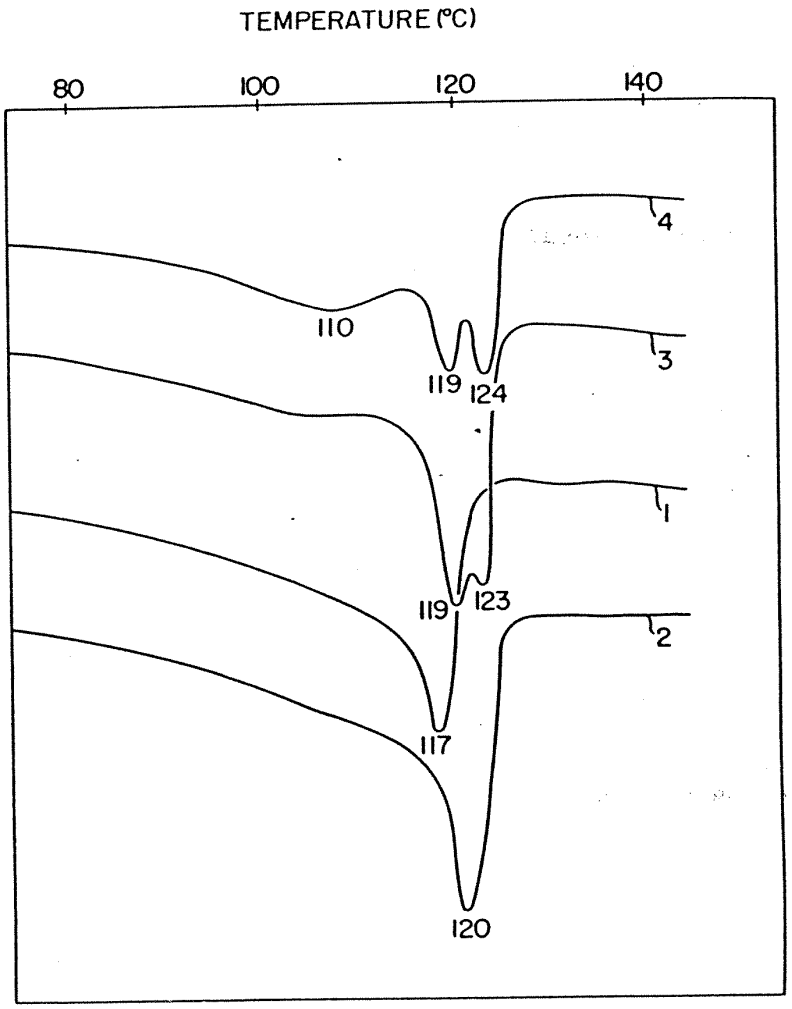
(2) a density of 0.91 to 0.94 g/cm³; and

(3) a xylene absorption per unit amorphous region (Y) satisfying the formula:

$$Y < -0.80X + 0.67$$

wherein X is the degree of the crystallinity of the copolymer. By satisfying the above requirements, the copolymer can give a film packaging material having excellent transparency, impact strength and opening property (anti-blocking property) in combination.

10 Claims, 1 Drawing Figure


TEMPERATURE (°C)
80
100
120
140
4
110
3
119
124
1
119
123
2
117
120

ETHYLENE COPOLYMER

BACKGROUND OF THE INVENTION

The present invention relates to an ethylene copolymer exhibiting excellent transparency, impact resistance and opening property when it is formed into a bag (hereinafter merely referred to as opening property).

High-pressure polyethylene is known as a resin having a relatively high transparency. In order to make the best use of its transparency, high-pressure polyethylene is used as a material for films, hollow containers and the like. However, as far as the film application is concerned, a thin film made of high-pressure polyethylene is useless for practical purposes because it exhibits low tear strength and impact strength. Therefore, high-pressure polyethylene is limited in its film application.

On the other hand, it is known that a copolymer of ethylene with an α-olefin having 3 or more carbon atoms, which is prepared by copolymerizing the ethylene with the α-olefin in the presence of a Ziegler catalyst or a Phillips catalyst under a low pressure, is a resin having an excellent mechanical strength and almost the same density as that of the high-pressure polyethylene. Ordinarily, in the production of the copolymer, titanium type catalysts are used as the Ziegler catalyst, or chromium type catalysts are used as the Phillips catalyst, and a pressure of 100 kg/cm^2 or less is used. The copolymers resulting from these processes are disadvantageous in that they exhibit poor transparency and opening property.

In this connection, there has been proposed a process for improving the transparency of the copolymers as disclosed in Japanese Patent Application Laid-open No.53-92887. However, as far as we know, the copolymer obtained by such a process is still unsatisfactory in its opening property.

The opening property is one of important qualities for a packaging film. If a bag has a poor opening property, it is impossible to pack efficiently an article thereinto. With regard to polymeric films, the index of blocking is used to indicate the adhesion of the polymeric films to each other. The index "opening property" as used herein signifies nothing but blocking when the polymeric films are in a specific form of product, i.e., bags.

SUMMARY OF THE INVENTION

Under these circumstances, we concentrated our efforts on the development of an ethylene copolymer which is excellent in respect to all of transparency, impact resistance, and opening property. As a result of this, we have found that such a copolymer can be produced and that such a copolymer is a special polymer product which has never been produced to date. More specifically, we have found that when the percentage of xylene absorption of the ethylene copolymer is reduced to less than that of a conventional polyethylene, the above mentioned object can be attained.

Accordingly, the copolymer of ethylene and a minor proportion of an α-olefin having 4 to 10 carbon atoms according to the present invention is characterized by having in combination the following properties:

(1) Melt Flow Rate (MFR): 0.1 to 100 g/10 min.,

(2) Density: 0.91 to 0.94 g/cm^3, and

(3) A xylene absorption per unit amorphous region (Y) satisfying the following formula.

$$Y < -0.80X + 0.67$$

wherein X is the degree of the crystallinity of the copolymer.

The copolymer of the present invention can be said to be more advanced than conventional ethylene polymers in that it is improved in both transparency and opening property. In addition, the copolymer of the present invention has far greater impact resistance than the conventional copolymers prepared by using Ziegler catalysts under low pressure.

BRIEF DESCRIPTION OF THE DRAWING

In the drawing, the single FIGURE is a reproduction of a graph showing heat absorption curves of the copolymers of Examples 1 and 2 and Comparative Examples 4 and 5 which were obtained by the differential thermal analysis (DSC).

DETAILED DESCRIPTION OF THE INVENTION

1. Copolymer

The ethylene copolymer of the present invention is defined by a number of physical properties.

(1) Composition

The copolymer is a copolymer of ethylene and a minor proportion of an α-olefin having 4 to 10 carbon atoms.

The term "minor proportion" as used herein refers to about 0.5 to 8 mole%, preferably, about 1 to 5 mole%, of the α-olefin, based on the total of the α-olefin units and the ethylene units.

An actual product represented by the term "polyethylene" is mostly a copolymer containing a small amount of modifying monomer units. Therefore, the term "copolymer of ethylene and a minor proportion of an α-olefin having 4 to 10 carbon atoms" as used herein is intended to include copolymers comprising, in addition to these two monomer units, a minor proportion, e.g., up to 10 mole%, preferably, up to 4.0 mole%, based on the total of the ethylene monomer units and the α-olefin units, of copolymerizable monomers such as propylene. Because the polymer of the present invention contains a significant amount of the comonomer (α-olefin) units, it is referred to as copolymer throughout the specification. However, the copolymer of the present invention may also be called polyethylene according to the above mentioned practice.

The α-olefins having 4 to 10 carbon atoms which are usable for the present invention are selected from those having a linear or branched chain. Examples of such α-olefins are 1-butene, 1-pentene, 1-hexene, 4-methyl-1-pentene, 1-octene, 1-decene and mixtures thereof. α-olefins having 4 to 8 carbon atoms, particularly, 6 to 8 carbon atoms, are preferable.

(2) Density

The copolymer according to the present invention has a density of from 0.91 to 0.94 g/cm^3. The density is determined according to ASTMD-1505.

The upper limit of the density is determined so as to provide excellent transparency of the copolymer. The preferable upper limit is about 0.93 g/cm^3.

On the other hand, the lower limit of the density is determined so as to provide the excellent opening prop-

erty of the copolymer. The preferable lower limit is about 0.915 g/cm^3.

The density of the copolymer is somewhat variable depending on the composition of the copolymer. However, as long as the α-olefin unit content in the copolymer is within the above stated range, the density of the copolymer falls within the above mentioned range.

(3) Melt Flow Rate (MFR)

The MFR of the copolymer of the present invention is in the range of from 0.1 to 100 g/10 min. The MFR is determined according to ASTMD-1238.

The upper limit of the MFR is determined so as to provide the excellent mechanical properties of the copolymer. The preferable upper limit is 10 g/10 min.

On the other hand, the lower limit of the MFR is determined so as to provide the excellent moldability of the copolymer. The preferable lower limit is 0.5 g/10 min.

(4) Xylene absorption

The xylene absorption per unit amorphous region (Y) is the most important factor distinguishing the copolymer of the present invention from other similar polymers. In accordance with the present invention, the xylene absorption per unit amorphous region (Y) should satisfy the following expression in relation to the degree of crystallinity (X) of the copolymer:

$$Y < -0.80X + 0.67$$

Preferably, this relationship is represented by the following formula:

$$Y \leqq -0.92X + 0.70$$

With regard to conventional polyethylenes, the above stated relationship is represented by the following formula:

$$Y \geqq -0.80X + 0.67$$

In this regard, the xylene absorption per unit amorphous region (Y) and the degree of crystallinity (X) are determined according to the following methods.

(1) Xylene absorption per unit amorphous region (Y)

A test piece consisting of a press sheet having a thickness of 1 mm and a weight of W_1 is immersed in a temperature-controlled bath filled with xylene at a temperature of 23° C. for 24 hours. After the immersion, the weight W_2 of the test piece is determined. The xylene absorption (S) is determined as the weight gain of the test piece calculated by the equation:

$$S = \frac{W_2 - W_1}{W_1}$$

In terms of the degree of crystallinity X of the test piece, the xylene absorption per unit amorphous region (Y) of the test piece is represented by the following equation:

$$Y = S/(1 - X)$$

(2) Degree of crystallinity (X)

The degree of crystallinity (X) is determined from the density according to the following equation:

$$D = \rho_c X + \rho_a (1 - X)$$

wherein:

D is the density of the specimen,

ρ_c is the density of the crystal region of the polyethylene: 1.014 g/cm^3

ρ_a is the density of the amorphous region of the polyethylene: 0.850 g/cm^3

Examinations by us indicated that there is a significant correlation between the rate of xylene absorption per unit amorphous region and the opening property. That is, although the correlation between the xylene absorption per unit amorphous region and the opening property and other qualities is not fully clear, it is considered that a low xylene absorption per unit amorphous region corresponds to a high density of the amorphous region, which results in a reduction in stickiness due to the amorphous region, whereby an excellent opening property is obtained. This consideration is based on the fact that, generally, the higher the density of a film, the lower is the stickiness thereof. The density per unit amorphous region tends to become high as the polymerization pressure becomes high, although the mechanism of this phenomenon is not clear.

As stated above, the opening property is synonymous with the blocking property. For commercial purposes, it is desirable that a polymer film have a blocking value of 300 g/10 cm^2 or less, preferably 100 g/10 cm^2 or less. The copolymer having an excellent opening property according to the present invention can satisfy the above mentioned blocking value range.

(5) Thermal property and other features

Another feature of the copolymer of the present invention, in its preferred embodiment, is that it exhibits a single melting point based on differential thermal analysis. In this regard, the copolymer of the present invention is clearly distinguishable from the low-density polyethylenes prepared by using Ziegler catalysts or chromium catalysts under a low pressure. That is, when a low-density polyethylene having a density of 0.940 or less is subjected to differential thermal analysis (DSC) under conditions such that the cooling rate of the sample is 10° C./min. and the heating rate of the sample during the measuring operation is 10° C./min., there is obtained a heat absorption curve having a plurality of sharp peaks (in most cases, 2 to 3) within a temperature range of from 100° to 130° C., which peaks correspond to melting points thereof.

The singularity of the melting point of a polymer signifies that the polymer has a single crystalline form. A polymer having a single crystalline form is considered to be more homogeneous than a polymer having a plurality of crystalline forms.

Thus, the copolymer of the present invention, in its preferred embodiment, has a highest melting point (T_{MPE}) higher than the melting point of high-pressure polyethylene but lower than the melting point of polyethylene prepared by using Ziegler catalysts under low pressure. More specifically, the relationship between the highest melting point (T_{MPE}) and the density (D) of the copolymer of the present invention is as follows.

$$700D - 536 < T_{MPE} < 50D + 77$$

The fact that a polymer has a single melting point has an important meaning particularly when the polymer is

a copolymer. When a plurality of monomers are copolymerized with each other, it is difficult to produce a copolymer having a single crystalline form. This is because the polymerizabilities of the monomers are usually different from each other. The copolymer of the present invention having a single melting point contains the comonomers (α-olefin monomers) uniformly dispersed therein. Therefore, even if the copolymer of the present invention contains a comonomer unit content lower than that of the conventional copolymer prepared by using a Ziegler catalyst under a low pressure, it exhibits a density lower than that of the conventional copolymer.

The copolymer of the present invention generally has a very narrow molecular weight distribution. For example, according to a preferred embodiment of the invention, the copolymer has a Q value ($\overline{M}_W/\overline{M}_N$) of from 2.0 to 5.0, preferably, from 2.0 to 4.0, more preferably, from 2.0 to 3.5. The narrow molecular weight distribution is probably not unrelated to the singularity of the melting point.

(6) Use

The copolymer of the present invention has excellent transparency, tear resistance and impact resistance all superior to those of high-pressure polyethylene, and its transparency, impact resistance and opening property are superior to those of copolymers prepared by using Ziegler catalysts or Phillips catalysts under low pressure. Accordingly, the copolymer of the present invention is suitable for use in producing a film.

The copolymer of the present invention can be formed into a film having a high degree of transparency by both the T-die method and the inflation method.

The copolymer of the present invention may be formed into various shaped articles by blow molding, injection molding, extrusion molding, and like techniques. As one specific example of extrusion molding, the copolymer of the present invention may be extrusion coated on other films or film-like materials (metal foil, paper, fabric, etc.) to produce a multi-layered film. Also, other resins may be extrusion coated on a film made of the copolymer of the present invention.

Because the copolymer of the present invention falls within the category of thermoplastic resins, it may be blended with other thermoplastic resins conventionally used for this type of resin, such as polyethylene, polypropylene, and ethylene-vinyl acetate copolymers. The copolymer of the present invention may have admixed therein other additives such as petroleum resins, waxes, stabilizers, antistatic agents, ultraviolet light absorbers, synthetic rubbers and natural rubbers, lubricants and inorganic fillers.

2. Preparation of copolymer

The copolymer of the present invention is prepared by subjecting the required monomers to copolymerization conditions. In order to ensure that the resulting copolymer will have the above enumerated physical properties, the choice of the catalysts and polymerization conditions used is important.

(1) Catalyst used

The catalyst used is selected from those which belong to the category of so-called Ziegler-type catalysts and are composed of a combination of the following components A and B.

(1) Component A

The component A is an organometallic compound.

The organometallic compound used as a cocatalyst in the present invention may be selected from organometallic compounds of metals of Groups I to III of the periodic table which are known as cocatalysts for the Ziegler-type catalysts. Particularly, organoaluminum compounds are preferable.

The organoaluminum compounds include those which have the formula:

$$R^1_{3-p}AlX^1_p$$

wherein: R^1 represents hydrogen or a hydrocarbon residue having 1 to 20 carbon atoms, preferably, 1 to 6 carbon atoms; X^1 represents hydrogen, halogens or an alkoxy group having 1 to 20 carbon atoms, preferably, 1 to 6 carbon atoms; and p represents a value of $0 \leqq p \leqq 2$, preferably, $0 < p \leqq 1.5$. Examples of such an organoaluminum compound are (a) trialkylaluminums such as trimethylaluminum, triethylaluminum, triisobutylaluminum, trioctylaluminum and tridecylaluminum; (b) dialkylaluminum monohalides such as diethylaluminum monochloride and diisobutylaluminum monochloride; (c) alkylaluminum sesquihalides such as ethylaluminum sesquihalide; (d) dialkylaluminum hydrides such as diethylaluminum hydride and diisobutylaluminum hydride; and (e) alkylaluminum alkoxides such as diethylaluminum ethoxide, diethylaluminum butoxide and diethylaluminum phenoxide.

These organoaluminum compounds of items (a) through (e) may be used singly or in mixtures of two or more of these compounds. In the polymerization under high temperature and pressure according to the present invention, a dialkylaluminum monohalide or an organoaluminum compound mixture of a dialkylaluminum monohalide with an organoaluminum compound of item (a), (c), (d) or (e) is preferably used. With regard to the amount of the organoaluminum compounds used, there is no specific limitation. However, it is desirable that the organoaluminum compound is used in a quantity such that the atomic ratio of Al/Ti with respect to a solid catalyst component as described hereinafter is in the range of from 3 to 200, preferably, from 6 to 20.

(2) Component B

The component B is a contact product of a magnesium compound defined as a component (a) and a titanium compound defined as a component (b).

(a) Magnesium compound

A magnesium compound which is suitable for use in the present invention is any of magnesium compounds in the form of a solid or a liquid.

Examples of such a magnesium compound are (i) magnesium halides such as magnesium dichloride, magnesium dibromide and magnesium diiodide; (ii) halohydrocarbyloxymagnesiums such as magnesiumethoxychloride and magnesium-hydroxychloride; (iii) magnesium dialcoholates such as magnesium diethoxide and magnesium dimethoxide; (iv) magnesium oxide and magnesium carbonate, and (v) organomagnesium compounds such as diethylmagnesium and ethylmagnesium chloride. Among these, the magnesium compounds of items (i), (ii) and (v) are preferable; and magnesium dichloride is particularly preferable. It is desirable that the solid magnesium compound have a specific surface

area of at least 5 m^2/g for the purpose of providing a highly active catalyst.

As the magnesium compound, use may also be made of those obtained by subjecting magnesium halides, such as magnesium dichloride, to dissolution in a suitable solvent and then to re-precipitation from the solution. Such re-precipitated magnesium compounds can be prepared by dissolving a magnesium halide in the presence or absence of an organic solvent in a medium selected from alcohols ROH wherein R represents a hydrogen residue having 3 to 10 carbon atoms; ethers R—O—R' wherein R and R' represent a hydrocarbon residue having 2 to 8 carbon atoms, or R and R' form a ring system containing a 5- to 8-membered ring; phosphoric esters $PO(OR)_3$ wherein R represents a hydrocarbon residue having 2 to 10 carbon atoms; and titanic acid esters $Ti(OR)_4$ wherein R represents a hydrocarbon residue having 3 to 10 carbon atoms and by adding a halogenating agent such as $TiCl_4$ and $SiCl_4$ or a reducing agent such as an alkylsiloxane or a derivative thereof to the resultant solution thereby to cause re-precipitation.

(b) Titanium compound

A titanium compound suitable for the present invention is selected from halides, oxyhalides, alcoholate and alkoxyhalides of titanium. Examples of these compounds are as follows.

(i) Compounds of tetravalent titanium

$TiCl_4$, $TiBr_4$, $Ti(OC_2H_5)Cl_3$, $Ti(O\text{-}n\text{-}C_4H_9)_3Cl$, $Ti(O\text{-}n\text{-}C_4H_9)_4$, etc.

(ii) Compounds of trivalent titanium

$TiCl_3$, $TiBr_3$, $Ti(OC_2H_5)Cl_2$, etc.

When a tetravalent titanium compound in the form of a liquid is used in the polymerization under high temperature and pressure according to the present invention, the resulting catalyst exhibits a high catalytic activity which leads to the production of a desirable copolymer.

The above mentioned magnesium compound and titanium compound are essential components in the present invention. The component B may contain an auxiliary component, if necessary. The use of an auxiliary component may be effective for further enhancing the uniformity of the resulting copolymer. Examples of auxiliary components are electron donors such as alcohols, ethers and esters; metal halide compounds such as $SiCl_4$ and $AlCl_3$; and polysiloxanes such as alkylhydropolysiloxanes and dialkylpolysiloxanes. A suitable method of using these auxiliary components is described in concrete terms in Japanese Patent Application Laid-open Nos. 55-21435 and 55-40745.

Contact condition

The contact between the component (a) and the component (b) may be carried out under any conditions conventionally known. However, it is desirable that the contact of these components with each other be carried out at a temperature of from −50° to 200° C., in general. The contact time is usually in a range of from about 10 minutes to about 5 hours. It is preferable that the contact between the components (a) and (b) be carried out with stirring. The use of a mechanical pulverization means such as a ball mill or a vibration mill may serve to afford a more thorough contact between the components (a) and (b).

The contact between the components (a) and (b) may also be carried out in the presence of a dispersion medium. Examples of suitable dispersion mediums for the contact are hydrocarbons, halogenated hydrocarbons and dihydrocarbylpolysiloxanes. Examples of hydrocarbons are hexane, heptane, benzene, toluene and cyclohexane. Examples of halogenated hydrocarbons are n-butyl chloride, 1,2-dichloroethane, chloroform, carbon tetrachloride, o-chlorotoluene, m-chlorotoluene, p-chlorotoluene, benzyl chloride, benzylidene chloride and iodobenzene. Examples of dihydrocarbylpolysiloxanes are dialkylpolysiloxanes such as dimethylpolysiloxane and methylphenylpolysiloxane.

Quantity ratio

The quantity of each component used may be arbitrary as long as the advantages of the present invention can be attained. Generally, the following range is preferable. The mole ratio of Mg/Ti, on which the quantity ratio of the component (a) to the component (b) depends, is in the range of, ordinarily, from 0.5 to 50, preferably, from 1 to 20.

It is preferable that the catalyst obtained by the above mentioned synthetic method have a fine particle configuration and a fine particle size. This is because such a catalyst ordinarily has a tendency to provide a copolymer having excellent uniformity. Accordingly, in order to produce a copolymer having excellent uniformity, it is desirable that the particle size of the catalyst be preferably 10 microns or less, more preferably, 5 microns or less.

(3) Quantity ratio between components A and B

The quantity ratio between the components A and B is not basically limited but is preferably within the range of 3 to 200, particularly 6 to 20, in terms of the Al/Ti atomic ratio.

(4) Preparation of catalyst

The catalyst is prepared by combining the components A and B within or outside the polymerization zone. The component A alone or a combination of the components A and B is injected into the polymerization zone under a high pressure by means of a high-pressure pump. For this reason, these components should be in the form of a liquid, or fine powder or its slurry and, if they are powdery, their particle size should preferably be of the order of 10μ or less, particularly of the order of 1 to 5μ.

(2) Polymerization of ethylene

(1) Polymerization apparatus

The polymerizaton of ethylene is preferably carried out in a continuous manner. The polymerization apparatus used for the polymerization reaction may be a continuous stirred tank reactor or a continuous tubular reactor, both of which are conventionally used for the high-pressure radical polymerization of ethylene.

The polymerizaton reaction may be carried out by using a single reactor of the above mentioned type in the form of a single compartment. Alternatively, a plurality of such reactors connected to each other in series to which a condenser is optionally connected may also be used. As another alternative, a single reactor of the above mentioned type may be effectively divided into a plurality of compartments in such a manner that the polymerization reaction can be carried out in a multi-compartment mode. In the multi-compartment mode polymerization method, the composition of monomers,

the concentration of the catalyst, the concentration of a molecular weight modifier, reaction conditions and the like are ordinarily controlled separately in the respective reactors or reaction compartments so that the properties of the polymers to be produced in the respective reactors or reaction compartments can be separately controlled. In the case where a plurality of reactors are connected to each other in series, in addition to a combination of two or more continuous stirred tank reactors, or two or more continuous tubular reactors, a combination of one or more continuous stirred tank reactor and one or more continuous tubular reactor may be used.

The polymer produced in one or more reactors is separated from the unreacted monomers. The resulting polymer can be treated without removing the residual catalyst in the same manner as in the case of the production of conventional high-pressure polyethylene. The unreacted monomer mixture is blended with an additional amount of the same monomer component, and the resulting blend is recycled under pressure into the reactor. The monomer component to be added has a composition such that the resulting blend will have the same composition as that of the original feed. Generally, the additional monomer component has a composition substantially equivalent to the composition of the polymer separated from the polymerization reactor.

The catalyst is, for example, dispersed in a suitable inert liquid to prepare a fine dispersion. Then, this fine dispersion is poured directly into the reactor by means of a high-pressure pump. Examples of suitable inert liquids usable in the present invention are white spirit, hydrocarbon oil, pentane, hexane, cyclohexane, heptane, toluene, higher branched saturated aliphatic hydrocarbons and mixtures thereof. In order to prevent contact of the dispersion with water and air before it is introduced into the reactor, the dispersion is preferably stored under a nitrogen seal. Furthermore, the ethylene and the other monomers should not contain substantial amounts of water and oxygen.

As stated above, the resultant polymer can be treated without removing the catalyst remaining in the polymer. This is because the catalyst used has very high activity, which makes it possible to attain a high conversion of the monomers to a desired polymer with a very small quantity of the catalyst.

(2) Polymerization condition

(i) Polymerization pressure

The pressure used in the polymerization process is more than 200 kg/cm^2, preferably, from 500 to 4000 kg/cm^2, more preferably, from 700 to 3000 kg/cm^2.

(ii) Polymerization temperature

The polymerization temperature is at least 125° C., preferably, in the range of from 150° to 350° C., more preferably, from 200° to 320° C.

(iii) Residence time

The average residence time in the reactor is related to the time during which the catalyst used retains its catalytic activity under the reaction conditions. The half life of the catalyst used depends on the reaction conditions, particularly, temperature. As the life of the catalyst becomes longer, the residence time of the monomers in the reactor is preferably extended. The average residence time used is in the range of from 2 to 600 seconds, preferably, from 10 to 150 seconds, more preferably, from 10 to 120 seconds.

(iv) Other features and particulars

The polymerization process of the present invention comes under the category of a high-pressure polymerization process for ethylene from the viewpoints of polymerization temperature and pressure. Therefore, the present polymerization process is carried out with substantially no liquid dispersion medium except for a small amount of the liquid medium to be introduced as a dispersion medium for the catalyst or for other purposes. Accordingly, this polymerization process requires separation of only the non-reacted monomers from the resulting polymer after the polymerization reaction has been completed. Separation of any liquid medium from the resulting polymer and refining of the separated liquid medium are unnecessary.

In accordance with this polymerization process, the resulting polymer contains only a trace of the residual catalyst, so that it is unnecessary to decompose and refine the residual catalyst. The resulting polymer is separated from the unreacted monomers in a separator. In this manner, a polymer product is obtained. This product may be used directly as it is. Alternatively, the product may be subjected to various post-treatment procedures such as those which have been already used for products obtained by the high-pressure radical polymerization process.

3. Experimental examples

The methods of measurements used for evaluation of the quality of the copolymer of the present invention were as follows.

(1) MFR: ASTM D-1238

(2) Density: ASTM D-1505

(3) Haze: ASTM D-1003

(4) Bag drop impact strength:

A test bag of blown film of a thickness of 30 microns, which is filled with 2,250 grams (g) of sand per 100 mm of flat width of the bag, is freely dropped from progressively increased heights onto the floor. The maximum height (cm) at which the bag does not rupture is taken as the bag-drop impact strength (BDI).

(5) Opening property:

A loading pressure of 15 kg/cm^2 is applied on a test piece of a blown film (tube) of a thickness of 30 microns at a temperature of 45° C. for 24 hours. Thereafter, the force (in g/10 cm^2) necessary for separating the opposed walls of the film is determined. This force value represents the blocking value.

(6) Differential thermal analysis (DSC)

A Perkin-Elmer DSC type 2 differential thermal analyzer is used. 5 mg of a sample is melted by heating it to a temperature of 150° C. Then the melt is cooled at a cooling rate of 10° C./min. and crystallized. The crystallized sample is again heated from 50° to 150° C. at a heating rate of 10° C./min., and measurement is carried out. The melting points of the sample are determined from the temperatures corresponding to the respective peaks in the resulting heat absorption curve. The melting point at the highest temperature represents the highest melting point (T_{MPE}).

EXAMPLE 1 (and Comparative Examples 3 through 4)

Preparation of catalyst component

A reactor equipped with an agitator and an external jacket, whose inside atmosphere was replaced by nitrogen gas (N_2), was charged with 1 l of n-heptane which had been thoroughly degassed and refined. Then 0.67 mole of anhydrous $MgCl_2$ and 0.2 mole of $Ti(O\text{-}nC_4H_9)_4$ were introduced into the reactor. The resulting mixture was agitated at a temperature of 70° C. for 1 hour. Then, 0.53 mole of $n\text{-}C_4H_9OH$ was introduced into the reactor, and the resulting mixture was agitated for 1 hour. Thereafter, 0.13 mole of $AlCl_3$ was introduced into the reactor, and the resulting mixture was agitated for 1 hour. In addition, 0.13 mole of $TiCl_4$ and 1 mole of methylhydropolysiloxane (MHPS) having a viscosity of 21 centistokes were introduced into the reactor, and the resulting mixture was agitated at a temperature of 70° C. for 2 hours. After the reaction was completed, a solid component was obtained as a solid catalyst component without being washed with n-heptane.

Preparation of catalyst dispersion

A catalyst preparation vessel equipment with an agitator, the atmosphere within which was replaced by nitrogen gas (N_2), was charged with 25 l of n-hexane which had been thoroughly degassed and refined. Then 5 g of the solid catalyst component prepared as described above and 124 millimole of diethylaluminum chloride were added to the reactor, and the solid catalyst component in the resulting mixture was preactivated so as to provide an atomic ratio Al/Ti of 16. Thereafter, hexene-1, which had been thoroughly degassed and refined, was added to the reactor in an amount such as to provide a mole ratio of hexene-1/Ti of 20. The resulting mixture was agitated for 2 hours thereby to produce a fine catalyst suspension.

High-pressure polymerization of ethylene

A continuous reactor of autoclave type with agitator having an internal volume of 1.5 l was continuously charged with 12.5 kg/hr of ethylene, 27.8 kg/hr of 1-butene, 5 l/hr of hydrogen, and 1.2 l/hr of the catalyst suspension at a polymerization temperature of 240° C. and a polymerization pressure of 1,600 kg/cm^2, thereby to produce a copolymer.

The resulting copolymer had a density of 0.920 g/cm^3, an MFR of 0.7, a 1-butene content of 3.8 mole%, a molecular weight M_N of 38,000, a Q value (M_W/M_N) of 4.4, one peak at a temperature of 117° C. measured by DSC, a degree of crystallinity of 48.3% determined from its density, and a xylene absorption per unit amorphous region of 0.25.

The copolymer was formed into a film having a width of 30 mm and a thickness of 30 microns by means of a commercially available high-pressure polyethylene film forming machine (manufactured by Modern Machinery K.K.). The forming operation was carried out at a resin temperature of 220° C. at a rotational speed of the screw of 50 rpm.

The evaluation results of the copolymer were as shown in Table 1 appearing hereinafter together with the polymerization conditions. In addition, two types of commercially available low-density polyethylenes were formed into films according to the same procedure as that described above. The evaluation results of the polyethylenes were as shown in Table 2 (Comparative Examples 3 and 4).

The copolymer of Example 1 and the polyethylenes of Comparative Examples 3 and 4 are all ethylene/1-butene copolymers. However, the copolymer of the present invention is superior to the commercial polyethylenes with respect to transparency, opening property, and impact strength.

EXAMPLES 2 and 7 (and Comparative Examples 5 and 6)

In each of Examples 2 and 7, a copolymer of the present invention in which 1-hexene was used as a comonomer was prepared.

Commercially available copolymers shown in Table 2 as Comparative Examples 5 and 6, are those obtained by using 4-methyl-1-pentene having the same carbon atoms of 6 as a comonomer.

The copolymers of the present invention are superior in transparency and opening property of the comparative copolymers and exhibit an impact strength BDI exceeding 5 m which is remarkably superior to that of the comparative copolymers.

EXAMPLE 3

The same polymerization reactor as that described in Example 1 was operated under the conditions indicated in Table 1 and a polymerization pressure of 2,000 kg/cm^2.

As is apparent from Table 1, the resulting copolymer exhibited remarkably good transparency and opening property.

EXAMPLE 4

The same polymerization reactor as that described in Example 1 was operated under the conditions indicated in Table 1 and a polymerization pressure of 300 kg/cm^2.

The physical properties of the resulting copolymer having a high MFR were as shown in Table 1.

EXAMPLE 5

The same polymerization reactor as that described in Example 1 was operated under the conditions indicated in Table 1. In this case, 1-octene was used as the comonomer.

The physical properties of the resulting copolymer were as shown in Table 1.

EXAMPLE 6

The same polymerization reactor as that described in Example 1 was operated under the conditions indicated in Table 1. In this case, 1-butene was used as the comonomer.

The physical properties of the resulting product having a low density were as shown in Table 1.

EXAMPLE 8

The same polymerization reactor as that described in Example 1 was operated under the conditions indicated in Table 1. In this case, 4-methyl-1-pentene was used as the comonomer.

The physical properties of the resulting copolymer were as shown in Table 1.

Comparative Examples 1 and 2

Two types of commercially available high-pressure polyethylenes were evaluated. Both of these polyethylenes exhibited poor impact strength.

TABLE 1

	Example No.							
	1	2	3	4	5	6	7	8
Polymerization pressure, Kg/cm^2	1600	1600	2000	300	700	1600	1600	1600
Polymerization temperature, °C.	240	240	205	240	240	240	240	240
Ethylene feed, kg/hr.	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5
Type of comonomer	1-butene	1-hexene	1-hexene	1-hexene	1-octene	1-butene	1-hexene	4-methyl-1-pentene
Comonomer feed, kg/hr.	27.8	33.5	30	50	18.0	48	35	35
Hydrogen feed, l/hr.	5	5	0	50	10	15	5	5
Catalyst feed, l/hr	1.2	0.9	0.7	1.3	1.5	1.0	0.9	
MFR, g/10 min.	0.7	1.2	0.2	80	2.5	4.0	0.8	0.8
D, g/cm^3	0.920	0.922	0.925	0.918	0.938	0.912	0.920	0.920
Comonomer content, mole %	3:8	2.7	2.3	3.6	0.8	5.6	3.3	3.3
M_N	38000	32000	54000	8600	26000	24000	34000	33800
$Q(M_W/M_N)$	4.4	3.2	3.8	2.8	2.9	2.7	2.8	2.9
Number of DSC peak(s)	1	1	1	1	1	1	1	1
Temperature of DSC peak, °C.	117	120	122	115	125	117	122	122
Degree of crystallization (X)	0.483	0.497	0.518	0.469	0.607	0.426	0.483	0.483
Xylene absorption per unit amorphous region (Y) 30μ blown film	0.25	0.23	0.21	0.27	0.15	0.32	0.24	0.25
Haze, %	3.8	3.5	1.3	3.0	4.1	1.8	2.1	2.6
Opening property, $g/10\ cm^2$	90	40	0	130	0	250	60	180
BDI, cm	320	510	590	110	220	380	530	490

TABLE 2

	Comparative Example No.					
	1	2	3	4	5	6
Sample of commercially available polyethylene	YUKALON NH-50 mfd. by Mitsubishi Yuka K.K.	YUKALON YF 30 mfd. by Mitsubishi Yuka K.K.	A	B	C	D
MFR, g/10 min.	2.8	1.0	1.5	3.5	2.3	2.2
D, g/cm^3	0.925	0.920	0.920	0.922	0.921	0.926
Type of comonomer	—	—	1-butene	1-butene	4-methyl-1-pentene	4-methyl-1-pentene
Comonomer content, mole %	—	—	4.2	3.9	3.3	2.7
M_N	22000	18000	20500	29300	28800	32100
$Q(M_W/M_N)$	6.5	9.3	4.2	3.3	2.8	2.8
Number of DSC peak(s)	1	1	2	2	3	3
Temperature(s) of DSC peak(s), °C.	113	108	118 121	119 123	110 119 124	110 122 127
Degree of crystallization	0.518	0.483	0.483	0.497	0.490	0.539
Xylene absorption per unit amorphous region 30μ blown film	0.30	0.32	0.35	0.33	0.31	0.36
Haze, %	6.5	12.0	12.8	15.2	4.5	6.5
Opening property, $g/10cm^2$	280	190	480	400	800	650
BDI, cm	150	120	105	90	400	350

What we claim is:

1. A copolymer of ethylene and a minor proportion of an α-olefin having 4 to 10 carbon atoms, characterized by having in combination the properties of:

(1) a melt flow rate (MFR) of 0.1 to 100 g/10 min.;

(2) a density of 0.91 to 0.94 g/cm^3; and

(3) a xylene absorption per unit amorphous region (Y) satisfying the following formula:

$$Y < -0.80X + 0.67$$

wherein X is the degree of crystallinity of the copolymer.

2. A copolymer as claimed in claim 1, wherein the xylene absorption per unit amorphous region (Y) satisfies the formula:

$$Y \leqq -0.92X + 0.70.$$

3. A copolymer as claimed in claim 1 or 2, wherein the MFR and the density are as follows:

MFR: 0.5 to 10 g/10 min.;

Density: 0.915 to 0.930.

4. A copolymer as claimed in claim 1, wherein the content of the α-olefin having 4 to 10 carbon atoms is in the range of from 1.0 to 5.0 mole% of the total of the ethylene and the α-olefin contents.

5. A copolymer as claimed in claim 1, wherein the α-olefin has 6 to 8 carbon atoms.

6. A copolymer as claimed in claim 1, which has a molecular weight distribution Q value ($\overline{M}_W/\overline{M}_N$) of from 2.0 to 4.0.

7. A copolymer as claimed in claim 1, which has a single melting point as determined by the differential thermal analysis.

8. A copolymer as claimed in claim 7, wherein the relationship between the highest melting point (T_{MPE}, degrees in Celsius) determined by the differential ther-

mal analysis and the density (D) is represented by the following formula:

$$700D - 536 < T_{MPE} < 50D + 77.$$

9. A copolymer as claimed in claim 8, wherein the α-olefin has 6 to 8 carbon atoms.

10. A copolymer as claimed in claim 9, which has a molecular weight distribution Q value ($\overline{M}_W/\overline{M}_N$) of from 2.0 to 4.0.

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IP research publications

United States Patent [19]

Shibata et al.

[11] **4,429,079**

[45] **Jan. 31, 1984**

[54] **ETHYLENE/ALPHA-OLEFIN COPOLYMER COMPOSITION**

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[57] **ABSTRACT**

This invention relates to a composition comprising a mixture of at least two ethylene-rich ethylene/alpha-olefin copolymers (A) and (B) below which has excellent transparency and impact strength and improved properties, particularly low-temperature heat sealability, heat seal strength and flexural resistance.

(A) 95 to 40% by weight of a random copolymer of ethylene and an alpha-olefin having 5 to 10 carbon atoms which has a melt index of 0.1 to 20 g/10 min., a density of 0.910 to 0.940 g/cm³, a crystallinity by X-rays of 40 to 70%, a melting point of 115° to 130° C. and an ethylene content of 94 to 99.5 mole %; and

(B) 5 to 60% by weight of a random copolymer of ethylene and an alpha-olefin having 3 to 10 carbon atoms which has a melt index of 0.1 to 50 g/10 min., a density of 0.870 to 0.900 g/cm³, a crystallinity by X-rays of 5 to 40%, a melting point of 40° to 100° C. and an ethylene content of 85 to 95 mole %.

7 Claims, No Drawings

ETHYLENE/ALPHA-OLEFIN COPOLYMER COMPOSITION

FIELD OF TECHNOLOGY

This invention relates to an ethylene/alpha-olefin copolymer composition comprising a blend of ethylene/alpha-olefin copolymers which has excellent heat sealing properties and flexural resistance and improved properties suitable, for example, for packaging films.

BACKGROUND TECHNOLOGY

Techniques of setting off the defects of different kinds of films by laminating them into a composite have been known heretofore in the field of packaging bags. Particularly, in the field of packaging foodstuffs, laminated packaging bags composed of a resin layer having excellent transparency, mechanical properties, rigidity, heat resistance and gas-barrier property, such as polypropylene, a polyester, nylon, cellophane or an ethylene/vinyl alcohol copolymer, and a resin layer having good transparency and heat sealability, such as polyethylene, polypropylene or an ethylene/vinyl acetate copolymer have come into widespread use.

In order to produce such laminated packaging bags, there is usually employed a method which comprising heat-sealing the top and bottom end portions or all end portions of a film, and in the resulting bag, the innermost layer is a resin layer having good heat sealability. Accordingly, films use as the innermost layer of the packaging bags are required not only to have good heat sealing characteristics but also to be free from extraction or degradation of the resin components which may be caused by an article packaged therein. In recent years, there have been a variety of articles to be packed and a variety of modes of using the packaging materials and some problems have arisen with regard to films which have heretofore been used to form the heat sealed layer. These problems include, for example, the high and narrow heat-sealing temperature range of polypropylene films, the poor heat resistance, strength and oil resistance and acetic acid odor of ethylene/vinyl acetate copolymer films, the poor heat sealing strength and hot tack property of films of high-pressure low-density polyethylene, and the poor flexural resistance of each of such films which is likely to lead to the formation of pinholes in bags during handling in transportation, etc. and to cause leakage of the contents.

The present invention has successfully given a solution to the above new problems, and as will be described below in detail, provides an ethylene/alpha-olefin copolymer composition having excellent low-temperature heat sealability, heat seal strength, flexural resistance, transparency and impact strength and being suitable for packaging films.

DISCLOSURE OF THE INVENTION

The present inventors have made investigations about the solving of the above new problems, and found that a blend of at least two ethylene-rich ethylene/alpha-olefin random copolymers (A) and (B) having specified properties gives a solution to the above problems and exhibits excellent properties.

The investigations of the present inventors have led to the discovery that a blended composition of 95 to 40% of (A) a random copolymer of ethylene and an alpha-olefin having 5 to 10 carbon atoms which has a melt index of 0.1 to 20 g/10 min., a density of 0.910 to 0.940 g/cm^3, a crystallinity by X-rays of 40 to 70%, a melting point of 115° to 130° C. and an ethylene content of 94 to 99.5 mole% and 5 to 60% by weight of (B) a random copolymer of ethylene and an alpha-olefin having 3 to 10 carbon atoms which has a melt index of 0.1 to 50 g/10 min., a density of 0.870 to 0.900 g/cm^3, a crystallinity by X-rays of 5 to 40%, a melting point of 40° to 100° C. and an ethylene content of 85 to 95 mole% has excellent low-temperature heat sealability, heat seal strength and flexural resistance and other excellent properties, especially transparency and impact strength.

In the present invention, examples of the alpha-olefin having 5 to 10 carbon atoms to be copolymerized with ethylene in the copolymer (A) include 1-pentene, 1-hexene, 4-methyl-1-pentene, 1-octene and 1-decene, and mixtures of at least two of these alpha-olefins. Of these, alpha-olefins having 6 to 8 carbon atoms, especially 4-methyl-1-pentene and 1-octene, are preferred.

The melt index of the copolymer (A) should be in the range of 0.1 to 20 g/10 min., preferably 0.5 to 10 g/10 min. When the melt index is less than 0.1 g/10 min., the flowability of the resulting composition is poor and packaging bags of good quality are difficult to obtain. On the other hand, if the melt index exceeds 20 g/10 min., the resulting composition has poor impact strength, tear strength and heat seal strength, and does not suit the purpose of this invention. In view of a balance between the ease of polymerization and the impact strength and tear strength of the polymer, the copolymer (A) most preferably has a melt index of 1.0 to 5.0 g/10 min. The melt index, as used in this invention is a value measured at 190° C. under a load of 2160 g substantially in accordance with the method of ASTM-D-1238. The density of the copolymer (A) used in this invention should be not more than 0.940 g/cm^3, preferably not more than 0.935 g/cm^3, in order to ensure good hot tack property at heat sealing and impart good transparency and impact strength to packaging bags. The density of the copolymer in this invention is a value measured by the method of ASTM-D-1505. On the other hand, in order to provide films having excellent mechanical properties and oil resistance and being free from stickness, the copolymer (A) should have a density of at least 0.910 g/cm^3, preferably at least 0.920 g/cm^3. If the resin is sticky, films prepared therefrom undergo blocking, and therefore bags are difficult to make therefrom. If the oil resistance of the films is poor, they cannot be used as packaging bags for oily foods, etc. Thus, the purpose of the invention cannot be achieved.

The crystallinity by X-rays of the copolymer (A) of this invention has a correlation with its density, and should be in the range of 40 to 70%, preferably 50 to 65%. If the crystallinity of the copolymer (A) exceeds 70%, a mixture of it with the copolymer (B) does not have improved oil resistance. If the crystallinity is less than 40%, the resulting composition is soft and has poor mechanical properties.

The copolymer (A) has 1 or more, in many cases 2 or 3, and preferably 3, melting points (sharp peaks) determined from an endothermic curve measured by a differential scanning calorimeter (DSC) at a temperature raising rate of 10° C./min. the highest melting point of the copolymer (A) is 115° to 130° C., preferably 115° to 125° C. If the melting point is lower than 115° C., the resulting film has poor heat resistance, and if it exceeds

130° C., the resulting film has poor low-temperature heat sealability. The ethylene/alpha-olefin copolymer (A) used in this invention has an ethylene content of 94 to 99.5 mole%, preferably 95 to 99 mole%, more preferably 96 to 98 mole%.

The use of the copolymer (A) having a molecular weight distribution (the ratio of the weight average molecular weight to the number average molecular weight) of up to 6 in this invention is preferred because it will lead to a film having excellent transparency. For example, the molecular weight distribution is preferably about 1.5 to 6. The molecular weight distribution is a value determined by drawing a molecular weight distribution curve using a gel permeation chromatograph [the measuring device: Model 150C-LC/GPC, made of Waters Associates Company; the column: GMH-6, a product made by Toyo Soda Co., Ltd.; the solvent: o-dichlorobenzene; the measuring temperature: 135° C.], and calculating the weight average molecular weight (to be abbreviated as $\overline{M}_w$) and the number average molecular weight (to be abbreviated as $\overline{M}_n$) by a universal calibration method using polystyrene as a standard.

The distribution of the composition of the copolymer (A) used in this invention varies depending upon the catalyst used. The p-xylene soluble content (I) at room temperature and the boiling n-heptane-insoluble content are useful as measures of the range of the distribution of composition, and for example, in copolymers having the same average molecular weight and density, larger (I) values show a larger proportion of a portion having a low molecular weight and/or an amorphous portion. On the other hand, larger (II) values show a larger proportion of a polyethylene crystalline portion of the copolymer indicating that copolymerization has not taken place uniformly. Preferred as the copolymer (A) used in this invention are those copolymers which have a (I) value of not more than 10% by weight, especially not more than 7% by weight, and a (II) value of not more than 35% by weight with the sum of (I)+(II) being not more than 40% by weight. The boiling n-heptane-insoluble content and the p-xylene-soluble content at room temperature are measured by a Soxhlet extracting method.

An example of a suitable catalyst for the production of the copolymer (A) having the aforesaid properties used in this invention is a catalyst composed of a highly active titanium catalyst component formed of a magnesium compound and a titanium compound, such as a solid titanium catalyst component supported on a hydrocarbon-insoluble magnesium compound, and an organoaluminum compound. For example, the highly active titanium catalyst component may be a titanium-type catalyst supported on a magnesium-containing compound containing a magnesium-halide especially magnesium chloride, or magnesium oxide, which has a Cl/Ti weight ratio of preferably from 5 to 150, a Ti/Mg mole ratio of preferably from 3 to 90 and a surface area of at least 70 m^2/g, conveniently at least 150 m^2/g. Examples of such titanium catalyst component are the catalysts described in Japanese Patent Publication No. 32270/1975 (U.S. Pat. No. 4,071,674; West German OLS No. 2,346,471) and Japanese Laid-Open Patent Publication No. 95382/1975 (British Pat. No. 1,485,520; West German OLS No. 2,461,677), and these catalysts are preferred. Examples of the organoaluminum compound include organoaluminum compounds of the formula R_nAlX_{3-n} (wherein R represents a hydrocarbon group such as an alkyl group, n is a number represented by $1 \leqq n \leqq 3$, and X represents hydrogen, chlorine, or an alkoxy group having 2 to 4 carbon atoms) as cocatalysts. A mixture of two or more of such organoaluminum compounds may also be used if its average composition satisfies the above formula. As organoaluminum compounds advantageous for the formation of polymers having excellent transparency, alkyl aluminum sesquichlorides and/or dialkylaluminum halides, particularly an alkyl aluminum halide and a mixture of it with a dialkyl aluminum halide, can be cited as preferred examples. Other organoaluminum compounds such as trialkylaluminums, dialkyl aluminum hydrides, dialkyl aluminum alkoxides, or alkyl aluminum alkoxyhalides can also be used, but are not so good for the transparency of the resulting polymers.

A suitable method for obtaining the copolymer (A) used in this invention can be carried out preferably in the co-presence of a hydrocarbon solvent or using the monomers themselves as a solvent at a temperature above the melting point of the copolymer formed, preferably at a temperature of at least about 140° C., preferably under such conditions that the solvent and the copolymer form a homogeneous phase. Preferably, the copolymerization is carried out continuously while maintaining the monomer concentration constant. The range of conditions under which the solvent and the copolymer form a homogeneous phase varies depending upon the type of the solvent, the concentrations (pressures) of the monomer, hydrogen, etc. in the solution, the polymerization temperature, the molecular weight (intrinsic viscosity) of the copolymer, etc. Desirably, therefore, the range is predetermined by performing a preliminary experiment. The polymerization is carried out preferably under pressure. For example, there can be employed pressures of about 2 to about 100 kg/cm^2, preferably about 15 to about 70 kg/cm^2. One example of the production of an ethylene/alpha-olefin random copolymer suitable for use in this invention as above is by the method described in detail in Japanese Laid-Open Patent Publication No. 92887/1978 (U.S. Pat. No. 4,205,021; West German OLS No. 2,803,598) filed by the present applicant.

Examples of the alpha-olefin having 3 to 10 carbon atoms to be copolymerized with ethylene in the copolymer (B), the other component of the composition of this invention, are propylene, 1-butene, 1-pentene, 1-hexene, 4-methyl-1-pentene, 1-octene, 1-decene and mixtures of these. Alpha-olefins having 3 to 5 carbon atoms, particularly 1-butene, are preferred.

The melt index of the copolymer (B) should be in the range of 0.1 to 50 g/10 min., preferably 1 to 30 g/10 min. If the melt index is less than 0.1 g/10 min., the flow characteristics of the resulting composition is poor, and good packaging films are difficult to obtain. On the other hand, if it exceeds 50 g/10 min., the mechanical strength of the resulting composition is reduced. The density of the copolymer (B) should be in the range of 0.870 to 0.900 g/cm^3, preferably 0.875 to 0.895 g/cm^3. When a copolymer (B) having a density of more than 0.900 g/cm^3 is mixed with the copolymer (A), the resulting composition does not show an effect of imparting improved flexural resistance. On the other hand, if the density is lower than 0.870 g/cm^3, the resin is sticky, and when the resin (B) is mixed with the copolymer (A) and the mixture is formed into a packaging film, the film inconveniently undergoes blocking. The ethylene con-

tent of the copolymer (B) is 85 to 95 mole%, preferably 88 to 95 mole%.

The crystallinity by X-ray of the copolymer (B) has a correlation with its density, and should be in the range of 5 to 40%, preferably 7 to 30%. When a copolymer (B) having a crystallinity of more than 40% is mixed with the copolymer (A), the resulting mixture does not exhibit improved flexural resistance. On the other hand, if the crystallinity is lower than 5%, the resin is sticky, and when it is mixed with the copolymer (A) and the mixture is formed into a packaging film, the film inconveniently undergoes blocking.

The copolymer (B) should have a melting point, determined from an endothermic curve by DSC at a temperature raising rate of 10° C./min., of 40° to 100° C., preferably 60° to 90° C. If a copolymer (B) having a melting point of more than 100° C. is mixed with the copolymer (A), there is no appreciable effect of decreasing the heat sealing temperature. If the melting point is lower than 40° C., the resulting packaging film has reduced heat resistance.

One method of producing the copolymer (B) having the aforesaid properties for use in this invention comprises copolymerizing ethylene with an alpha-olefin having 3 to 10 carbon atoms in the presence of a solvent using a catalyst composed of a vanadium compound, for example at least one compound selected from the group consisting of vanadyl trichloride, vanadyl monoethoxydichloride, triethoxyvanadyl, vanadium oxydiacetylacetonate and vanadium triacetylacetonate, and an organoaluminum compound. As the organoaluminum compound, an organoaluminum compound represented by the formula R_nAlX_{3-n} (wherein R is a hydrocarbon group such as an alkyl group, n is a number represented by $0<n\leqq3$, and X is hydrogen, chlorine or an alkoxy group having 2 to 4 carbon atoms) is used conveniently as a co-catalyst. A mixture of two or more of such organoaluminum compounds may also be used if its average composition satisfies the above formula.

In order to obtain packaging films having excellent low-temperature heat sealability, heat seal strength, flexural resistance, transparency and impact strength from the composition of this invention, it is necessary that the ratio (wt. %) of the copolymer (A) to the copolymer (B) should be in the range of from 95:5 to 40:60, preferably from 90:10 to 60:40. If the proportion of the copolymer (B) is less than 5% by weight, the low-temperature heat sealability and flexural resistance of the films are not improved, and if the proportion of the copolymer (B) exceeds 60% by weight, the heat seal strength of the films is reduced.

Formation of packaging films from the composition of this invention may be effected by mixing the copolymer (A) and the copolymer (B) in the above-specified ratios, and molding the mixture into a film form. For example, it may be carried out by mixing the copolymers by a V-blender, a ribbon blender, a Henschel mixer, a tumbler blender, etc., and forming the mixture directly into a film by an ordinary film-forming method such as a T-die method or an inflation method. Or there can also be used a method which comprises kneading and granulating the aforesaid mixture by means of an extruder, a kneader, a Bunbury mixer, etc., and molding the granules into a film.

Various additives usually employed for polyolefins, such as weatherability stabilizers, heat stabilizers, antistatic agents, anti-clouding agents, anti-blocking agents, antislip agents, lubricants, pigments, dyes, and antistick agents may be added to the composition of this invention in an amount of the range not impairing the purpose of the invention.

Since the composition of this invention in the form of a film has excellent transparency, flexural resistance and impact strength, it can be used singly as a packaging film such as a food-packing wrap film, a stretch film, a shrink film or a general packaging film, an agricultural film, a protective film. Furthermore, by taking advantage of its low-temperature heat sealability, it can be laminated to various substrates to provide packaging films suitable for various uses. The thickness of the film can be selected properly. For example, when it is used singly, its preferred thickness is, for example, about 10 microns to about 100 microns, and when it is used as a laminate, its preferred thickness is, for example, about 1 to about 50 microns.

The substrate materials may, for example, be film-forming polymers, paper, aluminum foils, cellophane, etc. Examples of such polymers include olefinic polymers such as high-density polyethylene, medium-density polyethylene, low-density polyethylene, an ethylene/vinyl acetate copolymer, an ethylene/acrylate copolymer, an ionomer, polypropylene, poly-1-butene, or poly-4-methyl-1-pentene; vinyl-type polymers such as polyvinyl chloride, polyvinylidene chloride, polystyrene, polyacrylates, and polyacrylonitrile; polyamides such as nylon 6, nylon 66, nylon 7, nylon 10, nylon 11, nylon 12, nylon 610 and poly(m-xylylene adipamide); polyesters such as polyethylene terephthalate, polyethylene terephthalate-isophthalate, and polybutylene terephthalate; polyvinyl alcohol; an ethylene/vinyl alcohol copolymer; and polycarbonate. These polymers can be selected properly depending upon the purpose and an article to be packaged. For example, when the article to be packed is a perishable food, resins having excellent transparency, rigidity and gas-barrier property, such as polyamides, polyvinylidene chloride, an ethylene/vinyl alcohol copolymer, polyvinyl alcohol and polyesters, are selected. For packing confectionary and fibers, polypropylene having good transparency, rigidity and resistance to water permeation can, for example, be selected as the outside layer. When the substrate is a polymeric film or sheet, it may be monoaxially or biaxially stretched.

For the production of a composite film obtained by bonding the packaging film prepared from the ethylene/alpha-olefin copolymer composition of this invention to the substrate, various known methods, such as the dry laminating method, extrusion laminating method, sandwitch laminating method and co-extrusion method, can be used.

The packaging film composed of the ethylene/alpha-olefin copolymer composition of this invention has the advantage that it has better low-temperature heat sealability, heat seal strength, flexural resistance and hot tack property than high-pressure low-density polyethylene which is a conventional sealing material and better heat seal strength, heat resistance and rigidity than an ethylene/vinyl copolymer and is free from odor.

The composition of this invention can be used as packaging bags for packing various articles. Since it has excellent low-temperature heat sealability, hot tack property, impact strength, flexural resistance, tear strength, especially excellent impact strength and flexural strength at low temperatures, it can be suitably used for packing refrigerated foods, water-containing foods such as pickles, tofu and konjak, and oily foods

such as curry, meat roasting sauce, soup, butter and cheese. Furthermore, because of its excellent flexural resistance (resistance to pinholes), it can also be suitably used as packaging bags for transporting liquids.

The following examples illustrate the present invention in greater detail. The invention, however, is not restricted by these examples so long as it does not go beyond the scope of the invention.

EXAMPLE 1

Preparation of a Copolymer

(A): ethylene/4-methyl-1-pentene copolymer

A 200-liter continuous polymerization reactor was charged hourly with 80 liters of hexane as a solvent, 20 millimoles of a 2:3 mixture of diethyl aluminum chloride and triethylamine, and 0.28 millimole, calculated as titanium, of a catalyst prepared by adding dropwise 60 moles of ethanol, 27 moles of diethyl aluminum chloride and 100 moles of titanium tetrachloride in this order to 10 moles of anhydrous magnesium chloride in hexane to react them with each other. Simultaneously, 13.5 kg/hr of ethylene, 14.4 kg/hr of 4-methyl-1-pentene and 60 liters/hr of hydrogen were continuously fed into the polymerization reactor, and the monomers were copolymerized at a polymerization temperature of 145° C. and a total pressure of 30 kg/cm^2.G with a residence time of 1 hour under conditions such that the concentration of the polymer in the hexane solvent was 119 g/liter. The resulting copolymer [to be abbreviated as E-4MP copolymer (I)] had a melt index (190° C.) of 2.3, a crystallinity by X-rays of 51.0%, a melting point of 123.2° C. (a peak existed also at 118.7° C.), a molecular weight distribution ($\overline{M}_w/\overline{M}_n$) of 3.6, a density of 0.920 g/cm^3, an ethylene content of 96.2 mole%, an n-heptane-insoluble content of 20% by weight and a p-xylene-soluble content at room temperature of 6.5% by weight and contained 17.5 isobutyl groups per 1000 carbon atoms.

Preparation of a Copolymer

(B): ethylene/1-butene copolymer

Ethylene and 1-butene were copolymerized continuously in a 15-liter stainless steel polymerization vessel equipped with stirring blades. Specifically, hexane as a polymerization solvent was continuously fed at a rate of 10 liters/hr into the polymerization vessel from its top. In the meanwhile, from the bottom of the polymerization vessel, the polymer solution was continuously withdrawn so that the volume of the polymerization solution in the polymerization vessel was kept always at 5 liters. As catalysts, vanadium oxychloride was continuously fed into the polymerization vessel from its top so that the concentration of vanadium atom in the polymerization vessel was kept at 0.2 millimole/liter, and ethyl aluminum sesquichloride [$(C_2H_5)_{1.5}AlCl_{1.5}$] was continuously fed into the polymerization vessel from its top so that the concentration of aluminum atoms in the vessel became 2.0 millimoles/liter. A gaseous mixture of 68 mole% of ethylene and 32 mole% of 1-butene was fed into the vessel from its top at a rate of 470 Nl/hr and hydrogen gas as a molecular weight controller, at a rate of 4.0 Nl/hr. The copolymerization reaction was carried out at 40° C. by circulating hot water through a jacket attached to the outside of the polymerization vessel. At this time, the pressure of the inside of the polymerization vessel was 2.4 kg/cm^2. When the copolymerization is carried out under the aforesaid conditions, an ethylene/1-butene copolymer can be obtained as a uniform solution. A small amount of methanol was added to the polymer solution withdrawn from the bottom of the polymerization vessel to stop the polymerization reaction. The polymer solution was added to a large amount of methanol and the polymer was taken out. The polymer was dried under reduced pressure at 80° C. for a day. The above procedure gave the ethylene/1-butene copolymer at a rate of 320 g/hr. The resulting copolymer [to be abbreviated as EB copolymer (II)] had a melt index of 4.0 g/10 min., a density of 0.890 g/cm^3, an ethylene content of 91.5% mole%, a crystallinity of 17%, and a melting point of 72° C.

Molding of a Packaging Film

90% by weight of the E-4MP copolymer (I) was mixed with 10% by weight of the EB copolymer (II) together with a heat stabilizer by means of a Henschel mixer. The mixture was molded into a film having a width of 230 mm and a thickness of 60 microns by means of a commercial tubular film former for polyolefins.

The resin temperature at the time of molding was 180° C. The extruder used had a screw diameter of 50 mm, a screw rotating speed of 40 rpm, a die diameter of 100 mm and a die slit width of 0.8 mm. and included two cooling air rings (first air ring-second air ring=380 mm).

The properties of the packaging film were evaluated by the following methods.

Haze (%): ASTM D 1003

Tear strength (Elmendorf: kg/cm): JIS Z 1702

Impact strength (kg.cm/cm): ASTM D 3420

Peel strength of the heat sealed part (g/15 mm):

The film surface was folded, heat-sealed by means of a seal bar having a width of 5 mm at a temperature of 90° C., 100° C., 110° C., 120° C., 130° C. and 140° C. respectively under a pressure of 2 kg/cm^2 for one second, and then allowed to cool. A test sample having a width of 15 mm was cut away from the sealed product, and the heat sealed part was peeled off at a cross head speed of 200 mm/min. And the peel strength of the heat sealed part at this time was measured.

Flexural resistance (the number of pinholes):

A sample, 282.6 mm×220 mm in size, was fixed in cylindrical form to a movable disc and a fixed disc having a diameter of 90 mm and spaced from each other by a distance of 180 mm, and a reciprocating torsional motion was given to the sample 1500 times at a speed of 50 times/min. in an atmosphere kept at −10° C. The number of pinholes which occurred in the sample during this period was counted. The stroke of the movable disc was 152.4 mm. While it moved over 88.0 mm, it gave a torsion of 440° to the sample and thereafter advanced over 63.5 mm to bend the sample.

Flexural rigidity (kg/cm^2):

A sample, 140 mm×140 mm, was provided, and flexural stress was imparted to the sample by using a Handle-O-Meter (manufactured by Thwing Albert Company, U.S.A.) with the slit width being adjusted to 5 mm. The maximum stress was determined and the quotient obtained by dividing it by the thickness of the sample was defined as flexural rigidity (kg/cm^2). The flexural rigidity was measured both in the longitudinal and transverse directions of the sample.

The results are shown in Table 1.

EXAMPLES 2 TO 4

The procedure of Example 1 was followed except that the blending ratio between the E-4MP copolymer (I) and the EB copolymer (II) was changed as shown in Table 1. The results are shown in Table 1.

COMPARATIVE EXAMPLE 1

The procedure of Example 1 was followed except that the E-4MP copolymer (I) of Example 1 was used singly. The results are shown in Table 1.

COMPARATIVE EXAMPLE 2

The procedure of Example 1 was followed except that an ethylene/propylene copolymer [to be abbreviated as EP copolymer (III) hereinbelow] having a melt index of 3.1 g/10 min., a density of 0.865 g/cm^3, an ethylene content of 81.5 mole%, a crystallinity of 3% and a melting point of 48° C. was used instead of the EB copolymer (II) of Example 1. The results are shown in Table 1.

COMPARATIVE EXAMPLE 3

The procedure of Example 1 was followed except that the ratio of the E-4MP copolymer (I) to the EB copolymer (II) in Example 1 was changed to 30:70. The results are shown in Table 1.

TABLE 1

			Example (Ex.) or Comparative Example (CEx.)						
			Ex. 1	Ex. 2	Ex. 3	Ex. 4	CEx. 1	CEx. 2	CEx. 3
E-4MP copolymer (I)			80	90	70	50	100	80	30
EB copolymer (II)		wt. %	20	10	30	50	—	—	70
EP copolymer (III)			—	—	—	—	—	20	—
Haze		%	3.7	3.5	3.4	2.8	4.1	3.3	2.5
Tear strength	Longitudinal	kg/cm	115	120	115	95	145	100	70
	Transverse		135	145	130	110	160	120	90
Impact strength		kg-cm/cm	3600	3500	3600	3700	3500	3000	3800
Peel strength of the heat-sealed part	90° C.	g/15 mm	200	—	300	500	13	40	600
	100° C.		830	560	910	920	—	80	940
	110° C.		1060	1080	1090	1050	970	930	980
	120° C.		1150	1170	1220	1170	1160	1040	1000
	130° C.		1300	1240	1360	1280	1380	1140	1020
	140° C.		1370	1400	1380	1330	1480	1180	1050
Pinholes (at −10° C.)		Number	1	5	0	0	11	2.5	0
Flexural rigidity	Longitudinal	kg/cm^2	33	36	29	24	40	26	15
	Transverse		35	39	30	25	47	28	17

EXAMPLE 5

A packaging film was formed in the same way as in Example 1 except that an ethylene/1-octene copolymer (to be abbreviated as EO copolymer hereinbelow) having a melt index (190° C.) of 1.01, a density of 0.930 g/cm^3, an ethylene content of 97.9 mole%, a crystallinity by X-rays of 53.7%, a melting point of 123.9° C. (a peak existed also at 121.3° C.) and a molecular weight distribution ($\overline{M}_w/\overline{M}_n$) of 4.4 was used instead of the E-4MP copolymer of Example 1, and the mixing ratio of the EO copolymer to the EB copolymer (II) of Example 1 was adjusted to 70:30 by weight. The results are shown in Table 2.

EXAMPLES 6 AND 7

A film having a thickness of 20 microns was formed by the same molding machine as used in Example 1 from a 50:50 (by weight) mixture of each of the E-4MP copolymer (I) used in Example 1 and the EO copolymer used in Example 5 with the EB copolymer (II) used in Example 1. The properties of the films were evaluated respectively by the method described in Example 1. The results are shown in Table 2.

TABLE 2

			Example		
			5	6	7
E-4MP copolymer (I)			—	50	—
EO copolymer		wt. %	70	—	50
EB copolymer (II)			30	50	50
Haze		%	3.6	2.7	3.0
Tear Strength	Longitudinal	kg/cm	70	90	50
	Transverse		180	110	210
Impact strength		kg-cm/cm	2500	4000	3500
Peel strength of the heat-sealed part	90° C.	g/15 mm	—	250	200
	100° C.		300	380	350
	110° C.		970	400	370
	120° C.		1220	420	400
	130° C.		1340	430	410
	140° C.		1350	440	420
Pinholes (at −10° C.)		Number	0	0	0
Flexural rigidity	Longitudinal	kg/cm^2	41	17	20
Transverse		42	18	24	

What is claimed is:

1. An ethylene/alpha-olefin copolymer composition characterized by comprising a mixture of 95 to 40% by weight of (A) a random copolymer of ethylene and an alpha-olefin having 5 to 10 carbon atoms having a melt index of 0.1 to 20 g/10 min., a density of 0.910 to 0.940 g/cm^3, a crystallinity by X-rays of 40 to 70%, a melting point of 115° to 130° C. and an ethylene content of 94 to 99.5 mole%, and 5 to 60% by weight of (B) a random copolymer of ethylene and an alpha-olefin having 3 to 10 carbon atoms having a melt index of 0.1 to 50 g/10 min., a density of 0.870 to 0.900 g/cm^3, a crystallinity by X-rays of 5 to 40%, a melting point of 40° to 100° C. and an ethylene content of 85 to 95 mole%.

2. The ethylene/alpha-olefin copolymer composition set forth in claim 1 wherein the alpha-olefin of the random copolymer (A) is 4-methyl-1-pentene.

3. The ethylene/alpha-olefin copolymer composition set forth in claim 1 wherein the alpha-olefin of the random copolymer (A) is 1-octene.

4. The ethylene/alpha-olefin copolymer composition set forth in claim 1 wherein the random copolymer (A) has a molecular weight distribution of not more than 6.

research publications

5. The ethylene/alpha-olefin copolymer composition set forth in claim 1 wherein the crystallinity by X-rays of the random copolymer (A) is 50 to 65%.

6. The ethylene/alpha-olefin copolymer composition wherein the crystallinity by X-rays of the random copolymer (B) is 7 to 30%.

7. The ethylene/alpha-olefin copolymer composition set forth in claim 1 wherein the mixing ratio of the random copolymer (A) to the random copolymer (B) is from 90:10 to 60:40.

* * * * *

research publications

United States Patent [19]
Naito et al.

[11] **Patent Number: 4,981,760**
[45] **Date of Patent: Jan. 1, 1991**

[54] **ETHYLENE-ALPHA-OLEFIN COPOLYMER AND FILMS OBTAINED THEREFROM**

[75] Inventors: **Yukio Naito; Kokzoh Miyazaki; Yuji Gotoh; Masashi Hambe; Akio Imai; Kiyoyuki Sugimori, all of Chiba, Japan**

[73] Assignee: **Sumitomo Chemical Company, Limited, Osaka, Japan**

[21] Appl. No.: **378,000**

[22] Filed: **Jul. 11, 1989**

[30] **Foreign Application Priority Data**

Jul. 11, 1988 [JP] Japan 63-173148

[51] Int. Cl.[5] B32B 27/32; C08L 23/08; C08F 210/02

[52] U.S. Cl. 428/523; 428/500; 525/240; 526/143; 526/348.3; 526/348.5; 526/348.6; 526/352.2

[58] Field of Search 526/143, 348.1, 348.5, 526/348.6, 348.3, 352.2; 525/240; 428/212, 218, 500, 523

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Primary Examiner—Fred Teskin
Attorney, Agent, or Firm—Sughrue, Mion, Zinn, Macpeak & Seas

[57] **ABSTRACT**

An ethylene-α-olefin copolymer comprising ethylene and an α-olefin having from 3 to 10 carbon atoms, the copolymer having an α-olefin content of from 1.0 to 8.0 mol %, a density of from 0.900 to 0.930 g/cm^3, and a melt flow rate of from 0.1 to 100 g/10 min., the programed-temperature thermogram of said copolymer as determined with a differential scanning calorimeter after being completely melted and then gradually cooled showing an endothermic peak (a) in a range of from 75° to 100° C. and an endothermic peak (b) in a range of from 120° to 140° C., with the ratio of an endotherm at the endothermic peak (b), ΔHb, to an endotherm at the endothermic peak (a), ΔHa, i.e., ΔHb/ΔHa, being from 0.03 to 2.0. The copolymer provides a film exhibiting excellent physical properties required for packaging film.

8 Claims, 6 Drawing Sheets

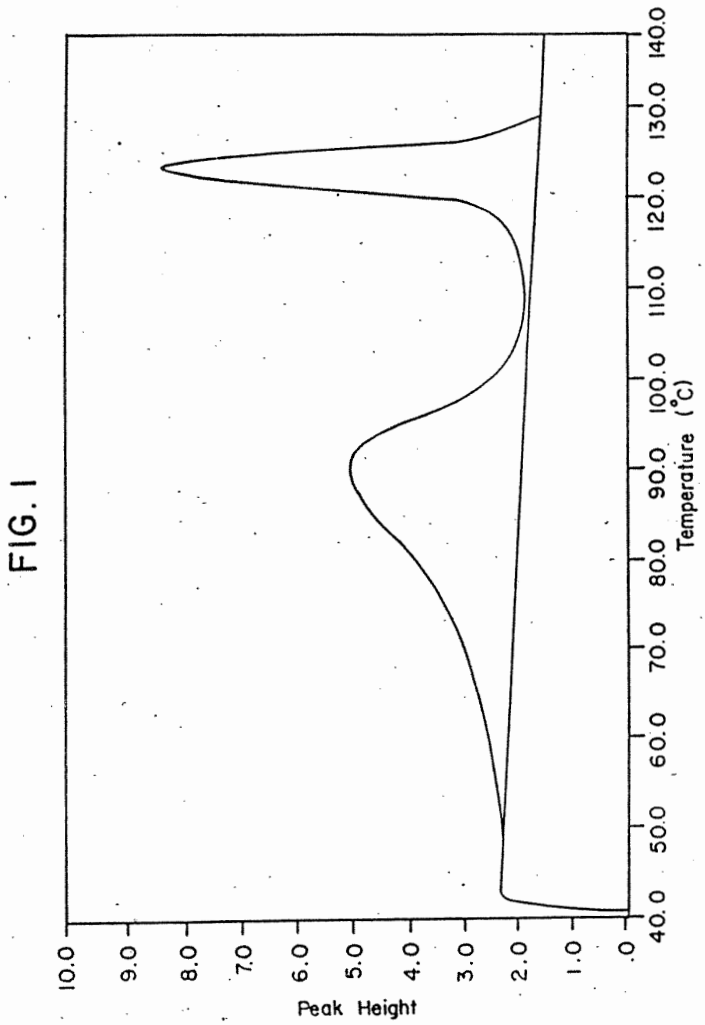

140.0
130.0
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Temperature (°C)
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Peak Height

FIG. 1

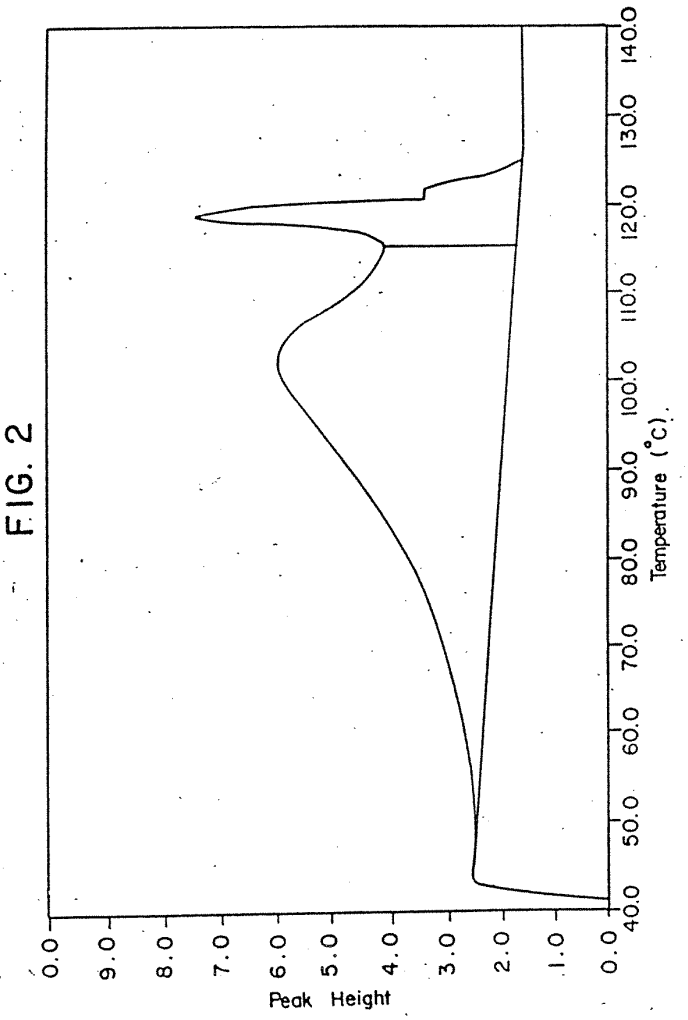

140.0
130.0
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Temperature (°C)
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1.0
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Peak Height

FIG. 2

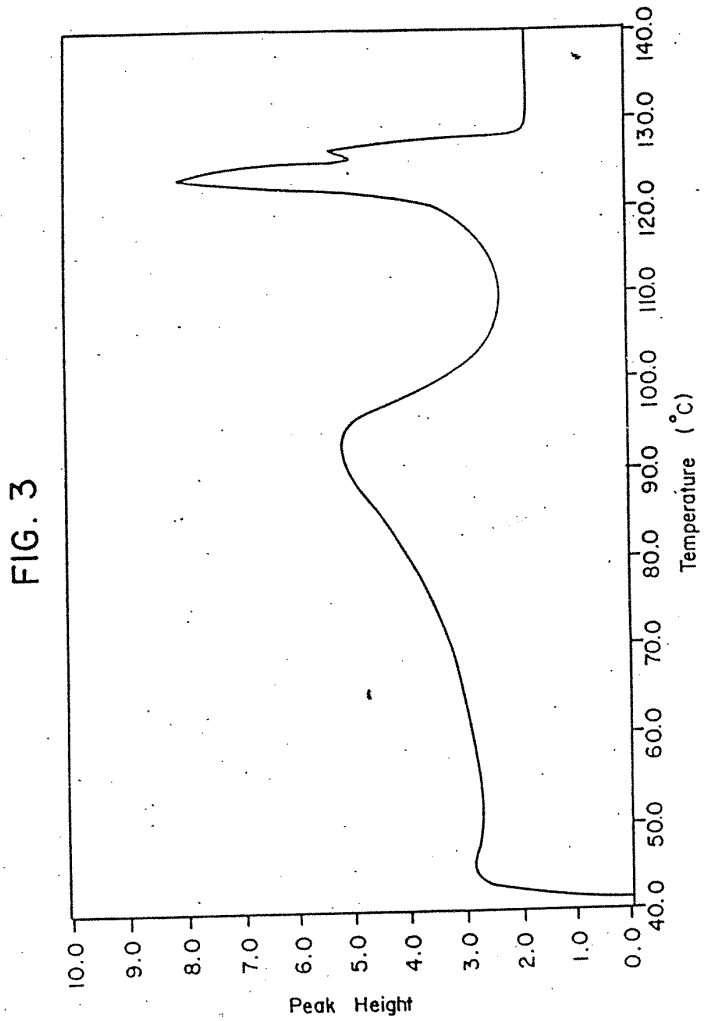

140.0
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Temperature (°C)
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1.0
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Peak Height

FIG. 3

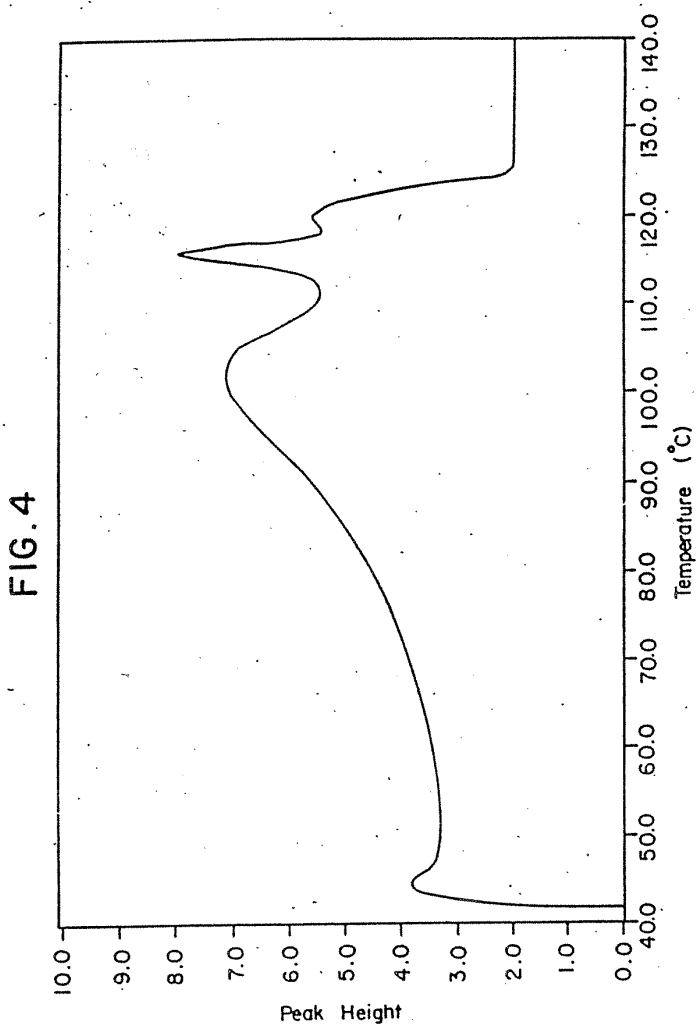

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9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
Peak Height
40.0
50.0
60.0
70.0
80.0
90.0
100.0
110.0
120.0
130.0
140.0
Temperature (°C)

FIG. 4

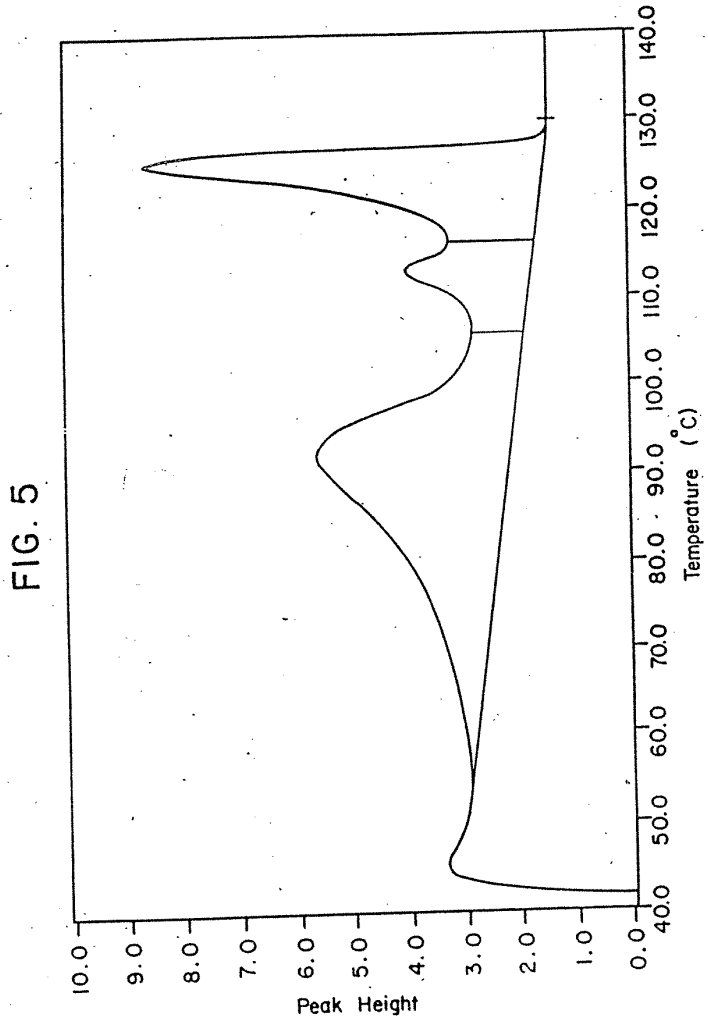

140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
Temperature (°C)
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
Peak Height

FIG. 5

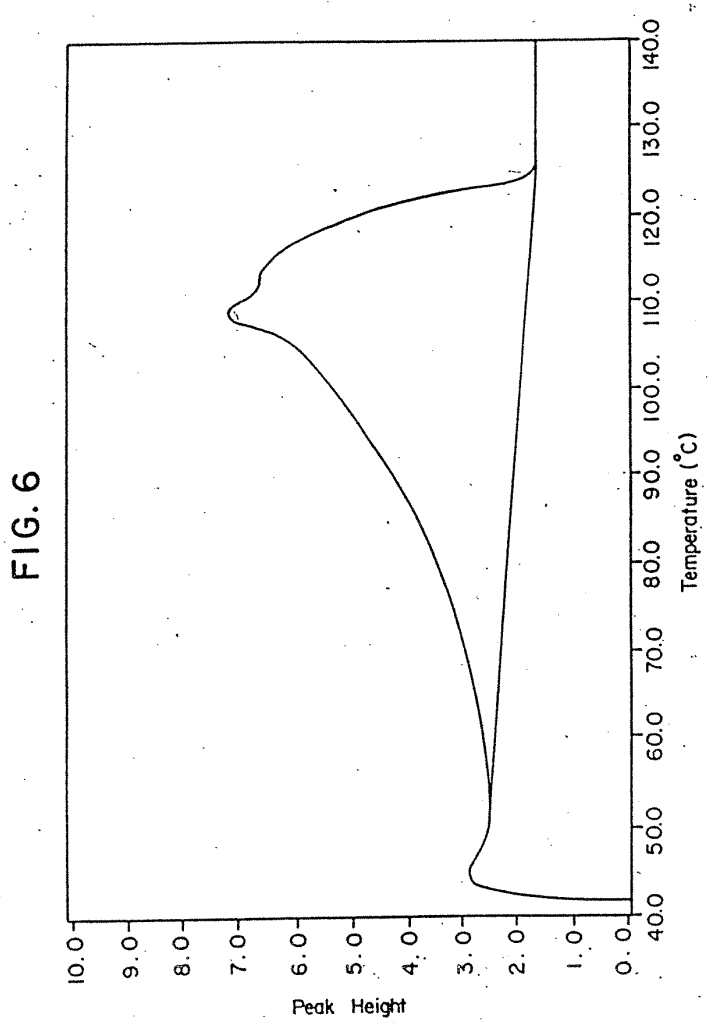

140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
Temperature (°C)
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
Peak Height

FIG. 6