EXHIBIT V

PART 16

UNITED STATES DEPARTMENT OF COMMERCE
Patent and Trademark Office
Address: COMMISSIONER OF PATENTS AND TRADEMARKS
Washington, DC 20231

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.
08/544,497	10/18/95	CHUM	C-40.121-AU

15M2/1219

OSBORNE K MCKINNEY
2301 BRAZOSPORT BLVD B-1211
FREEPORT TX 77541

EXAMINER	
WU, D	
ART UNIT	PAPER NUMBER
1505	20

DATE MAILED: 12/19/96

Please find below and/or attached an Office communication concerning this application or proceeding.

Commissioner of Patents and Trademarks

PTO-90C (REV. 2/95)

1-File Copy

☆U.S.GOVERNMENT PRINTING OFFICE 1995-319-826

Notice of Allowability	Application No. 08/544,597	Applicant(s) Chum et al.
	Examiner David Wu	Group Art Unit 1505

All claims being allowable, PROSECUTION ON THE MERITS IS (OR REMAINS) CLOSED in this application. If not included herewith (or previously mailed), a Notice of Allowance and Issue Fee Due or other appropriate communication will be mailed in due course.

☒ This communication is responsive to *October 9, 1996*.

☒ The allowed claim(s) is/are *1, 3-8, 17, 19-23, and 31-35*.

☐ The drawings filed on _____ are acceptable.

☐ Acknowledgement is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d).

☐ All ☐ Some* ☐ None of the CERTIFIED copies of the priority documents have been

☐ received.

☐ received in Application No. (Series Code/Serial Number) _____.

☐ received in this national stage application from the International Bureau (PCT Rule 17.2(a)).

*Certified copies not received: _____.

☐ Acknowledgement is made of a claim for domestic priority under 35 U.S.C. § 119(e).

A SHORTENED STATUTORY PERIOD FOR RESPONSE to comply with the requirements noted below is set to EXPIRE **THREE MONTHS** FROM THE "DATE MAILED" of this Office action. Failure to timely comply will result in ABANDONMENT of this application. Extensions of time may be obtained under the provisions of 37 CFR 1.136(a).

☐ Note the attached EXAMINER'S AMENDMENT or NOTICE OF INFORMAL APPLICATION, PTO-152, which discloses that the oath or declaration is deficient. A SUBSTITUTE OATH OR DECLARATION IS REQUIRED.

☒ Applicant MUST submit NEW FORMAL DRAWINGS

☐ because the originally filed drawings were declared by applicant to be informal.

☒ including changes required by the Notice of Draftsperson's Patent Drawing Review, PTO-948, attached hereto or to Paper No. 8.

☐ including changes required by the proposed drawing correction filed on _____, which has been approved by the examiner.

☐ including changes required by the attached Examiner's Amendment/Comment.

Identifying indicia such as the application number (see 37 CFR 1.84(c)) should be written on the reverse side of the *drawings. The drawings should be filed as a separate paper with a transmittal lettter addressed to the Official* Draftsperson.

☐ Note the attached Examiner's comment regarding REQUIREMENT FOR THE DEPOSIT OF BIOLOGICAL MATERIAL.

Any response to this letter should include, in the upper right hand corner, the APPLICATION NUMBER (SERIES CODE/SERIAL NUMBER). If applicant has received a Notice of Allowance and Issue Fee Due, the ISSUE BATCH NUMBER and DATE of the NOTICE OF ALLOWANCE should also be included.

Attachment(s)

☐ Notice of References Cited, PTO-892

☒ Information Disclosure Statement(s), PTO-1449, Paper No(s). 7

☐ Notice of Draftsperson's Patent Drawing Review, PTO-948

☐ Notice of Informal Patent Application, PTO-152

☐ Interview Summary, PTO-413

☐ Examiner's Amendment/Comment

☐ Examiner's Comment Regarding Requirement for Deposit of Biological Material

☒ Examiner's Statement of Reasons for Allowance

1. The following is an examiner's statement of reasons for allowance:

Claims 1, 3-8, 17, 19-23, and 31-35 are allowed because no prior art which anticipates or suggests fairly the instant claims has been located as of the date of this action.

Lai reference (U.S. Patent No. 5,408,004) which was thought to be the closest prior art discloses polyolefin blends comprising at least 10 percent, preferably at least 30 percent of at least one linear or substantially linear homogeneously branched polyethylene, such as one of a Tafmer TM, Exact TM or Insite TM (defined in column 3, lines 43-56), and the remainder of the blend comprises one or more heterogeneously branched polyethylene (defined in column 3, lines 3-14). In working examples 1-2, the polymer blend sample E-1 is prepared from a 50/50 of CGC resin (Sample C-1) and HDPE resin (Sample C-2), sample E-2 is also prepared from a 50/50 of CGC resin (Sample C-6) and HDPE resin (Sample C-7). Although Lai fails to disclose the property such as the slope of strain hardening coefficient of the substantially linear homogeneously branched polyethylene, in view of the same type of the polymer and made by the same technology taught by Lai reference and the instant disclosure, the Examiner has a reasonable basis to believe that Lai's substantially linear homogeneously branched polyethylene possesses substantially the same value of the slope of strain hardening coefficient. However, in view of Paper No. 9, the present application is entitled to the benefit of the filing date of its parent application 08/054,379, i.e., April 28, 1993, the Lai patent (U.S. 5,408,004, filed on August 17, 1993) is no longer a proper reference against the present invention.

The earlier reference made of record in the parent application (S.N. 08/378,998), WO 90/03,414, has been overcome based on the Markovich Declaration filed on February 6, 1996.

The 112, second paragraph rejection is now being removed in view of the amendment submitted on October 9, 1996.

Therefore, claims 1, 3-8, 17, 19-23, and 31-35 are allowed over WO 90/03,414.

Any comments considered necessary by applicant must be submitted no later than the payment of the issue fee and, to avoid processing delays, should preferably accompany the issue fee. Such submissions should be clearly labeled "Comments on Statement of Reasons for Allowance."

2. Any inquiry concerning this communication or earlier communications from the examiner should be directed to David Wu whose telephone number is (703) 308-2450.

David Wu

DAVID W. WU
PRIMARY EXAMINER
GROUP 1500

DWW
December 13, 1996

UNITED STATES DEPARTMENT OF COMMERCE
Patent and Trademark Office

Address: Box ISSUE FEE
ASSISTANT COMMISSIONER FOR PATENTS
Washington, D.C. 20231

NOTICE OF ALLOWANCE AND ISSUE FEE DUE

1542/0114

OSBORNE J MCKINNEY
2301 BRAZOSPORT BLVD B-1511
FREEPORT TX 77541

APPLICATION NO.	FILING DATE	TOTAL CLAIMS	EXAMINER AND GROUP ART UNIT	DATE MAILED
08/734,497	10/10/96	018	1505	01/14/97

First Named Applicant	

TITLE OF INVENTION: POROUS FIBERS MADE FROM POLYETHYLENE POLYMER BLENDS

ATTY'S DOCKET NO.	CLASS-SUBCLASS	BATCH NO.	APPLN. TYPE	SMALL ENTITY	FEE DUE	DATE DUE
5740.121-US	525-240.000	105	UTILITY	NO	$1290.00	04/14/97

THE APPLICATION IDENTIFIED ABOVE HAS BEEN EXAMINED AND IS ALLOWED FOR ISSUANCE AS A PATENT. PROSECUTION ON THE MERITS IS CLOSED.

THE ISSUE FEE MUST BE PAID WITHIN THREE MONTHS FROM THE MAILING DATE OF THIS NOTICE OR THIS APPLICATION SHALL BE REGARDED AS ABANDONED. THIS STATUTORY PERIOD CANNOT BE EXTENDED.

HOW TO RESPOND TO THIS NOTICE:

I. Review the SMALL ENTITY status shown above.
If the SMALL ENTITY is shown as YES, verify your current SMALL ENTITY status:

A. If the status is changed, pay twice the amount of the FEE DUE shown above and notify the Patent and Trademark Office of the change in status, or
B. If the status is the same, pay the FEE DUE shown above.

If the SMALL ENTITY is shown as NO:

A. Pay FEE DUE shown above, or

B. File verified statement of Small Entity Status before, or with, payment of 1/2 the FEE DUE shown above.

II. Part B of this notice should be completed and returned to the Patent and Trademark Office (PTO) with your ISSUE FEE. Even if the ISSUE FEE has already been paid by charge to deposit account, Part B should be completed and returned. If you are charging the ISSUE FEE to your deposit account, section "6b" of Part B should be completed.

III. All communications regarding this application must give application number and batch number. Please direct all communication prior to issuance to Box ISSUE FEE unless advised to the contrary.

IMPORTANT REMINDER: Patents issuing on applications filed on or after Dec. 12, 1980 may require payment of maintenance fees. It is patentee's responsibility to ensure timely payment of maintenance fees when due.

PART B—ISSUE FEE TRANSMITTAL

MAILING INSTRUCTIONS: This form should be used for t[illegible]mitting the ISSUE FEE. Blocks 2 through 6 should be c[illegible]pleted where appropriate. All further correspondence including the Issue Fee Receipt, the Patent, advance orde[illegible] and notification of maintenance fees will be mailed to addr[illegible]see entered in Block 1 unless you direct otherwise, by: (a) specifying a new correspondence address in Block 3 below; or (b) providing the PTO with a separate "FEE ADDRESS" for maintenance fee notifications with the payment of Issue Fee or thereafter. **See reverse for Certificate of Mailing, below.**

Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

Burden Hour Statement: This form is estimated to take 0.2 hours to complete. Time will vary depending on the needs of the individual case. Any comments on the amount of time required to complete this form should be sent to the Chief Information Officer, Patent and Trademark Office, Washington, D.C. 20231.
DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Box Issue Fee, Assistant Commissioner for Patents, Washington D.C. 20231

1. CORRESPONDENCE ADDRESS

15M2/0114

OSBORNE K MCKINNEY
2301 BRAZOSPORT BLVD B-1211
FREEPORT TX 77541

2. INVENTOR(S) ADDRESS CHANGE (Complete only if there is a change)

INVENTOR'S NAME
Street Address
City, State and ZIP Code
CO-INVENTOR'S NAME
Street Address
City, State and ZIP Code

RECEIVED
Publishing Division
APR 18 1997
03

☐ Check if additional changes are enclosed

APPLICATION NO.	FILING DATE	TOTAL CLAIMS	EXAMINER AND GROUP ART UNIT		DATE MAILED
08/544,497	10/18/95	018	WU, D	1505	01/14/97

First Named Applicant: CHUM, PAK-WING S.

TITLE OF INVENTION: FABRICATED ARTICLES MADE FROM ETHYLENE POLYMER BLENDS

ATTY'S DOCKET NO.	CLASS-SUBCLASS	BATCH NO.	APPLN. TYPE	SMALL ENTITY	FEE DUE	DATE DUE
1 C-40.121-AU	525-240.000	146	UTILITY	NO	$1290.00	04/14/97

3. Correspondence address change (Complete only if there is a change)

Stephen S. Grace
The Dow Chemical Company
P.O. Box 1967
Midland, Michigan 48641-1967

4. For printing on the patent front page, list the names of not more than 3 registered patent attorneys or agents OR, alternatively, the name of a firm having as a member a registered attorney or agent. If no name is listed, no name will be printed.

1 _____
2 _____
3 _____

5. ASSIGNMENT DATA TO BE PRINTED ON THE PATENT (print or type)

(1) NAME OF ASSIGNEE: The Dow Chemical Company
(2) ADDRESS: (CITY & STATE OR COUNTRY) Midland, Michigan USA

A. ☐ This application is NOT assigned.
☐ Assignment previously submitted to the Patent and Trademark Office.
☒ Assignment is being submitted under separate cover. Assignments should be directed to Box ASSIGNMENTS.

PLEASE NOTE: Unless an assignee is identified in Block 5, no assignee data will appear on the patent. Inclusion of assignee data is only appropriate when an assignment has been previously submitted to the PTO or is being submitted under separate cover. Completion of this form is NOT a substitute for filing an assignment.

6a. The following fees are enclosed:
☐ Issue Fee ☐ Advance Order - # of Copies _____

6b. The following fees should be charged to: 04-1512
DEPOSIT ACCOUNT NUMBER _____
(ENCLOSE A COPY OF THIS FORM)
☒ Issue Fee ☐ Advance Order - # of Copies _____
☒ Any Deficiencies in Enclosed Fees

The COMMISSIONER OF PATENTS AND TRADEMARKS is requested to apply the Issue Fee to the application identified above.

(Authorized Signature) [signature] Reg No. 40,084 (Date) 4/11/97

NOTE: The Issue Fee will not be accepted from anyone other than the applicant; a registered attorney or agent; or the assignee or other party in interest as shown by the records of the Patent and Trademark Office.

Certificate of Mailing

Note: If this certificate of mailing is used, it can only be used to transmit the Issue Fee. This certificate cannot be used for any other accompanying papers. Each additional paper, such as an assignment or formal drawing, must have its own certificate of mailing.

I hereby certify that this correspondence is being deposited with the United States Postal Service with sufficent postage as first class mail in an envelope addressed to: **Box ISSUE FEE**
Assistant Commissioner for Patents
Washington, D.C. 20231

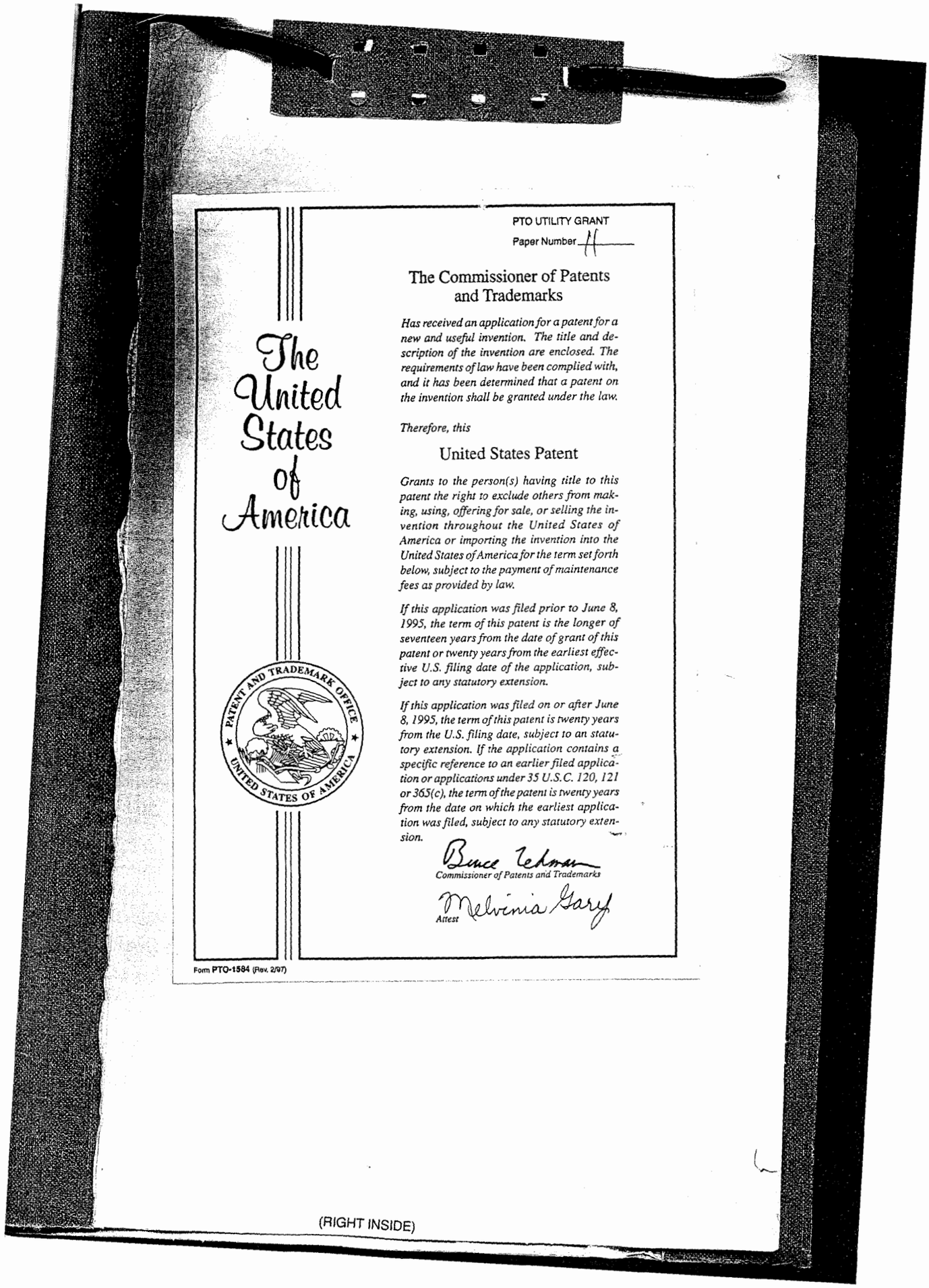
on: April 14, 1997 (Date)
Carrie Gray (Name of person making deposit)
Carrie Gray (Signature)
April 14, 1997 (Date)

810 BL 04-1512 05/20/97 08544497
01115 142 1.290.00CH

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JAN 20 1997
PATENT DEPT. TEXAS

1. TRANSMIT THIS FORM WITH FEE

PTOL-85B (REV.05-96) Approved for use through 05/31/96. OMB 0651-0033 **Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE**



PTO UTILITY GRANT

Paper Number 11

The Commissioner of Patents and Trademarks

Has received an application for a patent for a new and useful invention. The title and description of the invention are enclosed. The requirements of law have been complied with, and it has been determined that a patent on the invention shall be granted under the law.

Therefore, this

United States Patent

Grants to the person(s) having title to this patent the right to exclude others from making, using, offering for sale, or selling the invention throughout the United States of America or importing the invention into the United States of America for the term set forth below, subject to the payment of maintenance fees as provided by law.

If this application was filed prior to June 8, 1995, the term of this patent is the longer of seventeen years from the date of grant of this patent or twenty years from the earliest effective U.S. filing date of the application, subject to any statutory extension.

If this application was filed on or after June 8, 1995, the term of this patent is twenty years from the U.S. filing date, subject to an statutory extension. If the application contains a specific reference to an earlier filed application or applications under 35 U.S.C. 120, 121 or 365(c), the term of the patent is twenty years from the date on which the earliest application was filed, subject to any statutory extension.

The United States of America

PATENT AND TRADEMARK OFFICE · UNITED STATES OF AMERICA

Bruce Lehman
Commissioner of Patents and Trademarks

Attest Melvinia Gary

Form PTO-1584 (Rev. 2/97)

(RIGHT INSIDE)

cofc #12

*Attorney Docket No.*40121 AU

PATENT

OIPE IAP78 JUN 16 2006 PATENT & TRADEMARK OFFICE

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Patent No.:5,677,383

Application No.: 544,497

Issue Date: October 14, 1997

Inventors: Pak-Wing S. Chum et al.

Certificate JUN 20 2006 of Correction

Request FOR CORRECTION

Certificate of Correction Branch
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Dear Sir:

This is a Request for Correction pursuant to MPEP § 1480 to correct a mistake in the above-mentioned U.S. Patent, incurred through the fault of the U.S. Patent Office, which mistake is clearly disclosed in the records of the U.S. Patent Office.

Please note that although the printed copy of the above U.S. Patent includes the claim of priority, however, the PAIR System of the U.S. Patent Office fails to include such claim of priority. In addition, the front page of the above U.S. patent also fails to include such information.

Furthermore, attached please find a copy of the Email instruction that the Patentee has received from the U.S. Patent Office in connection with this error.

JUN 21 2006

Finally, attached please find a copy of the above U.S. Patent.

Accordingly, the patentee respectfully request the correction of the above-mentioned error.

Should there be any questions, please contact me.

Respectfully submitted,

Ray Ashburg
Attorney for Applicant
Reg. No. 53,956
THE DOW CHEMICAL CO.
2030 Dow Center
Midland, Michigan 48674
Phone No:(979) 238-4262

JUN 21 2006

Rubio, Monica

From: Ashburg, Ray (R)
Sent: Thursday, June 08, 2006 2:30 PM
To: Tipps, Tammy (TL)
Cc: Rubio, Monica
Subject: FW: Request to correct
Information Classification: DOW RESTRICTED - For internal use only

----Original Message-----
From: TSB1700_2900 IFW_PALM [mailto:TSB1700_2900IFW_PAL@USPTO.GOV]
Sent: Tuesday, June 06, 2006 2:49 PM
To: Ashburg, Ray (R)
Cc: Wagstaff, Mamye; Nutter, Nathan
Subject: Request to correct

In patent #'s 6,723,398; 6,111,023; 5,5677,383 there does appear to be an office error between what's printed on the patent and what's in public PAIRS. Certificate of Corrections branch would seem to be the area to correct the problem. Mary Diggs or Monyna Dorsey at 703-308-9390. Because it appears to be an office error there should be no fee. But you will probably have to file a Certificate of Correction paperwork to fix the problem. If you need more assistance, please contact Bob Warden at 571-272-1281.
Thanks

Janee Conley
PALM / IFW Contract Troubleshooter for TC1700
Remsen Bldg, Room 6B84
571-272-5523 Work Phone
571-273-5523 Fax
703-987-7067 Cell

UNITED STATES PATENT AND TRADEMARK OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 5,677,383
APPLICATION NO. : 08/544497
DATED : October 14, 1997
INVENTOR(S) : Pak-Wing S. Chum et al.

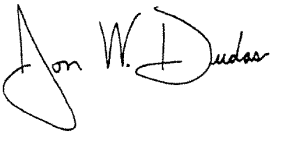
It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

"Related U .S. Application Data"

"(63) This application is a Rule 1.60 continuation application of application No. 08/378,998, filed Jan. 27, 1995, now abandoned, which was a Rule 1.62 continuation application of application No. 08/054,379, filed Apr. 28, 1993, now abandoned, which was a continuation-in-part application of 07/776,130, filed Oct. 15, 1991, now issued U.S. Pat; No. 5,272,236, the disclosures of each of which is incorporated herein in their entirety by reference. This application is also related to application number 08/501,527, filed Aug. 2, 1995, now U.S. Pat. No. 5,609,242 which is a continuation of 08/010,958, filed Jan. 29, 1993, now abandoned, the disclosure of which is incorporated herein by reference."

Signed and Sealed this

Twenty-first Day of November, 2006



JON W. DUDAS
Director of the United States Patent and Trademark Office

PTO/SB/44 (04-05)
Approved for use through 04/30/2007. OMB 0651-0033
U.S. Patent and Trademark Office: U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.
(Also Form PTO-1050)

UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 5,677,383

APPLICATION NO. : 08/544,497

ISSUE DATE : October 14, 1997

INVENTOR(S) : Pak-Wing S. Chum et al.

It is certified that an error appears or errors appear in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

"Related U.S. Application Data"

"(63) *This application is a* Rule 1.60 continuation application of application No. 08/378,998, filed Jan. 27, 1995, now abandoned, which was a Rule 1.62 continuation application of application No. 08/054,379, filed Apr. 28, 1993, now abandoned, which was a continuation-in-part application of 07/776,130, filed Oct. 15, 1991, now issued U.S. Pat. No. 5,272,236, the disclosures of each of which is incorporated herein in their entirety by reference. This application is also related to application number 08/501,527, filed Aug. 2, 1995, now U.S. Pat. No. 5,609,242 which is a continuation of 08/010,958, filed Jan. 29, 1993, now abandoned, the disclosure of which is incorporated herein by reference."

I hereby certify that this paper (along with any paper referred to as being attached or enclosed) is being deposited with the U.S. Postal Service on the date shown below with sufficient postage as First Class Mail, in an envelope addressed to: Attention: Certificate of Correction Branch, Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.

Dated: June 9, 2006 Signature: Monica Rubio (Monica Rubio)

MAILING ADDRESS OF SENDER (Please do not use customer number below):
Ray Ashburg
THE DOW CHEMICAL CO.
2030 Dow Center
Midland, Michigan 48674

1

JUN 21 2006

US005677383A

United States Patent [19]

Chum et al.

[11] Patent Number: 5,677,383

[45] Date of Patent: Oct. 14, 1997

[54] **FABRICATED ARTICLES MADE FROM ETHYLENE POLYMER BLENDS**

[75] Inventors: **Pak-Wing Steve Chum**, Lake Jackson; **Ronald P. Markovich**, Houston; **George W. Knight**, Lake Jackson; **Shih-Yaw Lai**, Sugar Land, all of Tex.

[73] Assignee: **The Dow Chemical Company**, Midland, Mich.

[21] Appl. No.: **544,497**

[22] Filed: **Oct. 18, 1995**

Related U.S. Application Data

[63] Continuation of Ser. No. 378,998, Jan. 27, 1995, abandoned, which is a continuation of Ser. No. 54,379, Apr. 28, 1993, abandoned, which is a continuation-in-part of Ser. No. 776,130, Oct. 15, 1991, Pat. No. 5,272,236.

[51] **Int. Cl.**[6] **C08L 23/06**

[52] **U.S. Cl.** **525/240**; 525/242; 525/320

[58] **Field of Search** 525/240, 242, 525/320

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ANTEC Proceedings, pp. 306–309 (1983), "Analysis of Long Chain Branching in High Density Polyethylene" by J.K. Hughes.

(List continued on next page.)

Primary Examiner—David W. Wu

[57] **ABSTRACT**

Fabricated articles made from formulated ethylene polymer compositions are disclosed. Films made from such formulated compositions have surprisingly good impact and tensile properties, and an especially good combination of modulus and toughness. The ethylene polymer compositions have at least one homogeneously branched substantially linear ethylene/α-olefin interpolymer and at least one heterogeneously branched ethylene polymer. The homogeneously branched substantially linear ethylene/α-olefin interpolymer has a density from about 0.89 to about 0.92 g/cm^3 and a slope of strain hardening coefficient greater than or equal to about 1.3.

18 Claims, 2 Drawing Sheets

OTHER PUBLICATIONS

Makromol. Chem., Rapid Commun., (5) pp. 225–228 (1984) "Influence of hydrogen on the polymerization of ethylene with the homogeneous Ziegler system bis(cyclopentadienyl)zirconiumdicholoride/aluminoxane" by Walter Kaminsky et al.

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FIG. 1

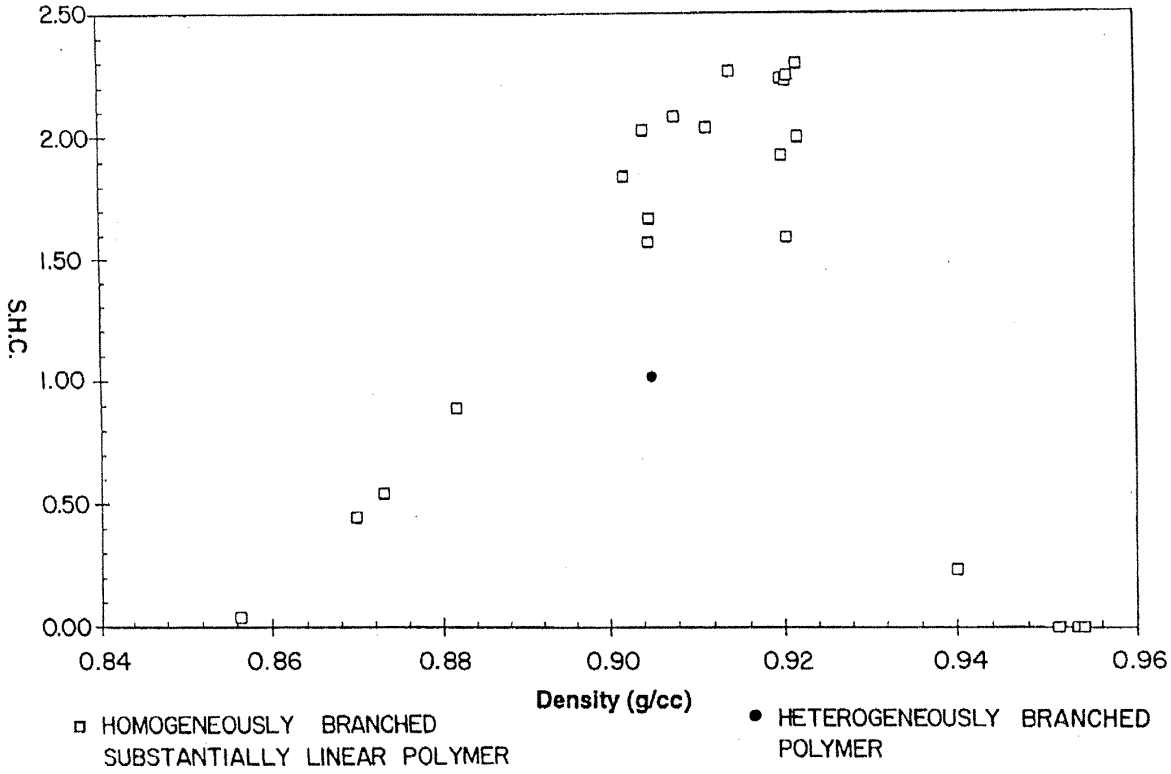
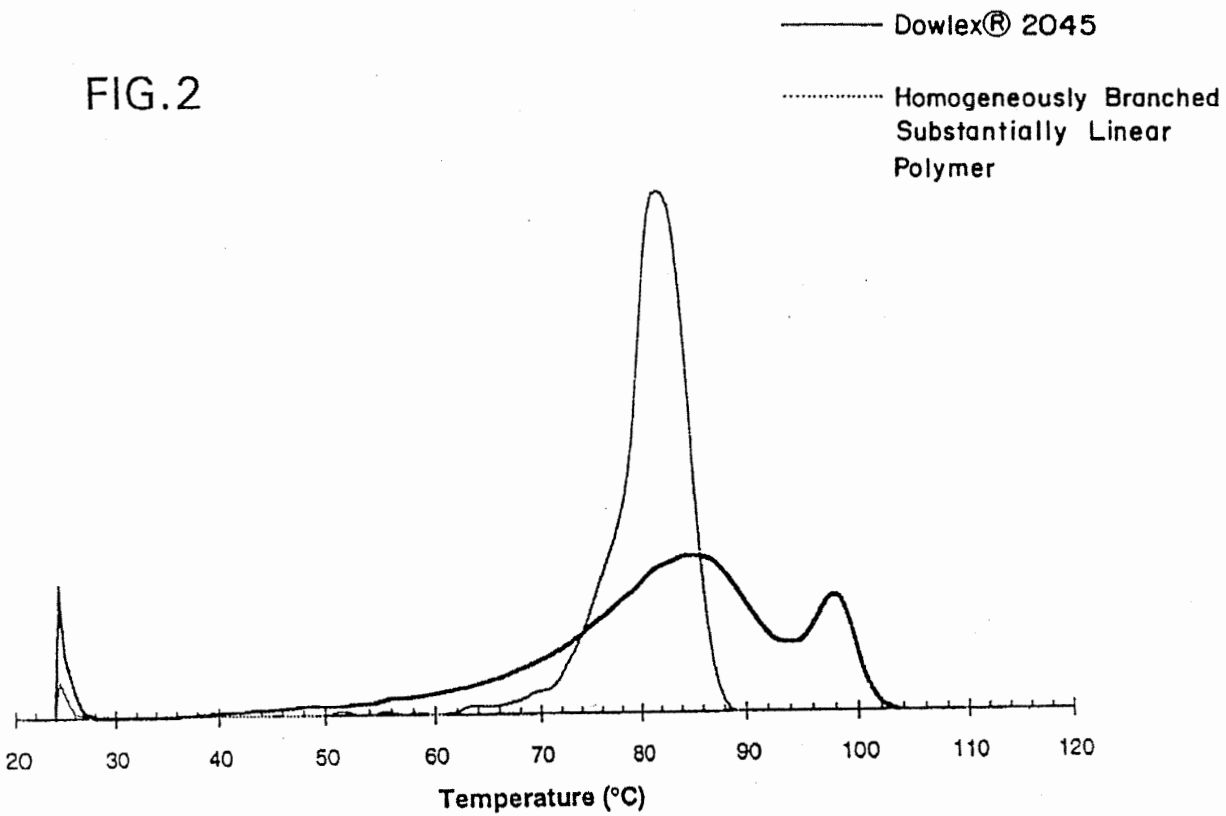

2.50
2.00
1.50
1.00
0.50
0.00
S.H.C.
0.84
0.86
0.88
0.90
0.92
0.94
0.96
Density (g/cc)
HOMOGENEOUSLY BRANCHED SUBSTANTIALLY LINEAR POLYMER
HETEROGENEOUSLY BRANCHED POLYMER

FIG. 2


Dowlex® 2045
Homogeneously Branched Substantially Linear Polymer
20
30
40
50
60
70
80
90
100
110
120
Temperature (°C)

FABRICATED ARTICLES MADE FROM ETHYLENE POLYMER BLENDS

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a Rule 1.60 continuation application of application No. 08/378,998, filed Jan. 27, 1995, now abandoned, which was a Rule 1.62 continuation application of application No. 08/054,379, filed Apr. 28, 1993, now abandoned, which was a continuation-in-part application of 07/776,130, filed Oct. 15, 1991, now issued U.S. Pat. No. 5,272,236, the disclosures of each of which is incorporated herein in their entirety by reference. This application is also related to application number 08/501,527, filed Aug. 2, 1995, now U.S. Pat. No. 5,609,242 which is a continuation of 08/010,958, filed Jan. 29, 1993, now abandoned, the disclosure of which is incorporated herein by reference.

FIELD OF THE INVENTION

This invention relates to compositions comprising specific ethylene/α-olefin polymer blends. The polymer blends preferably comprise:

(A) at least one homogeneously branched substantially linear ethylene/α-olefin interpolymer having specific processing characteristics, blended together with

(B) a heterogeneously branched ethylene polymer.

Such compositions are particularly useful in film applications (e.g., high strength thin gauge packaging film or heat sealable packaging film).

BACKGROUND OF THE INVENTION

Thin film products fabricated from linear low density polyethylene (LLDPE) and/or high density polyethylene (HDPE) are widely used for packaging applications such as merchandise bags, grocery sacks, and industrial liners. For these applications, films with high tensile strength, as well as high impact strength, are desired because film producers can down gauge their film products and still retain packaging performance.

Previous attempts were made to optimize film tensile strength and yield strength by blending various heterogeneous polymers together on theoretical basis. While such blends exhibited a synergistic response to increase the film yield strength, the film impact strength followed the rule of mixing, often resulting in a "destructive synergism" (i.e., the film impact strength was actually lower than film made from one of the two components used to make the blend).

For example, it is known that while improved modulus linear polyethylene resin can be produced by blending high density polyethylene with a very low density polyethylene (VLDPE), the impact strength of the resin blend follows the rule of mixing.

There is a continuing need to develop polymers which can be formed into fabricated articles (e.g., film) having these combinations of properties (e.g., improved modulus, yield strength, impact strength and tear strength). The need is especially great for polymers which can be made into film which can also be down gauged without loss of strength properties, resulting in savings for film manufacturers and consumers, as well as protecting the environment by source reduction.

Surprisingly, we have now discovered that film can have synergistically enhanced physical properties, when the film is made from a blend of at least one homogeneously branched ethylene/α-olefin interpolymer and a heterogeneously branched ethylene/α-olefin interpolymer.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 shows the relationship between the density and the slope of strain hardening coefficient for homogeneously branched substantially linear ethylene/α-olefin interpolymers used in the compositions disclosed herein, in comparison with a heterogeneously branched ethylene/α-olefin copolymer.

FIG. 2 shows the short chain branching distribution (as measured by analytical temperature rising elution fractionation (ATREF)) for a homogeneously branched substantially linear ethylene/1-octene copolymer used in the invention, in comparison with Dowlex™ 2045 (a heterogeneously branched ethylene/1-octene copolymer made by The Dow Chemical Company).

SUMMARY OF THE INVENTION

Formulated ethylene/α-olefin compositions have now been discovered to have improved physical and mechanical strength and are useful in making fabricated articles. Films made from these novel compositions exhibit surprisingly good impact and tensile properties, and an especially good combination of modulus, yield, ultimate tensile, and toughness (e.g., Dart impact).

The compositions comprise (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 polymer fraction, and

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

(B) at least one heterogeneously branched ethylene polymer having a density from about 0.93 g/cm^3 to about 0.965 g/cm^3.

In another aspect, the compositions comprise 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 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) at least one heterogeneously branched ethylene polymer having a density from about 0.93 g/cm^3 to about 0.965 g/cm^3.

Preferably, both the homogeneously branched substantially linear ethylene/α-olefin interpolymer and the homogeneously branched linear ethylene/α-olefin interpolymer each have a slope of strain hardening coefficient greater than or equal to about 1.3.

DETAILED DESCRIPTION OF THE INVENTION

The homogeneously branched ethylene/α-olefin interpolymer is preferably a homogeneously branched substantially linear ethylene/α-olefin interpolymer as described in U.S. Ser. No. 07/776,130, now U.S. Pat. No. 5,272,236. The homogeneously branched ethylene/α-olefin interpolymer can also be a linear ethylene/α-olefin interpolymer as described in U.S. Pat. No. 3,645,992 (Elston), the disclosure of which is incorporated herein by reference.

The substantially linear ethylene/α-olefin interpolymers are not "linear" polymers in the traditional sense of the term, as used to describe linear low density polyethylene (e.g., Ziegler polymerized linear low density polyethylene (LLDPE)), nor are they highly branched polymers, as used to describe low density polyethylene (LDPE).

The substantially linear ethylene/α-olefin interpolymers of the present invention are herein defined as in copending application Ser. No. 07/776,130, now U.S. Pat. No. 5,272,236 and in copending application entitled "Elastic Substantially Linear Olefin Polymers" filed Sep. 2, 1992 in the names of Shih-Yaw Lai, George W. Knight, John R. Wilson and James C. Stevens.

The homogeneously branched ethylene/α-olefin interpolymers useful for forming the compositions described herein are those in which the comonomer is randomly distributed within a given interpolymer molecule and wherein substantially all of the interpolymer molecules have the same ethylene/comonomer ratio within that interpolymer. The homogeneity of the interpolymers is typically described by the SCBDI (Short Chain Branch Distribution Index) or CDBI (Composition Distribution Branch Index) and is defined as the weight percent of the polymer molecules having a comonomer content within 50 percent of the median total molar comonomer content. The CDBI of a polymer is readily calculated from data obtained from techniques known in the art, such as, for example, temperature rising elution fractionation (abbreviated herein as "TREF") as described, for example, in Wild et al, *Journal of Polymer Science, Poly. Phys. Ed.*, Vol. 20, p. 441 (1982), in U.S. Pat. No. 4,798,081 (Hazlitt et al.), or in U.S. Pat. No. 5,089,321 (Chum et al.) the disclosures of all of which are incorporated herein by reference. The SCBDI or CDBI for the linear and for the substantially linear olefin polymers of the present invention is preferably greater than about 30 percent, especially greater than about 50 percent. The homogeneous ethylene/α-olefin polymers used in this invention essentially lack a measurable "high density" fraction as measured by the TREF technique (i.e., the homogeneously branched ethylene/α-olefin polymers do not contain a polymer fraction with a degree of branching less than or equal to 2 methyls/1000 carbons). The homogeneously branched ethylene/α-olefin polymers also do not contain any highly short chain branched fraction (i.e., the homogeneously branched ethylene/α-olefin polymers do not contain a polymer fraction with a degree of branching equal to or more than about 30 methyls/1000 carbons).

The substantially linear ethylene/α-olefin interpolymers for use in the present invention typically are interpolymers of ethylene with at least one C_3–C_{20} α-olefin and/or C_4–C_{18} diolefins. Copolymers of ethylene and 1-octene are especially preferred. The term "interpolymer" is used herein to indicate a copolymer, or a terpolymer, or the like. That is, at least one other comonomer is polymerized with ethylene to make the interpolymer. Ethylene copolymerized with two or more comonomers can also be used to make the homogeneously branched substantially linear interpolymers useful in this invention. Preferred comonomers include the C_3–C_{20} α-olefins, especially propene, isobutylene, 1-butene, 1-hexene, 4-methyl-1-pentene, 1-heptene, 1-octene, 1-nonene, and 1-decene, more preferably 1-butene, 1-hexene, 4-methyl-1-pentene and 1-octene.

The term "linear ethylene/α-olefin interpolymer" means that the interpolymer does not have long chain branching. That is, the linear ethylene/α-olefin interpolymer has an absence of long chain branching, as for example the linear low density polyethylene polymers or linear high density polyethylene polymers made using uniform (i.e., homogeneous) branching distribution polymerization processes (e.g., as described in U.S. Pat. No. 3,645,992 (Elston)) and are those in which the comonomer is randomly distributed within a given interpolymer molecule and wherein substantially all of the interpolymer molecules have the same ethylene/comonomer ratio within that interpolymer. The term "linear ethylene/α-olefin interpolymer" does not refer to high pressure branched (free-radical polymerized) polyethylene which is known to those skilled in the art to have numerous long chain branches. The branching distribution of the homogeneously branched linear ethylene/α-olefin interpolymers is the same or substantially the same as that described for the homogeneously branched substantially linear ethylene/α-olefin interpolymers, with the exception that the linear ethylene/α-olefin interpolymers do not have any long chain branching. The homogeneously branched linear ethylene/α-olefin interpolymers comprise ethylene with at least one C_3–C_{20} α-olefin and/or C_4–C_{18} diolefin. Copolymers of ethylene and 1-octene are especially preferred. Preferred comonomers include the C_3–C_{20} α-olefins, especially propene, isobutylene, 1-butene, 1-hexene, 4-methyl-1 -pentene, 1-heptene, 1-octene, 1-nonene, and 1-decene, more preferably 1-butene, 1-hexene, 4-methyl-1-pentene and 1-octene.

Both the homogeneously branched substantially linear and linear ethylene/α-olefin interpolymers have a single melting point, as opposed to traditional heterogeneously branched Ziegler polymerized ethylene/α-olefin copolymers having two or more melting points, as determined using differential scanning calorimetry (DSC).

The density of the homogeneously branched linear or substantially linear ethylene/α-olefin interpolymers (as measured in accordance with ASTM D-792) for use in the present invention is generally from about 0.89 g/cm^3 to about 0.935 g/cm^3, preferably from about 0.905 g/cm^3 to about 0.925 g/cm^3, and especially from about 0.905 g/cm^3 to less than about 0.92 g/cm^3.

The amount of the homogeneously branched linear or substantially linear ethylene/α-olefin polymer incorporated into the composition varies depending upon the heterogeneously branched ethylene polymer to which it is combined. However, about 50 percent (by weight of the total composition) of the homogeneous linear or substantially linear ethylene/α-olefin polymer is especially preferred in the novel compositions disclosed herein.

The molecular weight of the homogeneously branched linear or substantially linear ethylene/α-olefin interpolymers for use in the present invention is conveniently indicated using a melt index measurement according to ASTM D-1238, Condition 190° C./2.16 kg (formerly known as "Condition (E)" and also known as I_2). Melt index is inversely proportional to the molecular weight of the polymer. Thus, the higher the molecular weight, the lower the melt index, although the relationship is not linear. The lower

melt index limit for the homogeneously branched linear or substantially linear ethylene/α-olefin interpolymers useful herein is generally about 0.001 grams/10 minutes (g/10 min). The upper melt index limit for the homogeneously branched linear or substantially linear ethylene/α-olefin interpolymers is about 10 g/10 min, preferably less than about 1 g/10 min, and especially less than about 0.5 g/10 min.

Another measurement useful in characterizing the molecular weight of the homogeneously branched linear or substantially linear ethylene/α-olefin interpolymers is conveniently indicated using a melt index measurement according to ASTM D-1238, Condition 190° C./10 kg (formerly known as "Condition (N)" and also known as I_{10}). The ratio of the I_{10} and I_2 melt index terms is the melt flow ratio and is designated as I_{10}/I_2. Generally, the I_{10}/I_2 ratio for the homogeneously branched linear ethylene/α-olefin interpolymers is about 5.6. For the homogeneously branched substantially linear ethylene/α-olefin interpolymers used in the compositions of the invention, the I_{10}/I_2 ratio indicates the degree of long chain branching, i.e., the higher the I_{10}/I_2 ratio, the more long chain branching in the interpolymer. Generally, the I_{10}/I_2 ratio of the homogeneously branched substantially linear ethylene/α-olefin interpolymers is at least about 6, preferably at least about 7, especially at least about 8 or above. For the homogeneously branched substantially linear ethylene/α-olefin interpolymers, the higher the I_{10}/I_2 ratio, the better the processability.

Other additives such as antioxidants (e.g., hindered phenolics (e.g., Irganox® 1010 made by Ciba Geigy Corp.), phosphites (e.g., Irgafos® 168 also made by Ciba Geigy Corp.)), cling additives (e.g., PIB), antiblock additives, pigments, fillers, and the like can also be included in the formulations, to the extent that they do not interfere with the enhanced formulation properties discovered by Applicants.

Molecular Weight Distribution Determination

The molecular weight distribution of the linear or substantially linear olefin interpolymer product samples is analyzed by gel permeation chromatography (GPC) on a Waters 150° C. high temperature chromatographic unit equipped with three mixed porosity columns (Polymer Laboratories 10^3, 10^4, 10^5, and 10^6), operating at a system temperature of 140° C. The solvent is 1,2,4-trichlorobenzene, from which 0.3 percent by weight solutions of the samples are prepared for injection. The flow rate is 1.0 milliliter/minute and the injection size is 200 microliters. A differential refractometer is being used as the detector.

The molecular weight determination is deduced by using narrow molecular weight distribution polystyrene standards (from Polymer Laboratories) in conjunction with their elution volumes. The equivalent polyethylene molecular weights are determined by using appropriate Mark-Houwink coefficients for polyethylene and polystyrene (as described by Williams and Word in *Journal of Polymer Science*, Polymer Letters, Vol. 6, (621) 1968, incorporated herein by reference) to derive the following equation:

$$M_{polyethylene}=a*(M_{polystyrene})^b.$$

In this equation, a=0.4316 and b=1.0. Weight average molecular weight, M_w, is calculated in the usual manner according to the following formula: $M_w=\Sigma w_i * M_i$, where w_i and M_i are the weight fraction and molecular weight, respectively, of the i^{th} fraction eluting from the GPC column.

For both the homogeneously branched linear and substantially linear ethylene/α-olefin polymers, the molecular weight distribution (M_w/M_n) is preferably from about 1.8 to about 2.8, more preferably from about 1.89 to about 2.2 and especially about 2.

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 40× 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 used herein is greater than about 4×10^6 dyne/cm^2 and greater than about 2.8×10^6 dyne/cm^2, respectively.

Determination of the Slope of Strain Hardening Coefficient

The slope of strain hardening is measured by compression molding a plaque from the polymer to be tested. Typically, the plaque is molded at about 177° C. for 4 minutes under almost no pressure and then pressed for 3 minutes under a pressure of about 200 psi. The plaque is then allowed to cool at about 8° C./minute while still under 200 psi pressure. The molded plaque has a thickness of about 0.005 inches. The plaque is then cut into a dogbone shaped test piece using a steel rule die. The test piece is 0.315 inches wide and 1.063 inches long. The start of the curved portion of the dogbone shape begins at 0.315 inches from each end of the sample and gently curves (i.e., tapers) to a width of 0.09 inches. The curve ends at a point 0.118 inches from the start of the curve such that the interior portion of the dogbone test piece has a width of 0.09 inches and a length of 0.197 inches.

The tensile properties of the test sample is tested on an Instron Tensile Tester at a crosshead speed of 1 inch/minute. The slope of strain hardening is calculated from the resulting

tensile curve by drawing a line parallel to the strain hardening region of the resulting stress/strain curve. The strain hardening region occurs after the sample has pulled its initial load ((i.e., stress) usually with little or no elongation during the initial load) and after the sample has gone through a slight drawing stage (usually with little or no increase in load, but with increasing elongation (i.e., strain)). In the strain hardening region, the load and the elongation of the sample both continue to increase. The load increases in the strain hardening region at a much lower rate than during the initial load region and the elongation also increase, again at a rate lower than that experienced in the drawing region. FIG. 1 shows the various stages of the stress/strain curve used to calculate the slope of strain hardening. The slope of the parallel line in the strain hardening region is then determined.

The slope of strain hardening coefficient (SHC) is calculated according to the following equation:

$$SHC=(\text{slope of strain hardening})*(I_2)^{0.25}$$

where I_2=melt index in grams/10 minutes.

For both the homogeneously branched linear and substantially linear ethylene/α-olefin interpolymers used in the invention, the SHC is greater than about 1.3, preferably greater than about 1.5.

Surprisingly, the slope of strain hardening coefficient reaches a maximum for the linear or the substantially linear ethylene/α-olefin polymers at a density from about 0.89 g/cm^3 to about 0.935 g/cm^3. Heterogeneous ethylene/α-olefin polymers, in contrast, do not behave in the same manner. FIG. 1 graphically depicts the relationship between the density of the homogeneously branched substantially linear ethylene polymers and ethylene/α-olefin polymers as a function of their slope of strain hardening coefficient, and includes a heterogeneously branched ethylene/1-octene copolymer (polymer W** in Table 1) for comparison purposes. Table 1 displays the data of FIG. 1 in tabular form:

TABLE 1

Polymer	Melt Index (I_2) (g/10 min)	Density (g/cm^3)	I_{10}/I_2	SHC*
A	1	0.8564	7.36	0.004
B	1.03	0.8698	7.46	0.45
C	0.57	0.873	7.22	0.54
D	1.01	0.8817	7.36	0.89
E	1.06	0.9018	7.61	1.84
F	2.01	0.9041	8.07	2.03
G	0.77	0.9047	9.01	1.57
H	9.82	0.9048	7.03	1.67
I	4.78	0.9077	7.18	2.08
J	3.13	0.9113	7.67	2.04
K	2.86	0.9139	7.87	2.27
L	1.08	0.9197	8.07	2.24
M	0.96	0.9198	9.61	1.93
N	0.99	0.9203	9.09	2.23
O	1.11	0.9204	10.15	1.59
P	1.06	0.9205	9.08	2.25
Q	1.12	0.9216	8.94	2.3
R	30.74	0.9217	6.27	2
S	31.58	0.94	6.02	0.24
T	0.97	0.9512	12.11	0
U	0.97	0.9533	10.5	0
V	0.92	0.954	7.39	0
W**	0.8	0.905	8.7	1.02

*SHC = Slope of Strain Hardening Coefficient
**A comparative heterogeneously branched ethylene/1-octene copolymer

The Heterogeneously Branched Ethylene Polymer

The ethylene polymer to be combined with the homogeneous ethylene/α-olefin interpolymer is a heterogeneously branched (e.g., Ziegler polymerized) interpolymer of ethylene with at least one C_3–C_{20} α-olefin (e.g., linear low density polyethylene (LLDPE)).

Heterogeneously branched ethylene/α-olefin interpolymers differ from the homogeneously branched ethylene/α-olefin interpolymers primarily in their branching distribution. For example, heterogeneously branched LLDPE polymers have a distribution of branching, including a highly branched portion (similar to a very low density polyethylene), a medium branched portion (similar to a medium branched polyethylene) and an essentially linear portion (similar to linear homopolymer polyethylene). The amount of each of these fractions varies depending upon the whole polymer properties desired. For example, linear homopolymer polyethylene has neither branched nor highly branched fractions, but is linear. A very low density heterogeneous polyethylene having a density from about 0.9 g/cm^3 to about 0.915 g/cm^3 (such as Attane® copolymers, sold by The Dow Chemical Company and Flexomer® sold by Union Carbide Corporation) has a higher percentage of the highly short chain branched fraction, thus lowering the density of the whole polymer.

Heterogeneously branched LLDPE (such as Dowlex® sold by The Dow Chemical Company) has a lower amount of the highly branched fraction, but has a greater amount of the medium branched fraction. FIG. 2 graphically depicts the relative amounts of these various fractions (as measured using temperature rising elution fractionation) for Dowlex® 2045 (a heterogeneously branched ethylene/1-octene copolymer having a melt index (I_2) of about 1 g/10 min, a density of about 0.92 g/cm^3, a melt flow ratio (I_{10}/I_2) of about 7.93 and a molecular weight distribution (M_w/M_n) of about 3.34), as compared with a homogeneously branched substantially linear ethylene/1-octene copolymer having a melt index (I_2) of about 1 g/10 min, a density of about 0.92 g/cm^3, a melt flow ratio (I_{10}/I_2) of about 10.5 and a molecular weight distribution (M_w/M_n) of about 2.18. Note that the homogeneously branched polymer has a single relatively narrow peak at an elution temperature of about 85° C., while the Dowlex® 2045 polymer has a broad branching distribution, as represented by the breadth of elution temperatures over which the polymer fractions elute. Dowlex® 2045 also has a distinct peak at an elution temperature of about 98° C., indicating the "linear" fraction of the whole polymer. Increasing the fraction of the polymer which has the beneficial properties, without concomitantly increasing other fractions has not been demonstrated here-to-fore.

Preferably, however, the heterogeneously branched ethylene polymer is a heterogeneously branched Ziegler polymerized ethylene/α-olefin interpolymer having no more than about 10 percent (by weight of the polymer) of a polymer fraction having a SHC≧1.3.

More preferably, the heterogeneously branched ethylene polymer is a copolymer of ethylene with a C_3–C_{20} α-olefin, wherein the copolymer has:

(i) a density from about 0.93 g/cm^3 to about 0.965 g/cm^3,

(ii) a melt index (I_2) from about 0.1 g/10 min to about 500 g/10 min, and

(iii) no more than about 10 percent (by weight of the polymer) of a polymer fraction having a SHC≧1.3.

The heterogeneously branched ethylene/α-olefin interpolymers and/or copolymers also have at least two melting peaks, as determined using Differential Scanning Calorimetry (DSC).

The Formulated Compositions

The compositions disclosed herein can be formed by any convenient method, including dry blending the individual

components and subsequently melt mixing or by pre-melt mixing in a separate extruder (e.g., a Banbury mixer, a Haake mixer, a Brabender internal mixer, or a twin screw extruder).

Another technique for making the compositions in-situ is disclosed in pending U.S. Ser. No. 08/010,958, now abandoned entitled Ethylene Interpolymerizations, which was filed Jan. 29, 1993 in the names of Brian W. S. Kolthammer and Robert S. Cardwell, the disclosure of which is incorporated herein in its entirety by reference. U.S. Ser. No. 08/010,958, now abandoned describes, inter alia, interpolymerizations of ethylene and C_3–C_{20} alpha-olefins using a homogeneous catalyst in at least one reactor and a heterogeneous catalyst in at least one other reactor. The reactors can be operated sequentially or in parallel.

The compositions can also be made by fractionating a heterogeneous ethylene/α-olefin polymer into specific polymer fractions with each fraction having a narrow composition (i.e., branching) distribution, selecting the fraction having the specified properties (e.g., SHC≧1.3), and blending the selected fraction in the appropriate amounts with another ethylene polymer. This method is obviously not as economical as the in-situ interpolymerizations of U.S. Ser. No. 08/010,958, now abandoned but can be used to obtain the compositions of the invention.

Fabricated Articles Made from the Novel Compositions

Many useful fabricated articles benefit from the novel compositions disclosed herein. For example, molding operations can be used to form useful fabricated articles or parts from the compositions disclosed herein, including various injection molding processes (e.g., that described in *Modern Plastics Encyclopedia*/89, Mid October 1988 Issue, Volume 65, Number 11, pp. 264–268, "Introduction to Injection Molding" by H. Randall Parker and on pp. 270–271, "Injection Molding Thermoplastics" by Michael W. Green, the disclosures of which are incorporated herein by reference) and blow molding processes (e.g., that described in *Modern Plastics Encyclopedia*/89, Mid October 1988 Issue, Volume 65, Number 11, pp. 217–218, "Extrusion-Blow Molding" by Christopher Irwin, the disclosure of which is incorporated herein by reference), profile extrusion, calandering, pultrusion (e.g., pipes) and the like. Rotomolded articles can also benefit from the novel compositions described herein. Rotomolding techniques are well known to those skilled in the art and include, for example, those described in *Modern Plastics Encyclopedia*/89, Mid October 1988 Issue, Volume 65, Number 11, pp. 296–301, "Rotational Molding" by R. L. Fair, the disclosure of which is incorporated herein by reference).

Fibers (e.g., staple fibers, melt blown fibers or spunbonded fibers (using, e.g., systems as disclosed in U.S. Pat. Nos. 4,340,563, 4,663,220, 4,668,566, or 4,322,027, all of which are incorporated herein by reference), and gel spun fibers (e.g., the system disclosed in U.S. Pat. No. 4,413,110, incorporated herein by reference)), both woven and nonwoven fabrics (e.g., spunlaced fabrics disclosed in U.S. Pat. No. 3,485,706, incorporated herein by reference) or structures made from such fibers (including, e.g., blends of these fibers with other fibers, e.g., PET or cotton)) can also be made from the novel compositions disclosed herein.

Film and film structures particularly benefit from the novel compositions described herein and can be made using conventional hot blown film fabrication techniques or other biaxial orientation processes such as tenter frames or double bubble processes. Conventional hot blown film processes are described, for example, in *The Encyclopedia of Chemical Technology*, Kirk-Othmer, Third Edition, John Wiley & Sons, New York, 1981, Vol. 16, pp. 416–417 and Vol. 18, pp. 191–192, the disclosures of which are incorporated herein by reference. Biaxial orientation film manufacturing process such as described in a "double bubble" process as in U.S. Pat. No. 3,456,044 (Pahlke), and the processes described in U.S. Pat. No. 4,352,849 (Mueller), U.S. Pat. No. 4,597,920 (Golike), U.S. Pat. No. 4,820,557 (Warren), U.S. Pat. No. 4,837,084 (Warren), U.S. Pat. No. 4,865,902 (Golike et al.), U.S. Pat. No. 4,927,708 (Herran et al.), U.S. Pat. No. 4,952,451 (Mueller), U.S. Pat. No. 4,963,419 (Lustig et al.), and U.S. Pat. No. 5,059,481 (Lustig et al.), the disclosures of each of which are incorporated herein by reference, can also be used to make film structures from the novel compositions described herein. The film structures can also be made as described in a tenter-frame technique, such as that used for oriented polypropylene.

Other multi-layer film manufacturing techniques for food packaging applications are described in *Packaging Foods With Plastics*, by Wilmer A. Jenkins and James P. Harrington (1991), pp. 19–27, and in "Coextrusion Basics" by Thomas I. Butler, *Film Extrusion Manual: Process, Materials, Properties* pp. 31–80 (published by TAPPI Press (1992)) the disclosures of which are incorporated herein by reference.

The films may be monolayer or multilayer films. The film made from the novel compositions can also be coextruded with the other layer(s) or the film can be laminated onto another layer(s) in a secondary operation, such as that described in *Packaging Foods With Plastics*, by Wilmer A. Jenkins and James P. Harrington (1991) or that described in "Coextrusion For Barrier Packaging" by W. J. Schrenk and C. R. Finch, *Society of Plastics Engineers RETEC Proceedings*, Jun. 15–17 (1981), pp. 211–229, the disclosure of which is incorporated herein by reference. If a monolayer film is produced via tubular film (i.e., blown film techniques) or flat die (i.e., cast film) as described by K. R. Osborn and W. A. Jenkins in "Plastic Films, Technology and Packaging Applications" (Technomic Publishing Co., Inc. (1992)), the disclosure of which is incorporated herein by reference, then the film must go through an additional post-extrusion step of adhesive or extrusion lamination to other packaging material layers to form a multilayer structure. If the film is a coextrusion of two or more layers (also described by Osborn and Jenkins), the film may still be laminated to additional layers of packaging materials, depending on the other physical requirements of the final film. "Laminations Vs. Coextrusion" by D. Dumbleton (Converting Magazine (September 1992), the disclosure of which is incorporated herein by reference, also discusses lamination versus coextrusion. Monolayer and coextruded films can also go through other post extrusion techniques, such as a biaxial orientation process.

Extrusion coating is yet another technique for producing multilayer film structures using the novel compositions described herein. The novel compositions comprise at least one layer of the film structure. Similar to cast film, extrusion coating is a flat die technique. A sealant can be extrusion coated onto a substrate either in the form of a monolayer or a coextruded extrudate.

Generally for a multilayer film structure, the novel compositions described herein comprise at least one layer of the total multilayer film structure. Other layers of the multilayer structure include but are not limited to barrier layers, and/or tie layers, and/or structural layers. Various materials can be used for these layers, with some of them being used as more

than one layer in the same film structure. Some of these materials include: foil, nylon, ethylene/vinyl alcohol (EVOH) copolymers, polyvinylidene chloride (PVDC), polyethylene terephthalate (PET), oriented polypropylene (OPP), ethylene/vinyl acetate (EVA) copolymers, ethylene/acrylic acid (EAA) copolymers, ethylene/methacrylic acid (EMAA) copolymers, LLDPE, HDPE, LDPE, nylon, graft adhesive polymers (e.g., maleic anhydride grafted polyethylene), and paper. Generally, the multilayer film structures comprise from 2 to about 7 layers.

EXAMPLE 1

Seventy five percent (by weight of the total composition) of a homogeneously branched substantially linear ethylene/1-octene copolymer having I_2 of about 1 g/10 min, density of about 0.91 g/cm^3, I_{10}/I_2 of about 10, M_w/M_n of about 2, and SHC of about 1.81 is dry blended and then melt blended with 25 percent (by weight of the total composition) of a heterogeneously branched ethylene/1-octene copolymer having I_2 of about 1 g/10 min, density of about 0.935 g/cm^3, I_{10}/I_2 of about 7.8, and M_w/M_n of about 3.4. The heterogeneously branched ethylene/1-octene copolymer has a fraction of about 5 percent (by weight of the heterogeneously branched copolymer) having a SHC≧1.3. The dry blend is tumble blended in a 50 gallon drum for about 1 hour.

The melt blend is produced in a ZSK 30 twin screw extruder (30 mm screw diameter) and is then fabricated into film. The final blended composition has a density of about 0.919 g/cm^3.

The blended composition is then fabricated into blown film having a thickness of about 1 mil on an Egan Blown Film Line having a 2 inch diameter screw, a 3 inch die and at a 2.5 inch blow up ratio (BUR), as described in Table 2. For all film samples in Examples 1, 2, 4, and 6 and for comparative examples 3, 5, and 7, the targeted gauge is about 1 mil, using a blow-up ratio (BUR) of 2.5:1, a LLDPE screw design is used, a die gap of 70 mils is used, and a lay flat of about 11.875 inches is used.

Film properties are measured and reported in Table 3 with other examples of the invention and with comparative examples. Dart impact (type A) of the films is measured in accordance with ASTM D-1709–85; tensile strength, yield, toughness, and 2% secant modulus of the films is measured in accordance with ASTM D-882; Elmendorf tear (type B) is measured in accordance with ASTM D-1922; PPT tear is measured in accordance with ASTM D-2582; Block is measured in accordance with ASTM D-3354.

Puncture is measured by using an Instron tensiometer Tensile Tester with an integrator, a specimen holder that holds the film sample taut across a circular opening, and a rod-like puncturing device with a rounded tip (ball) which is attached to the cross-head of the Instron and impinges perpendicularly onto the film sample. The Instron is set to obtain a crosshead speed of 10 inches/minute and a chart speed (if used) of 10 inches/minute. Load range of 50% of the load cell capacity (100 lb. load for these tests) should be used. The puncturing device is installed to the Instron such that the clamping unit is attached to the lower mount and the ball is attached to the upper mount on the crosshead. Six film specimens are used (each 6 inches square). The specimen is clamped in the film holder and the film holder is secured to the mounting bracket. The crosshead travel is set and continues until the specimen breaks. Puncture resistance is defined as the energy to puncture divided by the volume of the film under test. Puncture resistance (PR) is calculated as follows:

$$PR=E/((12)(T)(A))$$

where PR=puncture resistance (ft-lbs/in^3)

E=energy (inch-lbs)=area under the load displacement curve

12=inches/foot

T=film thickness (inches), and

A=area of the film sample in the clamp=12.56 in^2.

EXAMPLE 2

Seventy five percent (by weight of the total composition) of a homogeneously branched substantially linear ethylene/1-octene copolymer having I_2 of about 0.5 g/10 min, density of about 0.915 g/cm^3, I_{10}/I_2 of about 11, M_w/M_n of about 2.4, and SHC of about 2.265 is dry blended and then melt blended (as described in Example 1) with 25 percent (by weight of the total composition) of a heterogeneously branched ethylene/1-octene copolymer having I_2 of about 1 g/10 min, density of about 0.935 g/cm^3, I_{10}/I_2 of about 7.8, and M_w/M_n of about 3.4. The heterogeneously branched ethylene/1-octene copolymer has a fraction of about 5 percent (by weight of the heterogeneously branched copolymer) having a SHC≧1.3. The final blended composition has a density of about 0.92 g/cm^3.

Blown film is made as described in Table 2 and film properties are measured and reported in Table 3 with other examples of the invention and with comparative examples.

COMPARATIVE EXAMPLE 3

A heterogeneously branched ethylene/1-octene copolymer having I_2 of about 1 g/10 min, density of about 0.92 g/cm^3, I_{10}/I_2 of about 7.93, and M_w/M_n of about 3.34 is made into film as described in Example 1. The heterogeneously branched ethylene/1-octene copolymer has a fraction of about 36 percent (by weight of the heterogeneous copolymer) having a SHC≧1.3. The entire heterogeneous ethylene/1-octene copolymer has a SHC of about 1.5.

Blown film is made as described in Table 2 and film properties are measured and reported in Table 3 with other examples of the invention and with comparative examples.

EXAMPLE 4

Example 4 is an in-situ blend made according to U.S. Ser. No. 08/010,958 now abandoned, wherein the homogeneously branched substantially linear polymer is made in a first reactor and is an ethylene/1-octene copolymer having a melt index (I_2) of about 0.5 g/10 min., and a density of about 0.9054 g/cm^3, a melt flow ratio (I_{10}/I_2) of about 8.27 and a molecular weight distribution (M_w/M_n) of about 1.979 and comprises about 50% (by weight of the total composition). A heterogeneously branched ethylene/1-octene copolymer is made in a second reactor operated sequentially with the first reactor and has a melt index (I_2) of about 1.5 g/10 min., and a density of about 0.944 g/cm^3 and comprises the remaining 50% (by weight of the total composition). The total composition has a melt index (I_2) of about 1 g/10 min., a density of about 0.9248 g/cm^3, a melt flow ratio (I_{10}/I_2) of about 7.22 and a molecular weight distribution (M_w/M_n) of about 2.641. This composition is made into blown film as described in Table 2 and the resultant film properties are reported in Table 3.

COMPARATIVE EXAMPLE 5

Comparative Example 5 is an ethylene/1-octene copolymer made according to U.S. Ser. No. 07/773,375, filed Oct.

7, 1991, now U.S. Pat. No. 5,250,612 the disclosure of which is incorporated herein by reference. About 15% (by weight of the total composition) is made in a first reactor, with the remaining portion of the composition polymerized in a second sequentially operated reactor. Both reactors utilize Ziegler type catalysts and make heterogeneously branched polymers. The total composition has a melt index (I_2) of about 0.56 g/10 min., a density of about 0.9256 g/cm^3, a melt flow ratio (I_{10}/I_2) of about 9.5 and a molecular weight distribution (M_w/M_n) of about 4.35. This composition is also made into blown film as described in Table 2 and the resultant film properties are reported in Table 3.

EXAMPLE 6

Example 6 is an in-situ blend made according to U.S. Ser. No. 08/010,958 now abandoned, wherein the homogeneously branched substantially linear polymer is made in a first reactor and is an ethylene/1-octene copolymer having a fractional melt index (I_2), a density of about 0.906 g/cm^3, a melt flow ratio (I_{10}/I_2) of about 8–10 and a molecular weight distribution (M_w/M_n) of about 2.2 and comprises about 43% (by weight of the total composition). A second heterogeneously branched ethylene/1-octene copolymer is made in a second reactor operated sequentially with the first reactor and has a melt index (I_2) of about 0.85 g/10 minutes, a density of about 0.938 g/cm^3 and comprises the remaining 57% (by weight of the total composition). The total composition has a melt index (I_2) of about 0.53 g/10 minutes, a density of about 0.9246 g/cm^3, a melt flow ratio (I_{10}/I_2) of about 7.83, and a molecular weight distribution (M_w/M_n) of about 2.8. This composition is made into blown film as described in Table 2 and the film properties are reported in Table 3.

COMPARATIVE EXAMPLE 7

Comparative Example 7 is an ethylene/1-octene copolymer made according to U.S. Ser. No. 07/773,375, filed Oct. 7, 1991, now U.S. Pat. No. 5,250,612 the disclosure of which is incorporated herein by reference. About 25% (by weight of the total composition) is made in a first reactor, with the remaining portion of the composition polymerized in a second sequentially operated reactor. Both reactors utilize Ziegler type catalysts and make heterogeneously branched polymers. The total composition has a melt index (I_2) of about 0.49 g/10 min., a density of about 0.9244 g/cm^3, a melt flow ratio (I_{10}/I_2) of about 10 and a molecular weight distribution (M_w/M_n) of about 4.78. This composition is also made into blown film as described in Table 2 and the resultant film properties are reported in Table 3.

COMPARATIVE EXAMPLE 8

Comparative example 8 is a heterogeneously branched ethylene/1-octene copolymer having a melt index (I_2) of about 1 g/10 minutes, a density of about 0.9249 g/cm^3, a melt flow ratio (I_{10}/I_2) of about 8 and a molecular weight distribution (M_w/M_n) of about 3.5.

Blown film is made as described in Table 2 and film properties are measured and reported in Table 3 with other examples of the invention and comparative examples.

TABLE 2

	Ex. 1	Ex. 2	Comp. Ex. 3	Ex. 4	Comp. Ex. 5	Ex. 6	Comp. Ex. 7	Comp. Ex. 8
Zone 1A (°F.)	300	300	300	300	300	300	300	300
Zone 1B (°F.)	450	451	475	474	475	475	475	474
Zone 1C (°F.)	450	450	475	475	475	475	475	475
Zone 2A (°F.)	450	450	475	474	475	475	475	475
Zone 2B (°F.)	450	450	455	475	475	475	475	475
Zone 2C (°F.)	450	450	47.5	475	475	475	475	475
Zone 3 (°F.)	451	452	474	477	477	476	476	474
Zone 4 (°F.)	450	450	473	475	475	475	475	475
Zone 5 (°F.)	450	450	475	475	475	475	475	475
Melt temp. (°F.)	475	477	515	501	502	499	499	497
Blower Air temp. (°F.)	47.3	45.7	57	44.4	86.5	47.6	NA	47.3
Chill Water temp. (°F.)	39	37.6	51.1	38.3	86.8	40	38.7	40.5
Extruder Die press. (psi)	2843	3427	1321	1874	1763	2893	2525	1952
Nozzle press. (in.)	3.2	4.5	4.38	4.4	4.9	4.6	4.6	4.3
Amps	27.3	33.1	37.7	39.9	40.2	50.1	42.6	38.6
Extruder speed (rpm)	27.6	28.8	21.5	23.1	21.1	21.5	22.1	21.7
Nip Roll speed (rpm)	33.1	36.9	39	39.8	36.2	37	36	37.8
Output (lbs/hr)	31	NR*	38.3	39	NR*	36	36	36
Frost line height (in.)	12.5	9	13	12	12	10.5	11	10.5

*NR = Not recorded

TABLE 3

	Ex. 1	Ex. 2	Comp. Ex. 3	Ex. 4	Comp. Ex. 5	Ex. 6	Comp. Ex. 7	Comp. Ex. 8
Yield (MD*) (psi)	1605	1595	1643	2040	2243	1973	1810	1782
Tensile (MD*) (psi)	8522	9525	7444	7794	7931	9325	8455	4928
Toughness (MD*) (ft-lbs/in^3)	1689	1773	1439	1671	1519	NR	NR	NR
Yield (CD**) (psi)	1530	1489	1706	2267	2407	1997	1809	1832
Tensile (CD**) (psi)	6252	7603	5807	7079	7458	7153	6326	4598
Toughness (CD**) (ft-lbs/in^3)	1282	1599	1358	1656	1495	NR	NR	NR
Elmendorf B (MD*) (grams)	288	216	334	317	194	320	398	297
Elmendorf B (CD**) (grams)	621	566	413	630	664	640	621	527
PPT Tear (MD*) (lbs.)	6.79	6.18	5.99	6.2	6.5	6.2	6.2	5.3
PPT Tear (CD**) (lbs.)	7.44	7.42	6.46	6.8	8.1	7.0	7.5	6.1
Dart Impact A (grams)	708	610	354	410	186	412	186	164
Puncture (ft-lbs/in^3)	316	349	251	231	256	2,50	227	237
Film Block g.	75	33	87	32	17	11.8	17	22
Film Gradient Density (g/cm^3)	0.9145	0.9153	0.9155	0.9205	0.9218	0.9198	0.9201	0.9207
Film Gauge (low) (mils)	0.9	0.9	0.9	0.85	0.8	0.98	0.95	1.05
Film Gauge (high) (mils)	1.2	1.05	1.1	0.95	1	1.08	1.05	1.15

*MD = Machine direction
**CD = Cross direction
NR = Not Recorded

In general, films made from the novel formulated ethylene/α-olefin compositions exhibit good impact and tensile properties, and an especially good combination of tensile, yield and toughness (e.g., toughness and dart impact). Further, films from the example resins exhibited significant improvements over films made from the comparative resins in a number of key properties.

For example, comparing examples 1 and 2 with comparative example 3, the data show films produced from the melt blends (examples 1 and 2) exhibited significantly higher values for the following film properties: dart impact, MD tensile, CD tensile, MD toughness, CD toughness MD ppt tear, CD ppt tear, CD Elmendorf tear B, puncture and significantly lower block.

Comparing example 4 to comparative example 5, the data shows films produced from the in-situ blend (made according to U.S. Ser. No. 08/010,958, now abandoned) exhibited significantly higher values for the following film properties: dart impact, MD toughness and CD toughness.

Comparing example 6 to comparative examples 7 (an ethylene/1-octene copolymer made according to U.S. Ser. No. 07/773,375 now U.S. Pat. No. 5,250,612) and 8 (an heterogeneously branched ethylene/1-octene copolymer), the data show films produced from the in-situ blend (made according to U.S. Ser. No. 08/010,958) exhibited significantly higher values for the following film properties: dart impact, MD yield, CD yield, MD tensile, CD tensile, CD Elmendorf tear B and puncture and significantly lower block.

We claim:

1. 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 stress at onset of gross melt fracture of greater than 4×10^6 dyne/cm^2, and

(vii) a slope of strain hardening coefficient from 1.3 to 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 1.3.

2. The film of claim 1 wherein the heterogeneously branched ethylene polymer is an interpolymer of ethylene with at least one C_3–C_{20} α-olefin.

3. The film of claim 2 wherein the heterogeneously branched ethylene polymer is a copolymer of ethylene and a C_3–C_{20} α-olefin.

4. The film of claim 3 wherein the heterogeneously branched ethylene polymer is a copolymer of ethylene and 1-octene.

5. The film of claim 1 wherein the homogeneously branched substantially linear ethylene/α-olefin interpolymer is an interpolymer of ethylene with at least one C_3–C_{20} α-olefin.

6. The film of claim 1 wherein the homogeneously branched substantially linear ethylene/α-olefin interpolymer is a copolymer of ethylene and a C_3–C_{20} α-olefin.

7. The film of claim 6 wherein the homogeneously branched substantially linear ethylene/α-olefin copolymer is a copolymer of ethylene and 1-octene.

8. 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 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 4×10^6 dyne/cm^2, and

(vii) a slope of strain hardening coefficient from 1.3 to 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 1.3.

9. The improvement of claim 8 wherein the homogeneously branched substantially linear ethylene/α-olefin interpolymer is an interpolymer of ethylene with at least one C_3–C_{20} α-olefin.

10. The improvement of claim 8 wherein the homogeneously branched substantially linear ethylene/α-olefin interpolymer is a copolymer of ethylene and a C_3–C_{20} α-olefin.

11. The improvement of claim 10 wherein the homogeneously branched substantially linear ethylene/α-olefin interpolymer is a copolymer of ethylene and 1-octene.

12. The improvement of claim 8 wherein the heterogeneously branched ethylene polymer is a copolymer of ethylene and a C_3–C_{20} α-olefin.

13. The improvement of claim 12 wherein the heterogeneously branched ethylene polymer is a copolymer of ethylene and 1-octene.

14. 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/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 4×10^6 dyne/cm^2, and

(vii) a slope of strain hardening coefficient from 1.3 to 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.

15. 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/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 4×10^6 dyne/cm^2, and

(vii) a slope of strain hardening coefficient from 1.3 to 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.

16. 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 from 1.3 to 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.

17. 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 from 1.3 to 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. The film of claims 14 or 16, or the composition of claims 15 or 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.

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(54) Method for the preparation of ethylene polymer compositions.

(57) The present invention provides a method for the preparation of an ethylene polymer composition having a density of 0.86-0.94 g/cm^3 and an intrinsic viscosity [η] of 1-6 dl/g using an olefin polymerization catalyst comprising a transition metal compound containing a ligand having a cydoal-kadienyl skeleton and an organoaluminium oxy-compound. A method for the preparation of an ethylene polymer composition having density of 0.87-0.93 g/cm^3 and an intrinsic viscosity [η] of 0.5-6 dl/g is also provided.

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METHOD FOR THE PREPARATION OF ETHYLENE POLYMER COMPOSITIONS

FIELD OF THE INVENTION

This invention relates to a method for the preparation of ethylene polymer compositions, particularly to a method for the preparation of ethylene polymer compositions by multi-stage polymerization, and more particularly to a method for the preparation of ethylene polymer compositions which are excellent in melt properties and favorable in processability at the time of melt molding.

The invention also relates to a method for the preparation of ethylene polymer compositions which are small in amount of their hydrocarbon solvent-soluble portion in spite of their having a low density and accordingly excellent in anti-block properties and also heat resistance.

BACKGROUND OF THE INVENTION

Recently, methods for the preparation of olefin polymers using a catalyst composed of a zirconocene compound and aluminoxane as a new type of Ziegler olefin polymerization catalysts have been proposed, for example, in Japanese Patent L-O-P Publns. Nos. 19309/1983, 35007/1985 and 221208/1986. According to these publications cited above, it is reported that ethylene polymers having a narrow molecular weight distribution and a narrow composition distribution and excellent in transparency are obtained. However, the polymers obtained by the use of such olefin polymerization catalysts as mentioned above have a narrow molecular weight distribution and are poor in processability on molding equipment, hence it is desired that the polymers shall be improved in melt properties according to the purpose for which they are used.

With the view of improving the above-mentioned methods, Japanese Patent L-O-P Publns. Nos. 35006/1985 and 35008/1985 propose a combination use of two or more kinds of metallocene compounds as the olefin polymerization catalysts, and Japanese Patent L-O-P Publns. No. 501369/1988 proposes a combination use of a metallocene compound and non-metallocene compound as the olefin polymerization catalysts. However, none of these proposals are found yet to be wholly satisfactory.

Furthermore, the polymers, particularly copolymers obtained by the use of the above-mentioned olefin polymerization catalysts are low in melting point and poor in heat resistance, hence it is desired said polymers or copolymers shall be improved in heat resistance.

On the one hand, ethylene copolymers obtained by the use of titanium based catalysts composed of a titanium compound and an organoaluminum compound are excellent in heat resistance, but have such drawback that when they are prepared so as to have a low density, the amount of their hydrocarbon solvent-soluble portion becomes large and they come to become poor in anti-block properties.

OBJECT OF THE INVENTION

The present invention has been made in view of the prior art mentioned above, and an object of the invention is to provide a method for the preparation of ethylene polymer compositions which are excellent in melt properties while retaining excellent characteristics of their own.

A further object of the invention is to provide a method for the preparation of ethylene polymer compositions which are excellent in anti-block properties and heat resistance while retaining excellent characteristics of their own.

SUMMARY OF THE INVENTION

The first method for the preparation of ethylene polymer compositions according to the present invention is characterized in that an ethylene polymer composition having a density of 0.86-0.94 g/cm^3 and an intrinsic viscosity of 1-6 dl/g is obtained by carrying out a multi-stage process comprising

a polymerization step (a): wherein ethylene is polymerized or ethylene and other α-olefin are copolymerized to form an ethylene polymer [I] having a density of higher than 0.88 g/cm^3 and an intrinsic viscosity [η] of 0.3-3 dl/g, and

a polymerization step (b): wherein ethylene and other α-olefin are copolymerized to form an ethylene copolymer [II] having a density not higher than that of the ethylene polymer [I] and an intrinsic viscosity [η] of at least 1.5 times that of the ethylene polymer [I] and of 1-10 dl/g, in the presence of an olefin polymerization catalyst [I] composed of a transition metal compound [A] containing a ligand having a cycloalkadienyl skeleton and an organoaluminum oxy-compound [B] in such a manner that the polymerization step (b) is carried out in

the presence of the polymerization product resulting from the polymerization step (a), or the polymerization step (a) is carried out in the presence of the polymerization product resulting from the polymerization step (b) so that the amount of polymerization in the above-mentioned two steps shall assume the proportion in terms of part by weight of the ethylene copolymer [II] to the ethylene polymer [I] being as 10-1000 to 100.

In accordance with the first method for the preparation of ethylene polymer compositions of the invention, there can be obtained ethylene polymer compositions excellent in melt properties.

The second method for the preparation of ethylene polymer compositions according to the present invention is characterized in that an ethylene polymer composition having a density of 0.87-0.93 g/cm³ and an intrinsic viscosity of 0.5-6 dl/g is obtained by carrying out a multi-stage process comprising

a polymerization step (c): wherein ethylene and other α-olefin are copolymerized in the presence of an olefin polymerization catalyst [II] composed of a transition metal compound [A] containing a ligand having a cycloalkadienyl skeleton and an organoaluminum oxy-compound [B] to obtain an ethylene copolymer [III] having a density lower than 0.91 g/cm³ and an intrinsic viscosity [η] of 0.5-C dl/g, and

a polymerization step (d): wherein ethylene, or ethylene and other α-olefin are polymerized or copolymerized in the presence of an olefin polymerization catalyst [III] composed of a titanium catalyst component [C] containing titanium, magnesium and halogen as its essential ingredients, an organoaluminum compound [D] and/or an organoaluminum oxy-compound [E] to form an ethylene polymer [IV] having a density higher than that of the above-mentioned ethylene copolymer [III] and an intrinsic viscosity [η] of 0.5-6 dl/g, in such a manner that the polymerization step (d) is carried out in the presence of the ethylene copolymer [III] resulting from the polymerization step (c), or the polymerization step (c) is carried out in the presence of the ethylene polymer [IV] resulting from the polymerization step (d) so that the amount of polymerization in the above-mentioned two steps shall assume the proportion in terms of part by weight of the ethylene polymer [IV] to the ethylene copolymer [III] being as 10-1000 to 100.

In accordance with the second method for the preparation of ethylene polymer compositions of the present invention, there can be obtained ethylene polymer compositions excellent in anti-block properties and heat resistance despite the fact that they are low in density.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 (a) and Fig. 1 (b) are each a rough schematic drawing illustrating the first process for the preparation of ethylene polymer composition of the present invention.

Fig. 2 is an IR spectrum of the benzene-insoluble organoaluminum oxy-compound.

Fig. 3 is an IR spectrum of the benzene-soluble organoaluminum oxy-compound.

Fig. 4 (a) and Fig. 4 (b) are each a rough schematic drawing illustrating the second process for the preparation of ethylene polymer composition of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

The first method for the preparation of ethylene polymer compositions according to the present invention is illustrated below in detail.

In the first method for the preparation of ethylene polymer compositions of the invention, the olefin polymerization catalyst [I] composed of the transition metal compound [A] containing a ligand having a cycloalkadienyl skeleton and the organoaluminum oxy-compound [B] is used.

Fig. 1 (a) and Fig. 1 (b) each show a rough schematic drawing illustrating the first process for the preparation of ethylene polymer compositions of the present invention.

First, the transition metal compound [A] containing a ligand having a cycloalkadienyl skeleton used in the present invention is explained as follows. This transition metal compound [A] is represented by the formula ML_x wherein M is a transition metal, L is a ligand coordinating to the transition metal, at least one of L is a ligand having a cycloalkadienyl skeleton, and when at least two or more ligands having a cycloalkadienyl skeleton are contained, at least two ligands having a cycloalkadienyl skeleton may be linked together via alkylene, substituted alkylene, silylene or substituted silylene, L other than the ligand having a cycloalkadienyl skeleton is hydrocarbon group of 1-12 carbon atoms, alkoxy of 1-12 carbon atoms, aryloxy having not more than 12 carbon atoms, halogen or hydrogen, and x is a valence of the transition metal.

In the above-mentioned formula, M which is a transition metal includes zirconium, titanium, hafnium, chromium or vanadium by preference, and particularly preferred are zirconium and hafnium.

The ligands having a cycloalkadienyl skeleton include, for example, cyclopentadienyl, alkyl-substituted cyclopentadienyl such as methylcyclopentadienyl, ethylcyclopentadienyl, n-butylcyclopentadienyl, t-butylcyclopentadienyl, dimethylcyclopentadienyl and pentamethylcyclopentadienyl, and indenyl and fluorenyl.

Two or more ligands having a cycloalkadienyl skeleton as mentioned above may coordinate to the transition metal and, in this case, at least two ligands having a cycloalkadienyl skeleton may be linked together via alkylene, substituted alkylene, silylene or substituted silylene. The alkylene group includes methylene, ethylene, trimethylene and tetramethylene, the substituted alkylene includes isopropylidene, tetramethylethylene, and the substituted silylene includes dimethylsilylene, ethylmethylsilylene and diphenylsilylene.

The ligand other than those having a cycloalkadienyl skeleton is a hydrocarbon group of 1-12 carbon atoms, an alkoxy group of 1-12 carbon atoms, an aryloxy group having not more than 12 carbon atoms, halogen or hydrogen.

The hydrocarbon group having 1-12 carbon atoms mentioned above includes, for example, alkyl, cycloalkyl, aryl and aralkyl, and the alkyl group includes methyl, ethyl, propyl, isopropyl and butyl.

The cycloalkyl group mentioned above includes, for example, cyclopentyl and cyclohexyl, the aryl group includes, for example, phenyl and tolyl, and the aralkyl group includes, for example, benzyl and neophyl.

The alkoxy group mentioned above includes, for example, methoxy, ethoxy and butoxy, and the aryloxy group includes, for example, phenoxy.

The halogen mentioned above includes, for example, fluorine, chlorine, bromine and iodine.

Listed below are typical representatives of the transition metal compounds having a cycloalkadienyl skeleton, represented by the aforementioned formula ML_x in which M is zirconium.

Bis(cyclopentadienyl)zirconium monochloride monohydride,
Bis(cyclopentadienyl)zirconium monobromide monohydride,
Bis(cyclopentadienyl)methyl zirconium hydride,
Bis(cyclopentadienyl)ethyl zirconium hydride,
Bis(cyclopentadienyl)phenyl zirconium hydride,
Bis(cyclopentadienyl)benzyl zirconium hydride,
Bis(cyclopentadienyl)neopentyl zirconium hydride,
Bis(methylcyclopentadienyl)zirconium monochloride hydride,
Bis(indenyl)zirconium monochloride monohydride,
Bis(cyclopentadienyl)zirconium dichloride,
Bis(cyclopentadienyl)zirconium dibromide,
Bis(cyclopentadienyl)methyl zirconium monochloride,
Bis(cyclopentadienyl)ethyl zirconium monochloride,
Bis(cyclopentadienyl)cyclohexyl zirconium monochloride,
Bis(cyclopentadienyl)phenyl zirconium monochloride,
Bis(cyclopentadienyl)benzyl zirconium monochloride,
Bis(methylcyclopentadienyl)zirconium dichloride,
Bis(dimethylcyclopentadienyl)zirconium dichloride,
Bis(n-butylcyclopentadienyl)zirconium dichloride,
Bis(indenyl)zirconium dichloride,
Bis(indenyl)zirconium dibromide,
Bis(cyclopentadienyl)zirconium dimethyl,
Bis(cyclopentadienyl)zirconium diphenyl,
Bis(cyclopentadienyl)zirconium dibenzyl,
Bis(cyclopentadienyl)zirconium methoxychloride,
Bis(cyclopentadienyl)zirconium ethoxychloride,
Bis(methylcyclopentadienyl)zirconium ethoxychloride,
Bis(cyclopentadienyl)zirconium phenoxychloride,
Bis(fluorenyl)zirconium dichloride,
Ethylenebis(indenyl)dimethyl zirconium,
Ethylenebis(indenyl)diethyl zirconium,
Ethylenebis(indenyl)diphenyl zirconium,
Ethylenebis(indenyl)methyl zirconium monochloride,
Ethylenebis(indenyl)ethyl zirconium monochloride,
Ethylenebis(indenyl)methyl zirconium monobromide,
Ethylenebis(indenyl)zirconium dichloride,
Ethylenebis(indenyl)zirconium dibromide,
Ethylenebis(4,5,6,7-tetrahydro-1-indenyl)dimethyl zirconium,
Ethylenebis(4,5,6,7-tetrahydro-1-indenyl)methyl zirconium monochloride,
Ethylenebis(4,5,6,7-tetrahydro-1-indenyl)zirconium dichloride,

Ethylenebis(4,5,6,7-tetrahydro-1-indenyl)zirconium dibromide,
Ethylenebis(4-methyl-1-indenyl)zirconium dichloride,
Ethylenebis(5-methyl-1-indenyl)zirconium dichloride,
Ethylenebis(6-methyl-1-indenyl)zirconium dichloride,
Ethylenebis(7-methyl-1-indenyl)zirconium dichloride,
Ethylenebis(5-methoxy-1-indenyl)zirconium dichloride,
Ethylenebis(2,3-dimethyl-1-indenyl)zirconium dichloride,
Ethylenebis(4,7-dimethyl-1-indenyl)zirconium dichloride,
Ethylenebis(4,7-dimethoxy-1-indenyl)zirconium dichloride,
Isopropylidene(cyclopentadienyl-fluorenyl)zirconium dichloride,
Isopropylidenebis(indenyl)zirconium dichloride,
Dimethylsilylenenbis(cyclopentadienyl)zirconium dichloride,
Dimethylsilylenebis(methylcyclopentadienyl)zirconium dichloride,
Dimethylsilylenebis(indenyl)zirconium dichloride.

There may also be used transition metal compounds obtained by replacing the zirconium metal in the above-exemplified zirconium compounds with titanium metal, hafnium metal, or vanadium metal.

Next, the organoaluminum oxy-compound [B] is explained below. This organoaluminum oxy-compound [B] may be known aluminoxane or a benzene-insoluble organoaluminum oxy-compound first discovered by the present inventors.

The above-mentioned aluminoxane may be prepared, for example, by the following procedures.

(1) The procedure for recovering aluminoxanes as their solution in hydrocarbons which comprises reacting organoaluminum compounds such as trialkylaluminum with suspensions in hydrocarbon solvents of compounds having absorbed water or salts containing water of crystallization, for example, hydrates of magnesium chloride, copper sulfate, aluminum sulfate, nickel sulfate or cerous chloride.

(2) The procedure for recovering aluminoxanes as their solution in hydrocarbons which comprises allowing organoaluminum compounds such as trialkylaluminum to interact directly with water, ice or water vapor in solvents such as benzene, toluene, ethyl ether and tetrahydrofuran.

In this connection, the above-mentioned solution of aluminoxane may contain small amount of organometallic components. Furthermore, the solution of aluminoxane recovered by the above-mentioned procedures may be distilled to remove therefrom the solvent or unreacted organoaluminum compound, followed by dissolving again in solvents.

The organoaluminum compounds used for preparing such solutions of aluminoxane as mentioned above include, for example, trialkylaluminum such as trimethylaluminum, triethylaluminum, tripropylaluminum, triisopropylaluminum, tri-n-butylaluminum, triisobutylaluminum, tri-sec-butylaluminum, tri-tert-butylaluminum, tripentylaluminum, trihexylaluminum, trioctylaluminum, tridecylaluminum, tricyclohexylaluminum, tricyclooctylaluminum; dialkylaluminum halides such as dimethylaluminum chloride, diethylaluminum chloride, diethylaluminum bromide and diisobutylaluminum chloride; dialkylaluminum hydrides such as diethylaluminum hydride and diisobutylaluminum hydride; dialkylaluminum alkoxides such as dimethylaluminum methoxide and diethylaluminum ethoxide; and dialkylaluminum aryloxides such as diethylaluminum phenoxide.

Of the organoaluminum compounds as exemplified above, particularly preferred is trialkylaluminum.

Furthermore, there may also be used as the organoaluminum compound isoprenylaluminum represented by the general formula

$$(i\text{-}C_4H_9)_xAl_y(C_5H_{10})_z$$

wherein x, y and z are each a positive number, and $z \geq 2x$.

The organoaluminum compounds mentioned above may be used either singly or in combination.

Solvents used in the solutions of aluminoxane include aromatic hydrocarbons such as benzene, toluene, xylene, cumene and cymene; aliphatic hydrocarbons such as pentane, hexane, heptane, octane, decane, dodecane, hexadecane and octadecane; alicyclic hydrocarbons such as cyclopentane, cyclohexane, cyclooctane and methylcyclopentane; petroleum fractions such as gasoline, kerosene and gas oil. In addition thereto, there may also be used ethers such as ethyl ether and tetrahydrofuran. Of these solvents as exemplified above, particularly preferred are aromatic hydrocarbons.

The benzene-insoluble organoaluminum oxy-compounds used in the first process of the present invention contain Al component which dissolves in benzene at 60°C in an amount of less than 10%, preferably less than 5% and further desirably less than 2% in terms of Al atom, and they are insoluble or sparingly soluble in benzene.

Solubility in benzene of such organoaluminum oxy-compounds as mentioned above is obtained by suspending in 100 ml of benzene the organoaluminum oxy-compound in an amount corresponding to 100 mg atoms in terms of Al atom, mixing the resulting suspension at 60°C for 6 hours, filtering the resulting mixture with G-5

glass filter equipped with a jacket kept at 60 °C, and washing four times the solids portion separated on the filter with 50 ml of benzene at 60°C to measure the amount (x mmol) of Al atoms present in the whole filtrate.

When the benzene-insoluble organoaluminum oxy-compounds of the present invention are analyzed by infrared spectrophotometry (IR), a ratio (D_{1260}/D_{1220}) of an absorbance (D_{1260}) at around 1260 cm^{-1} to an absorbance (D_{1220}) at around 1220 cm^{-1} is preferably less than 0.09, more preferably less than 0.08 and particularly in the range of from 0.04 to 0.07.

Infrared spectrophotometric analysis of the organoaluminum oxy-compounds as referred to in the present specification is carried out in the following manner.

First, the organoaluminum oxy-compound is ground, together with nujol, in a nitrogen box to paste.

Next, the paste-like sample thus obtained is put between KBr plates, and IR spectrum is measured in a nitrogen atmosphere by means of IR-810 manufactured and sold by Nippon Bunko K.K.

IR spectrum of the organoaluminum oxy-compound according to the first process of the present invention as obtained is shown in Fig. 2.

From the thus obtained IR spectrum, a D_{1260}/D_{1220} ratio is sought, and a value of said ratio is obtained in the following manner.

(a) A line connecting a maximum point at around 1280 cm^{-1} and a maximum point at around 1240 cm^{-1} is taken as a base line L_1.

(b) A transmittance (T %) of an absorption minimum point at around 1260 cm^{-1} and an transmittance (T_0 %) of a point of intersection are read, said point of intersection being obtained by drawing a vertical line from said absorption minimum point to a wave number abscissa axis (abscissa) and crossing said vertical line with said base line L_1, whereby an absorbance ($D_{1260}=\log T_0/T$) is calculated.

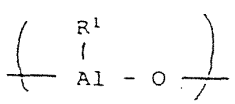
(c) Similarly, a line connecting maximum points at around 1280 cm^{-1} and at around 1180 cm^{-1} is taken as a base line L_2.

(d) A transmittance (T' %) of an absorption minimum point at around 1220 cm^{-1} and a transmittance (T'_0 %) of a point of intersection are read, said point of intersection being obtained by drawing a vertical line from said absorption minimum point to a wave number abscissa axis (abscissa) and crossing said vertical line with said base line L_2, whereby an absorbance ($D_{1220}=\log T'_0/T'$) is calculated.

(e) From these values as obtained, D_{1260}/D_{1220} is calculated.

IR spectrum of a known benzene-soluble organoaluminum oxy-compound is shown in Fig. 3. As can be seen from Fig. 3, the benzene-soluble aluminum oxy-compound has a value of D_{1260}/D_{1220} of being virtually 0.10-0.13, and thus the benzene-insoluble organoaluminum oxy-compound of the present invention is apparently different in the value of D_{1260}/D_{1220} from the known benzene-soluble organoaluminum oxy-compound.

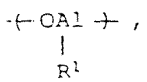
The benzene-insoluble organoaluminum oxy-compounds used in the present invention are presumed to have an alkyloxyaluminum unit represented by the formula



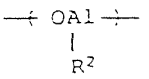
wherein R^1 is a hydrocarbon group of 1 to 12 carbon atoms.

In the above-mentioned alkyloxyaluminum unit, R^1 includes, for example, methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, pentyl, hexyl, octyl, decyl, cyclohexyl and cyclooctyl. Of these hydrocarbon groups exemplified above, preferred are methyl and ethyl, and particularly preferred is methyl.

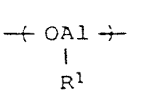
In addition to the alkyloxyaluminum unit of the formula



the benzene-insoluble organoaluminum oxy-compounds of the present invention may contain an oxyaluminum unit represented by the formula



wherein R^1 is as defined above, and R^2 is a hydrocarbon group of 1 to 12 carbon atoms, an alkoxyl group of 1 to 12 carbon atoms, an aryloxy group of 6 to 20 carbon atoms, a hydroxyl group, halogen or hydrogen, provided that R^1 and R^2 are different from each other. In that case, the organoaluminum oxy-compounds desirably contain the alkyloxyaluminum unit



in a proportion of at least 30 mol%, preferably at least 50 mol% and particularly at least 70 mol%.

The processes for preparing the benzene-insoluble organoaluminum oxy-compounds of the present invention are illustrated below in detail.

The benzene-insoluble organoaluminum oxy-compounds is obtained by bringing a solution of aluminoxane into contact with water or active hydrogen containing compounds.

The active hydrogen containing compounds include alcohols such as methanol, ethanol, n-propanol and isopropanol; diols such as ethylene glycol and hydroquinone; and organic acids such as acetic acid and propionic acid. Of these compounds, preferred are alcohols and diols, and especially preferred are alcohols.

Water or the active hydrogen containings compounds with which the solution of aluminoxane is brought into contact may be used as solutions or dispersions in hydrocarbon solvents such as benzene, toluene and hexane, ether solvents such as tetrahydrofuran or amine solvents such as triethylamine, or may be used in the form of vapor or solid. The water with which the solution of aluminoxane is brought into contact may be water of crystallization of salts such as magnesium chloride, magnesium sulfate, copper sulfate, nickel sulfate, iron sulfate and cerous chloride, or absorbed water absorbed to inorganic compounds such as silica, alumina and aluminum hydroxide or polymers.

Reaction of the solution of aluminoxane with water or the active hydrogen containing compounds is carried out usually in solvents, for example, hydrocarbon solvents. The solvents used in this case are aromatic hydrocarbons such as benzene, toluene, xylene, cumene and cymene; aliphatic hydrocarbons such as pentane, hexane, heptane, octane, decane, dodecane, hexadecane and octadecane; alicydic hydrocarbons such as cydopentane, cydohexane, cydooctane and methylcydohexane; petroleum fractions such as gasoline, kerosene and gas oil; halogenated hydrocarbons such as halides of the above-mentioned aromatic hydrocarbons, aliphatic hydrocarbons and alicydic hydrocarbons, particularly, chlorides and bromides; and ethers such as ethyl ether and tetrahydrofuran. Of these solvents as exemplified above, particularly preferred are aromatic hydrocarbons.

In the reaction as mentioned above, water or the active hydrogen containing compound is used in an amount of 0.1-5 moles, preferably 0.2-3 moles to 1 mole of Al atoms present in the solution of aluminoxane. A concentration in terms of aluminum atom in the reaction system is desirably 1×10^{-3} - 5 gram atom/l, preferably 1×10^{-2} - 3 gram atom/l, and a concentration of water in the reaction system is desirably 2×10^{-4} - 5 mol/l, preferably 2×10^{-3} - 3 mol/l.

The solution of aluminoxane may be brought into contact with water or the active hydrogen containing compound, for example, by the following procedures.

(1) The procedure which comprises bringing the solution of aluminoxane into contact with a hydrocarbon solvent containing water or the active hydrogen containing compound.

(2) The procedure which comprises blowing vapor of water or the active hydrogen containing compound into the solution of aluminoxane, thereby bringing the aluminoxane into contact with the vapor.

(3) The procedure which comprises bringing the solution of aluminoxane into contact directly with water, ice or the active hydrogen containing compound.

(4) The procedure which comprises mixing the solution of aluminoxane with a suspension of an absorbed water containing compound or a water of crystallization containing compound in hydrocarbon, or with a suspension of a compound, to which the active hydrogen containing compound has been absorbed, in hydrocarbon, thereby bringing the aluminoxane into contact with the absorbed water or water of crystallization.

The solution of aluminoxane may contain other components so long as they do not exert adverse effects

on the reaction of aluminoxane with water or the active hydrogen containing compound.

The above-mentioned reaction of the solution of aluminoxane with water or the active hydrogen containing compound is carried out usually at -50 to 150°C, preferably 0-120°C and more desirably at 20-100°C. The reaction time employed is usually 0.5-300 hours, preferably 1-150 hours, though said reaction time varies largely depending upon the reaction temperature used.

The benzene insoluble organoaluminum oxy-compound may also be prepared by direct contact of organoaluminum with water. In the reaction mentioned above, water is used in such amount that the organoaluminum atom dissolved in the reaction system is less than 20 %, based on total organoaluminum atom.

Water with which the organoaluminum compound is brought into contact may be used as solutions or dispersions in hydrocarbon solvents such as benzene, toluene and hexane, ether solvents such as tetrahydrofuran or amine solvents such as triethylamine, or may be used in the form of vapor or ice. The water with which the organoaluminum compound is brought into contact may be water of crystallization of salts such as magnesium chloride, magnesium sulfate, copper sulfate, nickel sulfate, iron sulfate and cerous chloride, or absorbed water absorbed to inorganic compounds such as silica, alumina and aluminum hydroxide or polymers.

Reaction of the organoaluminum compound with water is carried out usually in solvents, for example, hydrocarbon solvents. The solvents used in this case are aromatic hydrocarbons such as benzene, toluene, xylene, cumene and cymene; aliphatic hydrocarbons such as pentane, hexane, heptane, octane, decane, dodecane, hexadecane and octadecane; alicyclic hydrocarbons such as cyclopentane, cyclohexane, cyclooctane and methylcyclohexane; petroleum fractions such as gasoline, kerosene and gas oil; halogenated hydrocarbons such as halides of the above-mentioned aromatic hydrocarbons, aliphatic hydrocarbons and alicyclic hysrocarbons, particulary, chlorides and bromide; and ethers such as ethyl ether and tetrahydrofuran. Of these solvents as exemplified above, particularly preferred are aromatic hydrocarbons.

A concentration of organoaluminum compound in the reaction system in terms of aluminum atom is desirably 1×10^{-3} - 5 gram atom/l, preferably 1×10^{-2} - 3 gram atom/l, and a concentration of water in the reaction system is desirably 1×10^{-3} - 5 mol/l, preferably 1×10^{-2} - 3 mol/l.

In the reaction mentioned above, the organoaluminum atom dissloved in the reaction system is less than 20 %, preferably less than 10 %, more preferably 0 to 5 % based on total organoaluminum atom.

The organoaluminum compound may be brought into contact with water, for example, by the following procedures.

(1) The procedure which comprises bringing the hydrocarbon solution of organoaluminum into contact with a hydrocarbon solvent containing water.

(2) The procedure which comprises blowing vapor of water into the hydrocarbon solution of organoaluminum, thereby bringing the organoaluminum into contact with the vapor.

(3) The procedure which comprises mixing the hydrocarbon solution of organoaluminum with a suspension of an absorbed water containing compound or a water of crystallization containing compound in hydrocarbon, thereby bringing the organoaluminum into contact with the absorbed water or water of crystallization.

(4) The procedure which comprises bringing the hydrocarbon solution of organoaluminum into contact direcly with ice.

The hydrocarbon solution of organoaluminum may contain other components so long as they do not exert adverse effects on the reaction of organoaluminum with water.

The above-mentioned reaction of the organoaluminum with water is carried out usually at -100 to 150 °C, preferably -70 to 100 °C and more desirably at -50 to 80°C. The reaction time empolyed is usually 1 to 200 hours, preferably 2 to 100 hours, though the reaction time varies largely depending upon the reaction temperature used.

The first series of olefin polymerization catalysts according to the first method of the invention, if necessary, may contain an organoaluminum [C].

The organoaluminum compound [C] used herein includes such organoaluminum compounds, for example, as represented by the formula $R^a_nAlX_{3-n}$ wherein R^a is hydrocarbon of 1-12 carbon atoms, X is halogen or hydrogen, and n is 1-3.

In the above-mentioned formula, R^a is hydrocarbon of 1-12 carbon atoms, for example, alkyl, cycloalkyl or aryl, including concretely methyl, ethyl, n-propyl, isopropyl, isobutyl, pentyl, hexyl, octyl, cyclopentyl, cyclohexyl, phenyl, tolyl, etc.

The above-mentioned organoaluminum compounds will be exemplified below.

Trialkylaluminum such as trimethylaluminum, triethylaluminum, triisopropylaluminum, triisobutylaluminum, trioctylaluminum, tri-2-ethylhexylaluminum, etc.

Alkenylaluminum such as isoprenylaluminum, etc.

Dialkylaluminum halides such as dimethylaluminum chloride, diethylaluminum chloride, diisopropylaluminum chloride, diisobutylaluminum chloride, dimethylaluminum bromide, etc.

Alkylaluminum sesquihalides such as methylaluminum sesquichloride, ethylaluminum sesquichloride, butylaluminum sesquichloride, ethylaluminum sesquibromide, etc.

Alkylaluminum dihalides such as methylaluminum dichloride, ethylaluminum dichloride, isopropylaluminum dichloride, ethylaluminum dibromide, etc.

Alkylaluminum hydrides such as diethylaluminum hydride, di-isobutylaluminum hydride, etc.

Furthermore, there may also be used other organoaluminum compounds represented by the formula $R^6_nAlY_{3-n}$ wherein R^6 is as defined previously, Y is $-OR^7$, $-OSiR^8_3$, $-OAlR^9_2$, $-NR^{10}_2$, $-SiR^{11}_3$ or

$$-NAlR^{13}_2, \quad \begin{array}{l} | \\ R^{12} \end{array}$$

n is 1-2, R^7, R^8, R^9 and R^{13} are each methyl, ethyl, isopropyl, isobutyl, cyclohexyl or phenyl, R^{10} is hydrogen, methyl, ethyl, isopropyl, phenyl or trimethylsilyl, R^{11} and R^{12} are each methyl or ethyl.

The organoaluminum compounds as mentioned above include, in concrete, such compounds as enumerated below.

(i) Compounds of the formula $R^6_nAl(OR^7)_{3-n}$ such as dimethylaluminum methoxide, diethylaluminum ethoxide, diisobutylaluminum methoxide, etc.

(ii) Compounds of the formula $R^6_nAl(OSiR^8_3)_{3-n}$ such as $Et_2Al(OSiMe_3)$, $(iso\text{-}Bu)_2Al(OSiMe_3)$, $(iso\text{-}Bu)_2Al(OSiEt_3)$, etc.

(iii) Compounds of the formula $R^6_nAl(OAlR^9_2)_{3-n}$ such as $Et_2AlOAlEt_2$, $(iso\text{-}Bu)_2AlOAl(iso\text{-}Bu)_2$, etc.

(iv) Compounds of the formula $R^6_nAl(NR^{10}_2)_{3-n}$ such as Me_2AlNEt_2, $Et_2AlNHMe$, $Me_2AlNHEt$, $Et_2AlN(Me_3Si)_2$, $(iso\text{-}Bu)_2AlN(Me_3Si)_2$, etc.

(v) Compounds of the formula $R^6_nAl(SiR^{11}_3)_{3-n}$ such as $(iso\text{-}Bu)_2AlSiMe_3$, etc.

(vi) Compounds of the formula $R^6_nAl(NAlR^{13}_2)_{3-n}$ (with R^{12} on the NAl) such as

$Et_2AlNAlEt_2$ (Me), $(iso\text{-}Bu)_2AlNAl(iso\text{-}Bu)_2$ (Et), etc.

Of the organoaluminum compounds as exemplified above, preferred are those of the formula R^6_3Al, $R^6_nAl(OR^7)_{3-n}$ and $R^6Al(OAlR^9_2)_{3-n}$, particularly those in which R^6 is isoalkyl and n=2 are desirable. These organoaluminum compounds may be used in combination of two or more.

In this connection, the olefin polymerization catalysts as mentioned above may also be used after supporting them on a solid inorganic compound such as silica, alumina, magnesium oxide or magnesium chloride, or on a solid organic compound such as polyethylene, polypropylene or polystyrene.

In the first method of the present invention, ethylene polymers are prepared by a process divided into two stages, that is, the polymerization steps (a) and (b) as mentioned previously.

In the polymerization step (a), ethylene is homopolymerized or ethylene and other α-olefin are copolymerized to form an ethylene polymer [I] having a density of higher than 0.88 g/cm³, preferably 0.89-0.94 g/cm³ and an intrinsic viscosity [η] of 0.3-3 dl/g, preferably 0.5-2 dl/g.

In this ethylene polymer [I], it is desirable that the relationship between an amount (W) of the portion soluble at 23°C in n-decane and a density satisfies the following equation.

$\log W \leq -50 \times D + 46.4$, preferably

$\log W \leq -50 \times D + 46.3$ and especially

$\log W \leq -50 \times D + 46.2$.

In the polymerization step (b), ethylene and other α-olefin are copolymerized to form an ethylene copolymer [II]. Desirably, the density of the ethylene copolymer [II] is not higher than that of the ethylene polymer [I] obtained in the above-mentioned polymerization step (a), and is preferably lower by 0.005 g/cm³ than that of the ethylene polymer [I], and the intrinsic viscosity [η] of the ethylene copolymer [II] is at least 1.5 times, preferably 2-10 times that of the ethylene polymer [I], and is concretely 1-10 dl/g, preferably 1.5-7 dl/g.

Further, it is desirable that the relationship between a density D of the ethylene polymer [I], ethylene copolymer [II] or the whole polymer and a temperature T (°C) showing the highest peak in an endothermic curve

to be measured by a differential scanning calorimeter statisfies the following expression.

$T < 450 \times D - 297$, preferably

$T < 500 \times D - 344$ and especially

$T < 550 \times D - 391$.

The above-mentioned two polymerization steps (a) and (b) may be carried out in any order. That is, the ethylene copolymer [II] may be formed by carrying out the polymerization step (b) in the presence of the ethylene polymer [I] resulting from the polymerization step (a) first carried out, or the ethylene polymer [I] may be formed by carrying out the polymerization step (a) in the presence of the ethylene copolymer [II] resulting from the polymerization step (b) first carried out. In either case, these two steps must be carried out successively. In other words, the polymerization to be carried out in the latter stage must be carried out in the presence of the polymer formed by the polymerization carried out in the former stage. In this case, it is preferable in the latter polymerization step to use in succession the catalyst used in the former polymerization step without addition of a fresh catalyst, because there are obtained polymers in whith the development of fish-eye has been minimized.

In practicing the polymerization steps (a) and (b), it is desirable to form the ethylene copolymer [II] in the polymerization step (B) so as to amount to 10-1000 parts by weight, preferably 20-500 parts by weight when the amount of the ethylene polymer [I] obtained in the polymerization step (a) is taken as 100 parts by weight.

Further, the intrinsic viscosity [η] of the whole polymer (including the ethylene polymer [I] and ethylene copolymer [II]) is 1-6 dl/g, preferably 1.2-4 dl/g, and the density thereof is 0.86-0.94 g/cm^3, preferably 0.87-0.93 g/cm^3 and especially 0.88-0.92 g/cm^3. Furthermore, the (MFR_{10}/MFR_2) ratio of MFR_{10} as measured at 190°C under a load of 10 kg to MFR_2 as measured at 190°C under a load of 2.16 kg is more than 7, preferably from 8 to 40.

The density D of the ethylene polymer [I] or ethylene copolymer [II] as referred to in the present invention was determined by means of a density gradient tube using the strand obtained at the time of MFR measurement under a load of 2.16 kg which has been heated at 120°C for 1 hour, followed by gradual cooling up to room temperature over a period of 1 hour.

The intrinsic viscosity [η] of the above-mentioned polymer was measured at 135°C in decalin. Further, the amount of n-decane-soluble portion of the above-mentioned polymer was determined in the following manner.

About 3 g of the copolymer as weighed is dissolved at 145°C in 450 ml of n-decane, followed by gradual cooling up to 23°C. The solution is then filtered to remove a portion of the copolymer insoluble in n-decane therefrom, and the n-decane is distilled off from the filtrate, thereby obtaining an amount (percent by weight based on the whole copolymer) of an n-decane soluble portion of the copolymer.

The density (D_2), intrinsic viscosity $[\eta]_2$ and amount (W_2) of the polymer obtained in the second stage polymerization step were calculated according to the following equations, respectively.

$$[\eta]_2 = \frac{[\eta]_W - f_1\ [\eta]_1}{f_2}$$

wherein $[\eta]_W$, $[\eta]_1$ and $[\eta]_2$ represent an intrinsic viscosity of the whole polymer, that of the polymer obtained in the first step and that of the polymer obtained in the second step, respectively, and f_1 and f_2 represent the amount of polymerization in the first step and that of the polymerization in the second step, respectively, and $f_1 + f_2$ is 1.

$$D2 = \frac{f_2 D_W D_1}{D_1 - f_1 D_W}$$

wherein D_W, D_1 and D_2 represent a density of the whole polymer, that of the polymer obtained in the first stage, and that of the polymer obtained in the second stage, respectively.

$$W_2 = \frac{W_W - f_1 W_1}{f_2}$$

wherein W_W, W_1 and W_2 represent the amount of n-decane soluble portion of the whole polymer, that of the polymer obtained in the first stage, and that of the polymer obtained in the second stage, respectively.

In the present invention, moreover, pre-polymerization of olefin may also be carried out prior to the polymerization steps (a) and (b) as mentioned above. This pre-polymerization can be carried out under mild conditions using a suspension of olefin and the above-mentioned catalyst component [I] in an inert hydrocarbon medium.

The inert hydrocarbon medium used in this case may include, for example, aliphatic hydrocarbons such as propane, butane, pentane, hexane, heptane, octane, decane, dodecane, kerosine, etc.; alicyclic hydrocar-

bons such as cyclopentane, cyclohexane, methyl cyclopentane, etc.; aromatic hydrocarbons such as benzene, toluene, xylene, etc.; halogenated hydrocarbons such as ethylene chloride, chlorobenzene, etc.; or mixtures thereof. Of these inert hydrocarbon media as illustrated above, particularly preferred are aliphatic hydrocarbons. The pre-polymerization may be carried out by using the olefin as a medium or may also be carried out in a state substantially free from a medium.

Olefins used in the pre-polymerization may be the same as or different from those used in the main polymerization as will be mentioned later. Concretely, the olefin preferably used in the pre-polymerization is ethylene.

The reaction temperature employed in carrying out the pre-polymerization is usually from about -20° to +100°C, preferably from about -20° to +40°C.

In the pre-polymerization, a molecular weight modifier such as hydrogen may also be used. The molecular weight modifier is desirably used in such an amount that an intrinsic viscosity [η], as measured in decalin at 135°C, of the polymer obtained by the pre-polymerization becomes more than about 0.2 dl/g, preferably from about 0.5 to 10 dl/g.

The pre-polymerization is desirably carried out in such a manner that the polymer is formed in an amount, based on 1 g of the above-mentioned solid catalyst, of about 0.1-500 g, preferably about 0.3-300 g and especially 1-100 g. If the pre-polymerization amount is made excessively large, the production efficiency of the olefin polymer in the main polymerization sometimes decreases.

Usable as α-olefins other than ethylene in the first process of the present invention are those having 3-20 carbon atoms, for example, propylene, 1-butene, 1-pentene, 1-hexene, 4-methyl-1-pentene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene, 1-eicosene, cyclopentene, cycloheptene, norbornene, 5-methyl-2-norbornene, tetracyclododecene, 2-methyl-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene, etc.

In addition to such α-olefins as exemplified above, there may also be used styrene, vinylcyclohexane, diene, etc.

In the first process of the present invention, the polymerization may be carried out by any of polymerization techniques, for example, liquid phase polymerization such as solution or suspension polymerization or gas phase polymerization.

The reaction temperature of olefin using the olefin polymerization catalyst [I] is usually from -50° to 200°C, preferably from 0° to 150°C. The polymerization pressure is usually from ordinary pressure to 100 kg/cm², preferably from ordinary pressure to 50 kg/cm², and the polymerization reaction may be carried out by any of the batchwise, semicontinuous and continuous methods. The molecular weight of the olefin polymer obtained may be modified by the presence in the polymerization system of hydrogen or by changing the polymerization temperature employed.

In polymerizing olefin with the above-mentioned olefin polymerization catalyst [I], it is desirable to use the transition metal compound [A] containing a ligand having a cycloalkadienyl skeleton in an amount of usually 10^{-6} - 1 mmol, preferably 10^{-4} - 0.1 mmol, the organoaluminum oxy-compound [B] in an amount of usually 0.01-10 mmol, preferably 0.02-5 mmol, and the organoaluminum compound [C] in an amount of usually 0-10 mmol, preferably 0.1-5 mmol, each based on 1 liter of the reaction volume.

In the first process of the present invention, the olefin polymerization catalyst [I] may contains other components useful for olefin polymerization in addition to the above-mentioned components.

Next, the second method for the preparation of ethylene polymer compositions according to the present invention is illustrated below in detail.

Fig. 4 (a) and Fig. 4 (b) are each a rough schematic drawing illustrating the second process for the preparation of ethylene polymer compositions of the invention.

The second method for the preparation of ethylene polymer compositions of the invention comprises a polymerization step (c) and a polymerization step (d).

In the polymerization step (c), the olefin polymerization catalyst [II] composed of the transition metal compound [A] containing a ligand having a cycloalkadienyl skeleton and the organoaluminum oxy-compound [B] is used.

In the polymerization step (c), ethylene and other α-olefin are copolymerized with the olefin polymerization catalyst [II] to form an ethylene copolymer [III] having a density of not more than 0.91 g/cm³, preferably 0.86-0.905 g/cm³ more preferably 0.87-0.90 g/cm³ and an intrinsic viscosity [η] of 0.5-6 dl/g, preferably 0.7-4 dl/g.

In the polymerization step (c), the other α-olefin used may include those as used in the first method of the present invention.

This polymerization step (c) may be carried out by any of polymerization techniques, for example, liquid phase polymerization such as solution polymerization and suspension polymerization, and gas phase polymerization.

The polymerization of olefin with the olefin polymerization catalyst [II] may be carried out in the same man-

ner as in the first method of the present invention as mentioned previously.

In the polymerization step (d), the olefin polymerization catalyst [III] composed of the titanium catalyst component [C] containing titanium, magnesium and halogen as its essential ingredients, the organoaluminum compound [D] and/or the organoaluminum oxy-compound [E] is used.

The titanium catalyst component [C] containing titanium, magnesium and halogen as its essential ingredients contains further an electron donor, if necessary.

Titanium compound useful for the preparation of the solid titanium catalyst component [C] includes tetravalent titanium compounds usually represented by the formula $Ti(OR)_gX_{4-g}$ (wherein R is a hydrocarbon group, X is halogen, and $0 \leq g \leq 4$). More particularly, these titanium compounds include titanium tetrahalides such as $TiCl_4$, $TiBr_4$, and TiI_4;

alkoxytitanium trihalides such as $Ti(OCH_3)Cl_3$, $Ti(OC_2H_5)Cl_3$, $Ti(O\ n\text{-}C_4H_9)Cl_3$, $Ti(O\ iso\text{-}C_4H_9)Cl_3$, $Ti(OC_2H_5)Br_3$, and $Ti(O\ iso\text{-}C_4H_9)Br_3$;

alkoxytitanium dihalides such as $Ti(OCH_3)_2Cl_2$, $Ti(OC_2H_5)_2Cl_2$, $Ti(O\ n\text{-}C_4H_9)_2Cl_2$, and $Ti(OC_2H_5)_2Br_2$;

trialkoxytitanium monohalides such as $Ti(OCH_3)_3Cl$, $Ti(OC_2H_5)_3Cl$, $Ti(O\ n\text{-}C_4H_9)_3Cl$ and $Ti(OC_2H_5)_3Br$; and

tetraalkoxytitanium such as $Ti(OCH_3)_4$, $Ti(OC_2H_5)_4$, $Ti(O\ n\text{-}C_4H_9)_4$, $Ti(O\ iso\text{-}C_4H_9)_4$ and Ti(O 2-ethylhexyl)$_4$.

These titanium compounds may be used either singly or in admixture of two or more, and also they may be diluted, before use, with hydrocarbon compounds or halogenated hydrocarbon compounds.

Magnesium compounds useful for the preparation of the solid titanium catalyst component [C] used in the second process of the invention include those having reducing ability and those having no reducing ability.

The magnesium compounds having reducing ability as referred to herein include, for example, those having a magnesium-carbon bond or magnesium-hydrogen bond. Concrete examples of such magnesium compounds as having reducing ability include dimethylmagnesium, diethylmagnesium, dipropylmagnesium, dibutylmagnesium, diamylmagnesium, dihexylmagnesium, didecylmagnesium, ethylmagnesium chloride, propylmagnesium chloride, butylmagnesium chloride, hexylmagnesium chloride, amylmagnesium chloride, butyl ethoxy magnesium, ethyl butyl magnesium, octyl butyl magnesium, butylmagnesium halide, etc. The magnesium compounds exemplified above may be used singly, or may form complex compounds with organoaluminum compounds as will be mentioned later, and they also may be either liquid or solid.

Concrete examples of magnesium compounds having no reducing ability include halogenated magnesium such as magnesium chloride, magnesium bromide, magnesium iodide or magnesium fluoride; alkoxy magnesium halide such as methoxy magnesium chloride, ethoxy magnesium chloride, isopropoxy magnesium chloride, butoxy magnesium chloride or octoxy magnesium chloride; aryloxy magnesium halide such as phenoxy magnesium chloride, methylphenoxy magnesium chloride or dimethylphenoxy magnesium; alkoxy magnesium such as ethoxy magnesium, isopropoxy magnesium, butoxy magnesium, n-octoxy magnesium or 2-ethylhexoxy magnesium; and magnesium carboxylate such as magnesium laurate or magnesium stearate.

The magnesium compounds having no reducing ability exemplified above may be compounds derived from the above-mentioned magnesium compounds having reducing ability or compound derived at the time of preparation of catalyst component. The magnesium compound having no reducing ability may be derived from the magnesium compounds having reducing ability, for example, by bringing said magnesium compounds having reducing ability into contact with polysiloxane compounds, halogen containing silane compounds, halogen containing aluminum compounds or compounds such as esters, alcohols, etc.

The magnesium compounds used in the second process of the invention may also be complex or composite compounds of the above-mentioned magnesium compounds with other metals, or mixtures thereof. Further, the magnesium compounds used herein may also be mixtures of two or more of these compounds mentioned above.

Of these magnesium compounds exemplified above, preferred are those having no reducing ability, particularly halogen containing magnesium compounds. Of the halogen containing magnesium compounds, preferred are magnesium chloride, alkoxy magnesium halide and aryloxy magnesium halide.

In preparing the solid titanium catalyst component [C], it is preferable to use an electron donor. Useful electron donors include alcohols, amines, amides, ethers, ketones, esters, nitriles, phosphines, stibines, arsines, phosphoramides, thioethers, thioesters, acid anhydrides, acid halides, aldehydes, alcoholates, alkoxy(aryloxy)silanes and organic acids. Of these electron donors exemplified above, preferred are alcohols, amines, ethers, esters, acid anhydrides, alkoxy(aryloxy)silanes and organic acids.

The solid titanium catalyst component [C] may be prepared by bringing the above-mentioned magnesium compound (or metallic magnesium), titanium compound and, if necessary, electron donor into contact with one another. In preparing the solid titanium catalyst components, there may be employed the known method for the preparation of highly active titanium catalyst components from magnesium compounds, titanium com-

pounds and, if necessary, electron donors. The above-mentioned components may be brought into contact with one another in the presence of other reaction reagents, for example, silicon, phosphorus and aluminum.

Briefly illustrated below are several examples of the process for the preparation of these solid titanium catalyst components.

In the following processes for the preparation of the solid titanium catalyst component [C] as will be illustrated below, the electron donor is used, but the use of the electron donor is not always necessary.

(1) A process wherein a magnesium compound or a complex compound comprising the magnesium compound and electron donor is allowed to react with the titanium compound in the liquid phase. In carrying out this reaction, each reactant may be pretreated with a reaction assistant such as the electron donor and/or an organoaluminum compound or a halogen containing silicon compound. In this process, the above-mentioned electron donor is used at least one time.

(2) A process wherein a liquid magnesium compound having no reducing ability is allowed to react with a liquid titanium compound in the presence of an electron donor, thereby separating out a solid magnesium titanium composite.

(3) A process wherein the reaction product obtained in the process (2) is allowed to react further with a titanium compound.

(4) A process wherein the reaction product obtained in the process (1) or (2) is allowed to react further with an electron donor and a titanium compound.

(5) A process wherein a solid product obtained by pulverizing a magnesium compound or a complex compound comprising a magnesium compound and an electron donor in the presence of a titanium compound is treated with any of halogen, a halogen compound and an aromatic hydrocarbon. In carrying out this process, the magnesium compound or the complex compound comprising the magnesium compound and the electron donor may be pulverized in the presence of a pulverized assistant. Further, after pulverizing the magnesium compound or the complex compound comprising the magnesium compound and the electron donor in the presence of the titanium compound, the solid product obtained thereby is pretreated with a reaction assistant, followed by treatment with halogen or the like. The reaction assistant used herein includes an organoaluminum compound or a halogen containing silicon compound. In this process, the electron donor is used at least one time.

(6) A process wherein the compound obtained in the processes (1)-(4) is treated with halogen, a halogen compound or an aromatic hydrocarbon.

(7) A process wherein a contact reaction product of a metallic oxide with dihydrocarbyl magnesium and a halogen containing alcohol is brought into contact with an electron donor and a titanium compound.

(8) A process wherein a magnesium compound such as magnesium salt of an organic acid, alkoxy magnesium or aryloxy magnesium is allowed to react with an electron donor, a titanium compound and/or a halogen containing hydrocarbon.

(9) A process wherein a catalyst component contained in a hydrocarbon solution at least comprising a magnesium compound, alkoxy titanium and/or an electron donor such as alcohol or ether are allowed to react with a titanium compound and/or a halogen containing compound such as a halogen containing silicon compound.

(10) A process wherein a liquid magnesium compound having no reducing ability is allowed to react with an organoaluminum compound to separate a solid magnesium aluminum composite, followed by reaction with a titanium compound.

Of the above-mentioned processes (1) to (10) for the preparation of the titanium catalyst component [C], preferred are the processes (1) to (4) and (10).

Further, there may be used a solution containing the mixture of a liquid magnesium compound having no reducing ability and a titanium compound.

The amount of each of the above-mentioned components used in the preparation of the solid titanium catalyst component [C] cannot be indiscriminately defined, because it varies according to the process employed. For example, however, there may be used, based on 1 mole of the magnesium compound, the electron donor in an amount of about 0.01-20 moles, preferably 0.05-10 moles, and the titanium compound in an amount of about 0.01-500 moles, preferably 0.05-300 moles.

The solid titanium catalyst component thus obtained contains magnesium, titanium, halogen and, if necessary, an electron donor, as its essential ingredients.

In the solid titanium catalyst component [C], Halogen/Ti (atomic ratio) is about 4-200, preferably about 5-100, the above-mentioned electron donor/Ti (molar ratio) is about 0.1-50, preferably about 0.2-25, and Mg/Ti (atomic ratio) is about 1-100, preferably about 2-50.

In comparison with commercially available halogenated magnesium, the solid titanium catalyst component [C], contains halogenated magnesium having small crystal size whose specific surface area is usually larger

than about 10 m²/g, preferably about 30-1000 m²/g and especially about 50-800 m²/g. This solid titanium catalyst component [C] does not substantially change in composition when it is washed with hexane, because the above-mentioned components used in the titanium catalyst component [C] are integrated into an integrated catalyst component.

The processes for the preparation of such highly active titanium catalyst components [C] as mentioned above are disclosed, for example, in Japanese Patent L-O-P Publns. Nos. 108385/1975, 126590/1975, 20297/1976, 28189/1976, 64586/1976, 2885/1976, 136625/1976, 87489/1977, 100596/1977, 147688/1977, 104593/1977, 2580/1978, 40093/1978, 40094/1978, 43094/1978, 135102/1980, 135103/1980, 152710/1980, 811/1981, 11908/1981, 18606/1981, 83006/1983, 138705/1983, 138706/1983, 138707/1983, 138708/1983, 138709/1983, 138710/1983, 138715/1983, 23404/1985, 195108/1985, 21109/1986, 37802/1986 and 37803/1986.

The titanium catalyst component [C] is desirably to have a polymerization activity for ethylene of 200g-polymer/mmol-Tixhxatm and preferably 500g-polymer/mmol-Tixhxatm.

The organoaluminum compound [D] used herein includes such organoaluminum compounds, for example, as represented by the formula $R^6_nAlX_{3-n}$ wherein R^6 is hydrocarbon of 1-12 carbon atoms, X is halogen or hydrogen, and n is 1-3.

In the above-mentioned formula, R^6 is hydrocarbon of 1-12 carbon atoms, for example, alkyl, cycloalkyl or aryl, including concretely methyl, ethyl, n-propyl, isopropyl, isobutyl, pentyl, hexyl, octyl, decyl, cyclopentyl, cyclohexyl, phenyl, tolyl, etc.

The above-mentioned organoaluminum compounds will be exemplified below.

Trialkylaluminum such as trimethylaluminum, triethylaluminum, triisopropylaluminum, triisobutylaluminum, trihexylaluminum, trioctylaluminum, tri-2-ethylhexylaluminum, etc.

Alkenylaluminum such as isoprenylaluminum, etc

Dialkylaluminum halides such as dimethylaluminum chloride, diethylaluminum chloride, diisopropylaluminum chloride, diisobutylaluminum chloride, dimethylaluminum bromide, etc.

Alkylaluminum sesquihalides such as methylaluminum sesquichloride, ethylaluminum sesquichloride, isopropylaluminum sesquichloride, butylaluminum sesquichloride, ethylaluminum sesquibromide, etc.

Alkylaluminum dihalides such as methylaluminum dichloride, ethylaluminum dichloride, isopropylaluminum dichloride, ethylaluminum dibromide, etc.

Alkylaluminum hydrides such as diethylaluminum hydride, di-isobutylaluminum hydride, etc.

Furthermore, there may also be used other organoaluminum compounds represented by the formula $R^6_nAlY_{3-n}$ wherein R^6 is as defined previously, Y is $-OR^7$, $-OSiR^8_3$, $-OAlR^9_2$, $-NR^{10}_2$, $-SiR^{11}_3$ or

$$-N(R^{12})AlR^{13}_2,$$

n is 1-2, R^7, R^8, R^9 and R^{13} are each methyl, ethyl, isopropyl, isobutyl, cyclohexyl or phenyl, R^{10} is hydrogen, methyl, ethyl, isopropyl, phenyl or trimethylsilyl, R^{11} and R^{12} are each methyl or ethyl.

The organoaluminum compounds as mentioned above include, in concrete, such compounds as enumerated below.

(i) Compounds of the formula $R^6_nAl(OR^7)_{3-n}$ such as dimethylaluminum methoxide, diethylaluminum ethoxide, diisobutylaluminum methoxide, etc.

(ii) Compounds of the formula $R^6_nAl(OSiR^8_3)_{3-n}$ such as $Et_2Al(OSiMe_3)$, $(iso\text{-}Bu)_2Al(OSiMe_3)$, $(iso\text{-}Bu)_2Al(OSiEt_3)$, etc.

(iii) Compounds of the formula $R^6_nAl(OAlR^9_2)_{3-n}$ such as $Et_2AlOAlEt_2$, $(iso\text{-}Bu)_2AlOAl(iso\text{-}Bu)_2$, etc.

(iv) Compounds of the formula $R^6_nAl(NR^{10}_2)_{3-n}$ such as Me_2AlNEt_2, $Et_2AlNHMe$, $Me_2AlNHEt$, $Et_2AlN(Me_3Si)_2$, $(iso\text{-}Bu)_2AlN(Me_3Si)_2$, etc.

(v) Compounds of the formula $R^6_nAl(SiR^{11}_3)_{3-n}$ such as $(iso\text{-}Bu)_2AlSiMe_3$, etc.

(vi) Compounds of the formula $R^6_nAl(N(R^{12})AlR^{13}_2)_{3-n}$ such as

$Et_2AlNAlEt_2$, $(iso\text{-}Bu)_2AlNAl(iso\text{-}Bu)_2$, etc.
| |
Me Et

Of the organoaluminum compounds as exemplified above, preferred are those of the formula R^6_3Al, $R^6_nAl(OR^7)_{3-n}$ and $R^6Al(OAlR^6_2)_{3-n}$, particularly those in which R^6 is isoalkyl and n=2 are desirable. These organoaluminum compounds may be used in combination of two or more.

The organoaluminum oxy-compound [E] used in the polymerization step (d) is the same as the organoaluminum oxy-compound [B] used in the polymerization step (c).

The polymerization step (d) may also be carried out by using the olefin polymerization catalyst [III] containing the electron donor as mentioned above in addition to the above-mentioned titanium catalyst component [C], organoaluminum compound [D] and/or organoaluminum oxy-compound [E].

In the polymerization step (d), using the above-mentioned olefin polymerization catalyst [III], ethylene is homopolymerized or ethylene and other α-olefin are copolymerized to form an ethylene polymer [IV] having a density higher than that of the above-mentioned ethylene copolymer [III] formed in the polymerization step (c), preferably a density of 0.90-0.94 g/cm³ and especially 0.91-0.93 g/cm³, and an intrinsic viscosity [η] of 0.5-6 dl/g, preferably 0.7-4 dl/g. In the ethylene polymer [IV] thus formed, the amount of the portion soluble in n-decane at 23°C is desirably 0.1-10%.

Usable as α-olefins other than ethylene in the polymerization step (d) are those as exemplified in the case of the polymerization step (c).

The polymerization step (d) may be carried out by any of polymerization techniques, for example, liquid phase polymerization such as solution or suspension polymerization, or gas phase polymerization. Of these polymerization techniques, particularly preferred is solution polymerization.

The polymerization temperature of olefin using the above-mentioned olefin polymerization catalyst [III] is usually from 0°C to 250°C, preferably from 50°C to 200°C. The polymerization pressure is usually from ordinary pressure to 100 kg/cm², preferably from ordinary pressure to 50 kg/cm², and the polymerization reaction may be carried out by any of the batchwise, semi-continuous and continuous methods. The molecular weight of the olefin polymer obtained may be modified by the presence of hydrogen atoms or changing in the polymerization temperature employed.

In polymerizing olefin with the above-mentioned olefin polymerization catalyst [III], it is desirable to use the titanium catalyst component [C] in an amount, based on 1 liter of the polymerization volume, of usually about 10^{-4} - 0.5 mmol, preferably about 10^{-3} - 0.1 mmol in terms of Ti atom, the organoaluminum compound [D] in such an amount that aluminum atom becomes usually 1-2000 moles, preferably 5-500 moles based on 1 mole of titanium atom, and the organoaluminum oxy-compound [E] in such an amount that aluminum atom becomes usually 4-2000 moles, preferably 10-500 moles based on 1 mole of titanium atom.

The above-mentioned two polymerization step (c) and (d) may be carried out in any order. That is, the ethylene polymer [IV] may be formed by carrying out the polymerization step (d) in the presence of the ethylene copolymer [III] resulting from the polymerization step (c) first carried out, or the ethylene copolymer [III] may be formed by carrying out the polymerization step (c) in the presence of the ethylene copolymer [IV] resulting from the polymerization step (d) first carried out. In either case, these two steps must be carried out successively. In other words, the polymerization to be carried out in the latter stage must be carried out in the presence of the polymer formed by the polymerization carried out in the former stage. In the present invention, it is preferable to carry out first the polymerization step (c), followed by the polymerization step (d).

In practicing the polymerization step (c) and (d), it is desirable to form the ethylene polymer [IV] in the polymerization step (d) so as to amount to 10-1000 parts by weight, preferably 20-500 parts by weight when the amount of the ethylene copolymer [III] obtained in the polymerization step (c) is taken as 100 parts by weight.

Further, the intrinsic viscosity [η] of the whole polymer (including the ethylene polymer [III] and ethylene copolymer [IV]) is 0.5-6 dl/g, preferably 0.7-4 dl/g, and the density of the whole polymer is 0.87-0.94 g/cm³, preferably 0.88-0.93 g/cm³ and especially 0.89-0.92 g/cm³.

In the whole polymer as mentioned above, it is desirable that parts of the melt temperature curve as measured by means of DSC are observed at a level of 110°C or higher, preferably 115-125°C, and the relationship between the amount of portion soluble in n-decane at 23°C (Ww) and the density (Dw) satisfies $\log Ww \leq -50 \times Dw + 45.9$, preferably $\log Ww \leq -50 \times Dw + 45.8$ and especially $\log Ww \leq -50 \times Dw + 45.7$.

The density D, of the ethylene polymer [III] or ethylene copolymer [IV] obtained in the polymerization step (c) of the first stage as referred to in the present specification was determined by means of a density gradient tube using a strand obtained at the time of MFR measurement under a load of 2.16 kg, the strand having been heat treated at 120°C for 1 hour, followed by gradual cooling to room temperature over a period of 1 hour.

The intrinsic viscosity [η] and the amount of portion soluble in n-decane of the above-mentioned polymer were measured in accordance with the method illustrated already in the case of the first process of the present invention.

The copolymers are excellent in anti-block properties when they are found to have a smaller amount of portion soluble in n-decane.

The density (D_2), intrinsic viscosity $[\eta]_2$ and amount (W_2) of portion soluble in n-decane of the polymer obtained in the polymerization step (d) of the second stage as referred to in the present specification were also measured in the same manner as illustrated already in the case of the first process of the present invention.

A melting point of the copolymer as determined by means of DSC was used as a measure of heat resistance of said copolymer.

In the second method of the present invention, the olefin polymerization catalyst [II] or [III] used may contain also other components useful for olefin polymerization in addition to the above-mentioned components. The same pre-polymerization as mentioned previously may also be carried out in the second method of the present invention prior to the above-mentioned polymerization steps (c) and (d).

The present invention is illustrated below with reference to examples, but it should be construed that the invention is in no way limited to those examples.

Example 1

(Preparation of organoaluminum oxy-compound [B])

A 400 ml glass flask thoroughly purged with nitrogen was charged with 37.1 g of $Al_2(SO_4)_3.14H_2O$ and 133 ml of toluene, cooled to -5°C, and 47.9 ml of trimethylaluminum diluted with 152 ml of toluene was added dropwise over a period of 1 hour, followed by reaction at a temperature of from 0° to -5°C for 1 hour. The temperature of the flask was then elevated to 40°C over a period of 3 hours, and the reaction was continued at that temperature for 72 hours. After completion of the reaction, the reaction mixture was subjected to solid-liquid separation by filtration, and the toluene was removed from the filtrate to obtain a white solid organoaluminum oxy-compound.

(Polymerization)

A 2-liter stainless steel autoclave thoroughly purged with nitrogen was charged with 900 ml of 4-methyl-1-pentene, followed by rise in temperature of the system up to 55°C. Into the autoclave were then injected 1.0 mmol of triisobutylaluminum, 0.1 mg atom of the organoaluminum oxy-compound in terms of aluminum atom and 0.001 mmol of bis(methylcyclopentadienyl)zirconium dichloride together with ethylene to initiate polymerization. The polymerization was carried out at the total pressure of 8 kg/cm² G and 60°C for 10 minutes while continuously feeding ethylene to the polymerization system [step (b)]. Immediately after the 10-minute polymerization, 0.25 Nl of hydrogen together with ethylene was injected into the autoclave to carry out the polymerization at the total pressure of 12 kg/cm² G and 60°C for 25 minutes [step (a)]. The polymerization was stopped by the addition to the polymerization system of small amounts of methanol, and the resulting polymer solution was poured into large amounts of methanol to separate polymer therefrom. The polymer was then recovered and vacuum dried at 80°C overnight. As the result, there was obtained 53.5 g of an ethylene/4-methyl-1-pentene copolymer having [η] of 1.82 dl/g, a density of 0.901 g/cm³, MFR_2 of 0.82 g/10 min, MFR_{10}/MFR_2 of 10.5 a melting point at 95°C and an amount of portion of soluble in n-decane of 1.6% by weight.

Separately, only the above-mentioned step (b) was carried out. As the result, there was obtained 15.5 g of an ethylene/4-methyl-1-pentene copolymer having [η] of 3.30 dl/g, a density of 0.892 g/cm³, an amount of portion soluble in n-decane of 3.9% by weight and a melting point of 87°C. From the results obtained in the above step (b), it was found by calculation that the ethylene/4-methyl-1-pentene copolymer obtained in the above step (a) amounted to 38.0 g, having [η] of 1.22 dl/g, a density of 0.905 g/cm³ and an amount of portion soluble in n-decane of 0.66% by weight.

Comparative Example 1

(Polymerization)

Only the step (b) of Example 1 was repeated except that the polymerization was carried out at 100°C for 40 minutes and at the total pressure of 12 kg/cm² G, whereby 32.8 g of an ethylene/4-methyl-1-pentene copolymer having [η] of 1.85 dl/g, a density of 0.902 g/cm³, MFR_2 of 0.75 g/10 min, MFR_{10}/MFR_2 of 6.0, a melting

point of 94°C, and an amount of portion soluble in n-decane of 1.1% by weight was obtained.

Example 2

(Polymerization)

Immediately after completion of the step (b) of Example 1, the flask was charged with 0.2 Nl of hydrogen to carry out polymerization at the total pressure of 10 kg/cm² G and 60°C for 25 minutes [step (a)]. Thereafter, the same operation as in Example 1 was conducted to obtain 44.3 g of an ethylene/4-methyl-1-pentene copolymer having [η] of 1.87 dl/g, a density of 0.897 g/cm³, MFR_2 of 0.65 g/10 min, MFR_{10}/MFR_2 of 9.8, a melting point of 92°C, and an amount of portion soluble in n-decane of 2.4% by weight.

From the results obtained in the above step (a), it was found by calculation that the ethylene/4-methyl-1-pentene copolymer obtained in the step (a) amounted to 28.8 g, having [η] of 1.10 dl/g, a density of 0.900 g/cm³ and an amount of portion soluble in n-decane of 1.6% by weight.

Example 3

(Preparation of titanium catalyst component [C])

To a suspension of 1 mole of commercially available anhydrous magnesium chloride in 2 liters of hexane was added dropwise with stirring in a nitrogen atmosphere 6 moles of ethanol over a period of 1 hour, followed by reaction at room temperature for 1 hour. To the reaction mixture was added dropwise 2.6 moles of diethylaluminum chloride at room temperature, followed by stirring for 2 hours. After addition thereto of 6 moles of titanium tetrachloride, the temperature of the system was elevated to 80°C, and the reaction was carried out with stirring at that temperature for 3 hours. After completion of the reaction, solids formed were separated from the reaction mixture, followed by repeated washing with hexane. To 200 ml of a decane suspension containing 5 mmoles in terms of titanium atom of the thus obtained solid component (Ti: 3.4 wt%, Mg: 21 wt%) was added dropwise at room temperature 45.6 mmoles of ethanol, followed by reaction at 90°C for 1 hour. After cooling the system to room temperature, 15 mmoles of triethylaluminum, was added and reaction was carried out at room temperature for 1 hour to obtain the captioned titanium catalyst component [C].

(Preparation of organoaluminum oxy-compound [B])

A 400 ml glass flask thoroughly purged with nitrogen was charged with 37.1 g of $Al_2(SO_4)_3.14H_2O$ and 133 ml of toluene, cooled to -5°C, and 47.9 ml of trimethylaluminum diluted with 152 ml of toluene was added dropwise over a period of 1 hour, followed by reaction at a temperature of from 0° to -5°C for 1 hour. The temperature of the flask was then elevated to 40°C over a period of 3 hours, and the reaction was continued at that temperature for 72 hours. After completion of the reaction, the reaction mixture was subjected to solid-liquid separation by filtration, and the toluene was removed from the filtrate to obtain a white solid benzene-soluble organoaluminum oxy-compound.

A 400 ml glass flask was charged with 58.4 ml of a solution of the benzene-soluble organoaluminum oxy-compound obtained above in toluene (Al = 2.57 mol/l), 90.5 ml of toluene and 25 g of Teflon columns (1.2 mm of length x 2 mm of diameter). The temperature of the flask was cooled to -5°C, and 1.08 ml of water was added dropwise over a period of 20 minutes. In that case, the temperature inside the flask was maintained at from 0°C to -5°C. After completion of the dropwise addition of water the temperature of the flask was elevated up to 80°C over a period of 30 minutes, and the reaction was carried out at that temperature for 3 hours. Thereafter, the Teflon columns were removed by means of a 32-mesh screen from the reaction mixture to obtain a benzene-insoluble organoaluminum oxy-compound having a solubility in benzene at 60°C of 0.4 wt% and a D_{1260}/D_{1220} ratio as measured by IR of 0.053.

(Polymerization)

A 2-liter stainless steel autoclave thoroughly purged with nitrogen was charged with 900 ml of 4-methyl-1-pentene, followed by rise in temperature of the system up to 75°C. Into the autoclave were then injected 0.5 mmole of triisobutylaluminum, 0.1 mg atom in terms of aluminum atom of the benzene-insoluble organoaluminum oxy-compound and 0.001 mmole of bis(methylcyclopentadienyl)zirconium dichloride together with ethylene to initiate polymerization. The polymerization was carried out at the total pressure of 8 kg/cm².G and 80°C for 40 minutes while continuously feeding ethylene to the autoclave [step(c)]. Immediately thereafter, 180

ml of the polymer solution obtained above was injected together with ethylene into another autoclave having been used in the step (c), said another autoclave had been charged with 800 ml of cyclohexane, 0.5 Nl of hydrogen and 0.3 mmole of ethylaluminum sesquichloride, and heated to 170°C, and then 0.003 mg atom in terms of titanium atom of the titanium catalyst component prepared above was injected thereinto together with ethylene to initiate polymerization again. The polymerization was carried out at the total pressure of 25 kg/cm².G and 170°C for 15 minutes while continuously feeding ethylene to the autoclave [step (d)]. The polymerization was stopped by the addition to the polymerization system of small amounts of methanol, and the resulting polymer solution was poured in large amounts of methanol to separate polymer. The polymer was then recovered therefrom, and vacuum dried at 80°C overnight. As the result, there was obtained 25.3 g of an ethylene/4-methyl-1-pentene copolymer having [η] of 1.63 dl/g, a density of 0.905 g/cm³, an amount of portion soluble in n-decane of 2.7 wt%, and a peak of melting point, as measured by means of DSC, appearing at 122, 112 and 93°C.

Separately, only the step (c) mentioned above was repeated to recover the resulting polymer from 180 ml of the polymer solution obtained thereby. As the result, there was obtained 9.6 g of an ethylene/4-methyl-1-pentene copolymer having [η] of 1.80 dl/g, a density of 0.891 g/cm³, an amount of portion soluble in n-decane of 4.3 wt%, and a melting point of 83°C. From the results obtained in this step (c), it was found by calculation that the ethylene/4-methyl-1-pentene copolymer obtained in the step (d) mentioned above amounted to 15.7 g, having [η] of 1.53 dl/g, a density of 0.914 g/cm³, and an amount of portion soluble in n-decane of 1.7 wt%.

Comparative Example 2

A 2-liter stainless steel autoclave thoroughly purged with nitrogen was charged with 900 ml of 4-methyl-1-pentene, followed by rise in temperature of the system to 90°C. Into the autoclave were injected 1.0 mmole of triisobutylaluminum, 0.2 mg atom in terms of aluminum atom of the benzene-insoluble organoaluminum oxy-compound prepared in Example 3 and 0.002 mmole of bis(cyclopentadienyl)zirconium dichloride together with ethylene to initiate polymerization. The polymerization was carried out at the total pressure of 20 kg/cm².G and 100°C for 40 minutes while continuously feeding ethylene to the autoclave, whereby 91.0 g of an ethylene/4-methyl-1-pentene copolymer having [η] of 1.56 dl/g, a density of 0.907 g/cm³, an amount of portion soluble in n-decane of 0.65 wt%, and a melting point of 97°C was obtained.

Comparative Example 3

A 2-liter stainless steel autoclave thoroughly purged with nitrogen was charged with 200 ml of 4-methyl-1-pentene, 800 ml of cyclohexane and 0.5 Nl of hydrogen, followed by rise in temperature of the system to 160°C. Into the autoclave were then injected 0.35 mmole of ethylaluminum sesquichloride and 0.013 mg atom in terms of titanium atom of the titanium catalyst component prepared in Example 3 together with ethylene to initiate polymerization. The polymerization was carried out at the total pressure of 25 kg/cm².G and 170°C for 40 minutes while continuously feeding ethylene to the autoclave, whereby 115 g of an ethylene/4-methyl-1-pentene copolymer having [η] of 1.40 dl/g, a density of 0.908 g/cm³, an amount of portion soluble in n-decane of 3.9 wt%, and a melting point of 122.7, 112.6 and 96°C was obtained.

Example 4

The step (d) of the polymerization of Example 3 was repeated except that the amount of the titanium catalyst used was changed to 0.005 mg atom in terms of titanium atom, whereby 36.9 g of an ethylene/4-methyl-1-pentene copolymer having [η] of 1.55 dl/g, a density of 0.907 g/cm³, an amount of portion soluble in n-decane of 2.5 wt% and a melting point of 122, 114 and 94°C was obtained.

In this connection, it was found by calculation that the ethylene/4-methyl-1-pentene copolymer obtained in the step (d) amounted to 27.3 g, having [η] of 1.46 dl/g, a density of 0.913 g/cm³ and an amount of portion soluble in n-decane of 1.9 wt%.

Claims

1. A method for the preparation of an ethylene polymer composition, having a density of 0.86-0.94 g/cm³ and an intrinsic viscosity [η] of 1-6 dl/g, using an olefin polymerization catalyst [I] comprising a transition metal compound [A], which contains a ligand having a cycloalkadienyl skeleton, and an organoaluminum oxy-compound [B], wherein the method comprises carrying out a multi-stage process comprising

a polymerization step (a): wherein ethylene is homopolymerized or ethylene and another α-olefin are copolymerized to form an ethylene polymer [I] having a density greater than 0.88 g/cm³ and an intrinsic viscosity [η] of 0.3-3 dl/g, and
a polymerization step (b): wherein ethylene and another α-olefin are copolymerized to form an ethylene copolymer [II] having a density no higher than that of the ethylene polymer [I] and having an intrinsic viscosity of at least 1.5 times that of the ethylene polymer [I] and from 1 to 10 dl/g,
wherein the polymerization steps (a) and (b) are carried out such that step (a) is carried out first and step (b) is carried out in the presence of the ethylene polymer [I] or step (b) is carried out first and step (a) is carried out in the presence of the ethylene copolymer [II] so that the ethylene copolymer [II] amounts to 10-1000 parts by weight based on 100 parts by weight of the ethylene polymer [I].

2. A method according to Claim 1, wherein the amount of ethylene copolymer [II] in the polymerization step (b) is 20-500 parts by weight when the amount of ethylene polymer [I] obtained in the polymerization step (a) is taken as 100 parts by weight.

3. A method for the preparation of an ethylene polymer composition having a density of 0.87-0.93 g/cm³ and an intrinsic viscosity [η] of 0.5-6 dl/g, which comprises carrying out a multi-stage process comprising
a polymerization step (c): wherein ethylene and another α-olefin are copolymerized using an olefin polymerization catalyst [II], which comprises a transition metal compound [A] containing a ligand having a cycloalkadienyl skeleton and an organoaluminum oxy-compound [B], to form an ethylene copolymer [III] having a density of lower than 0.91 g/cm³ and an intrinsic viscosity [η] of 0.5-6 dl/g, and
a polymerization step (d): wherein ethylene is homopolymerized or ethylene and another α-olefin are copolymerized using an olefin polymerization catalyst [III], which comprises a titanium catalyst component [C] containing titanium, magnesium and halogen as its essential ingredients, an organoaluminum compound [D] and/or an organoaluminum oxy-compound [E] to form an ethylene copolymer [IV] having a density greater than that of the ethylene copolymer [III] and an intrinsic viscosity [η] of 0.5-6 dl/g,
wherein the polymerization steps (c) and (d) are carried out such that step (c) is carried out first and step (d) is carried out in the presence of the ethylene copolymer [III] or step (d) is carried out first and step (c) is carried out in the presence of the ethylene polymer [IV] so that the ethylene polymer [IV] amounts to 10-1000 parts by weight based on 100 parts by weight of the ethylene copolymer [III].

4. A method according to claim 3, wherein the polymerization steps (c) and (c) are carried out such that the step (d) is carried out in the presence of the ethylene polymer [III] obtained in the step (c) carried out previously.

5. A method according to claim 3 or 4, wherein the amount of the ethylene copolymer [IV] in the polymerization step (d) is 20-500 parts by weight when the amount of the ethylene polymer [III] obtained in the polymerization step (c) is taken as 100 parts by weight.

6. A method according to any one of the preceding claims wherein the transition metal of the transition metal compound [A] is zirconium, titanium, hafnium, chromium or vanadium.

FIG. 1 (a)

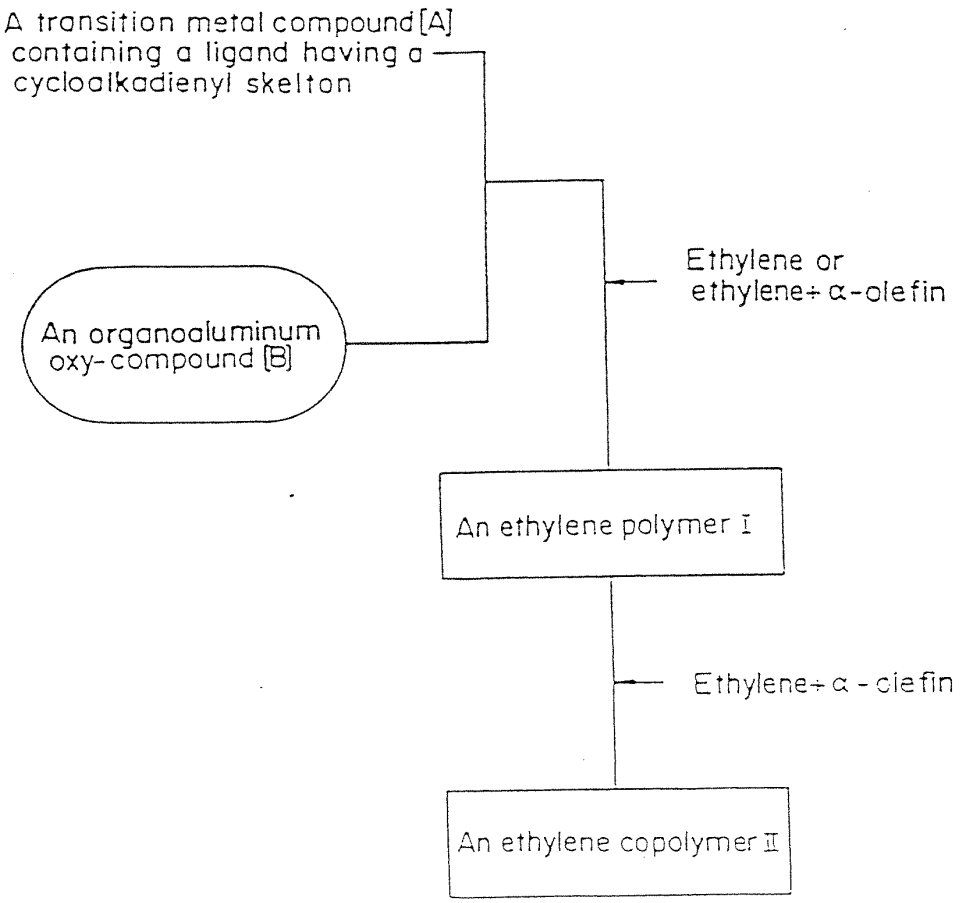

A transition metal compound [A] containing a ligand having a cycloalkadienyl skelton
An organoaluminum oxy-compound [B]
Ethylene or ethylene+α-olefin
An ethylene polymer I
Ethylene+α-olefin
An ethylene copolymer II

FIG. 1 (b)

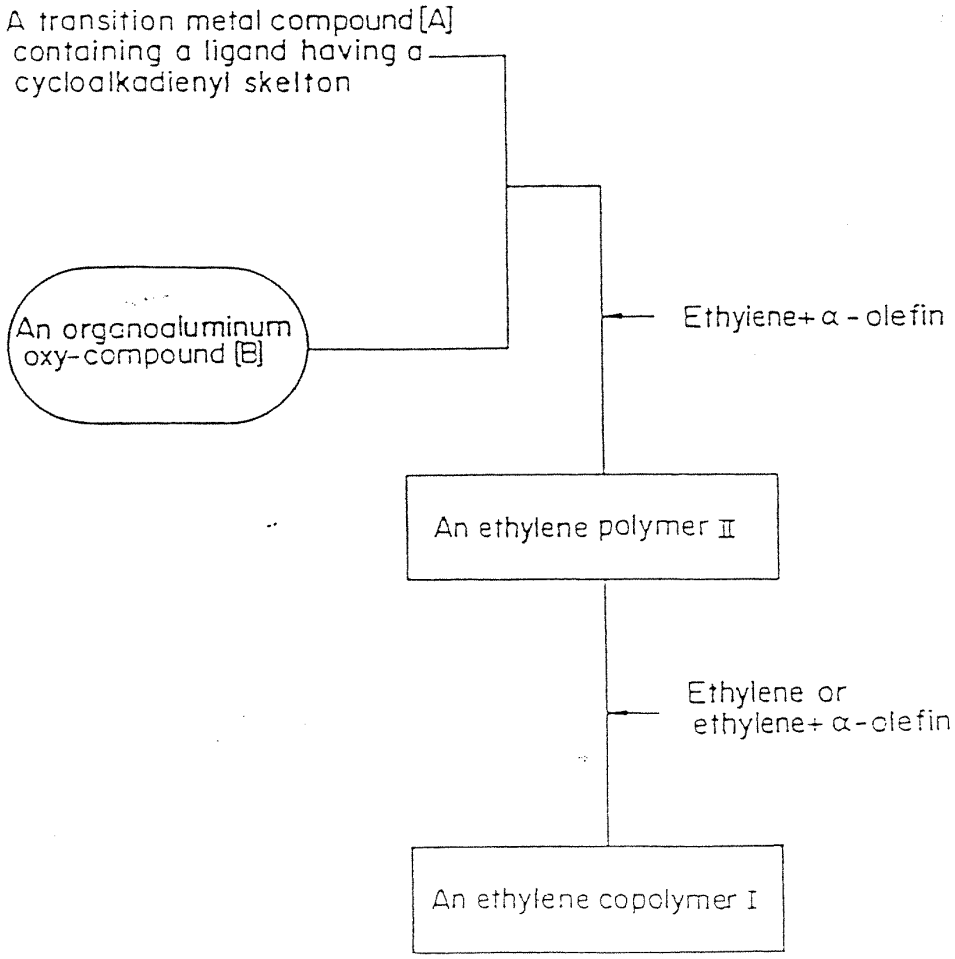

A transition metal compound [A] containing a ligand having a cycloalkadienyl skelton
An organoaluminum oxy-compound [B]
Ethylene+α-olefin
An ethylene polymer II
Ethylene or ethylene+α-olefin
An ethylene copolymer I

FIG. 2

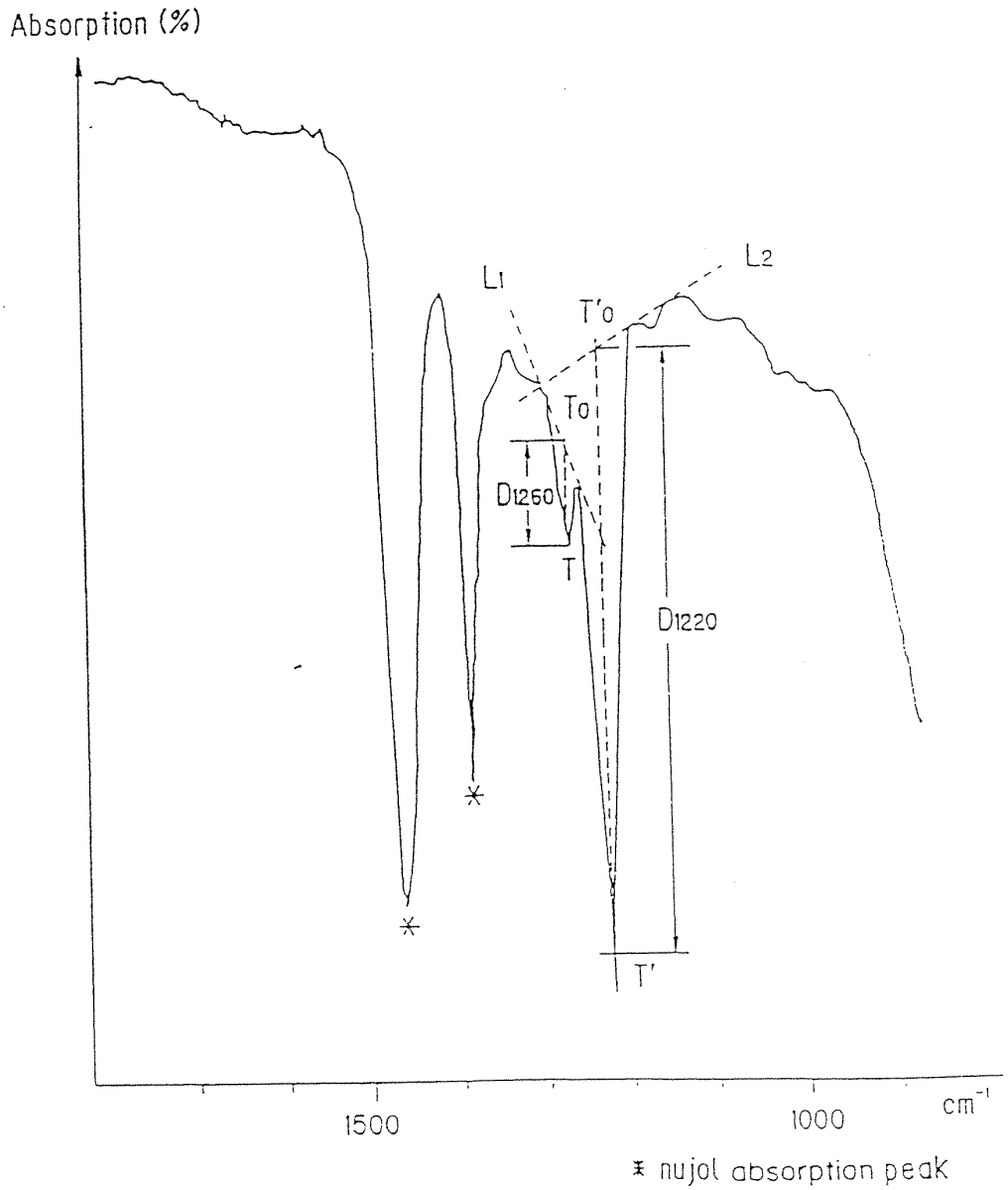

Absorption (%)
L1
L2
T'o
To
D1260
T
D1220
T'
1500
1000
cm⁻¹
* nujol absorption peak

FIG. 3

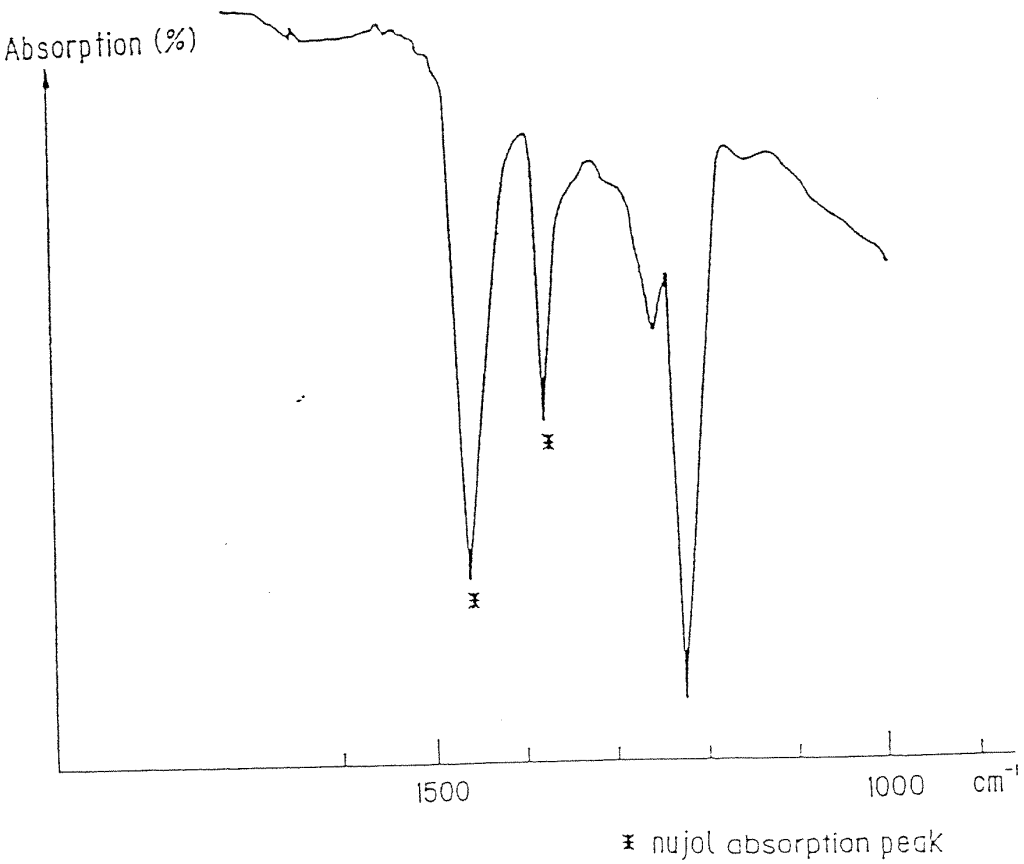


FIG. 4 (a)

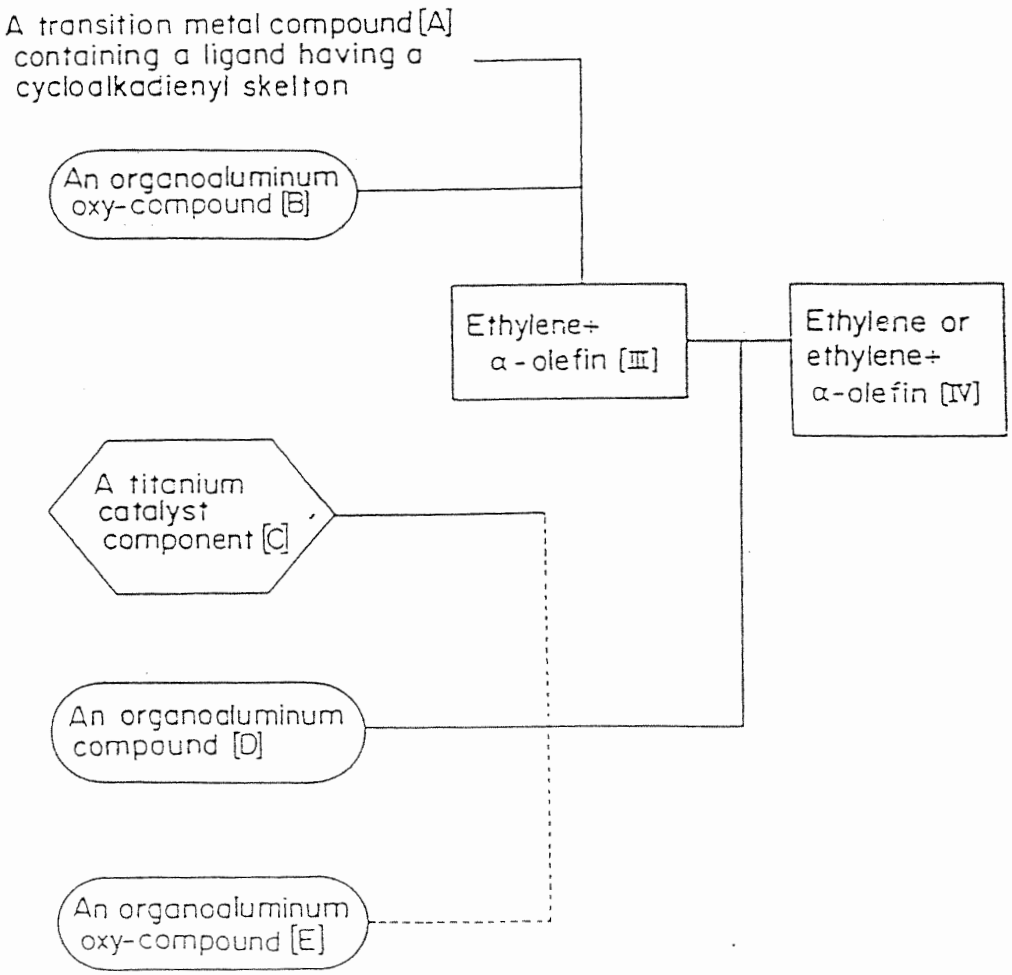
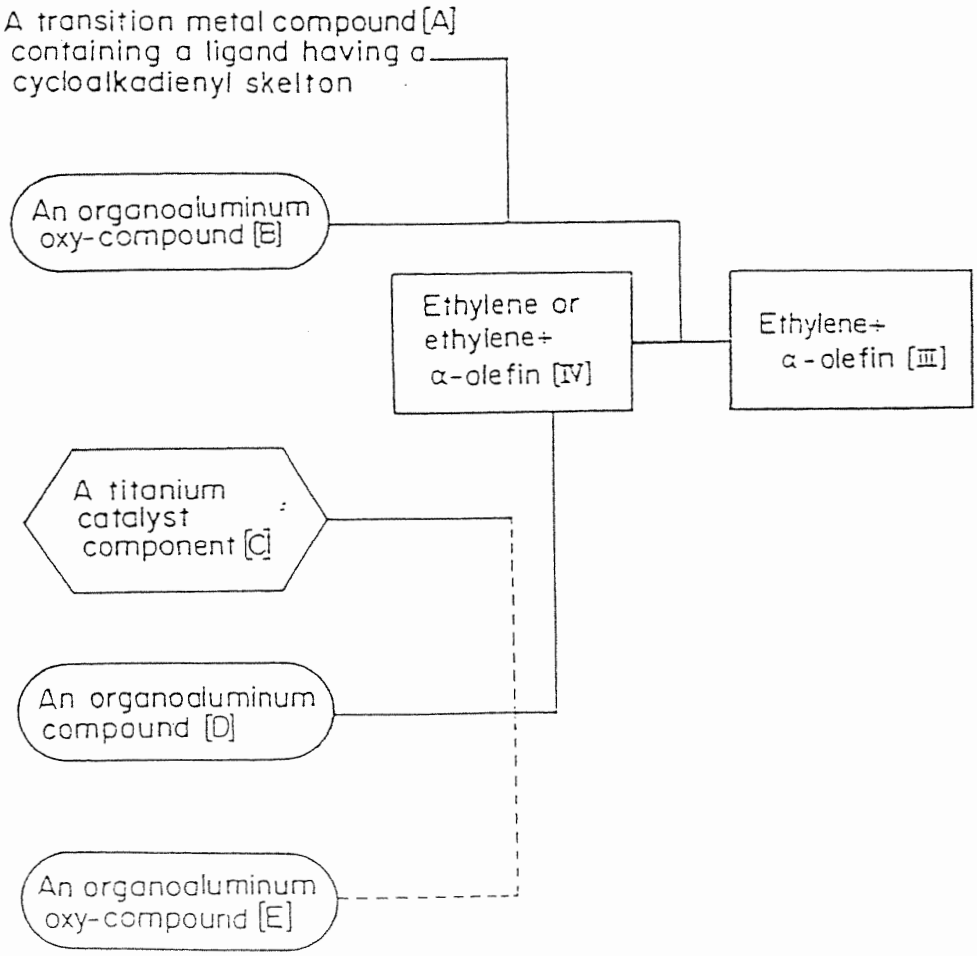

A transition metal compound [A] containing a ligand having a cycloalkadienyl skelton
An organoaluminum oxy-compound [B]
Ethylene+ α-olefin [III]
Ethylene or ethylene+ α-olefin [IV]
A titanium catalyst component [C]
An organoaluminum compound [D]
An organoaluminum oxy-compound [E]

FIG. 4 (b)


A transition metal compound [A] containing a ligand having a cycloalkadienyl skelton
An organoaluminum oxy-compound [B]
Ethylene or ethylene÷ α-olefin [IV]
Ethylene÷ α-olefin [III]
A titanium catalyst component [C]
An organoaluminum compound [D]
An organoaluminum oxy-compound [E]