EXHIBIT U

PART 3

INFORMATION ON HOW TO EFFECT DRAWING CHANGES

1. **Correction of Informalities—37 CFR 1.85**

File new drawing with the changes incorporated therein. The art unit number, serial number and number of drawing sheets should be written on the drawing in accordance with 37 CFR 1.84(l). Applicant may delay filing of the new drawings until receipt "Notice of Allowability" (PTOL-37). If delayed, the new drawings **MUST** be Filed within the **THREE MONTH** shortened statutory period set for response in the"Notice of Allowability" (PTOL-37). Extensions of time may be obtained under the provisions of 37 CFR 1.136. The drawing should be filed as a separate paper with a transmittal letter addressed to the Official Draftsperson.

Timing of Corrections

Applicant is required to submit **acceptable** corrected drawings within the three month shortened statutory period set in the "Notice of Allowability" (PTOL-37). Within the three month period, two weeks should be allowed for review by the Office of the correction.if a correction is determined to be unacceptable by the Office, applicant must arrange to have acceptable correction re-submitted within the original three month period to avoid the necessity of obtaining an extension of time and paying the extension fee. Therefore, applicant should file corrected drawings as soon as possible.

Failure to take corrective action within set (or extended) period will result in **ABANDONMENT** of the Application.

2. **Corrections other than Informalities Noted by the Draftsperson on the PTO-948**

All changes to the drawings, other than informalities noted by the Draftsperson, **Must** be made in the same manner as above except that, normally, a red ink sketch of the changes to be incorporated into the new drawings **MUST** be approved by the examiner before the application will be allowed. No changes will be permitted to be made, other than correction of informalities, unless the examiner has approved the proposed changes.

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant(s): Pak-Wing Steve Chum et al.

Serial No.: 08/378,998 Group Art Unit: 1505

Filed: January 27, 1995 Examiner: David Wu

For FABRICATED ARTICLES MADE FROM ETHYLENE POLYMER BLENDS

RECEIVED
SEP 21 1995
GROUP 1500

#12

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

Sir:

EXTENSION OF TIME

Applicant(s) hereby request(s) that the shortened statutory period for response now set to expire July 18, 1995 in this application be extended for a period of three (3) month(s), the extended period then expiring on October 18, 1995. This is a first request for an extension of time.

Please charge $870 to our Deposit Account No. 04-1512. If this estimate is incorrect, please charge or credit our account accordingly. Two duplicate copies of this sheet are enclosed.

Respectfully submitted,

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

Freeport, Texas 77541

OKM/mfg
C-40,121-AB

230 04-1512 09/22/95 08378998
23023 117 870.00CH
23024 102 76.00CH

RESPONSE UNDER 37 CFR 1.116
EXPEDITED PROCEDURE
EXAMINING GROUP 1505
PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants:	Pak-Wing Steve Chum, et al.		
Serial No.:	08/378,998	Art Unit:	1505
Filed:	January 27, 1995	Examiner:	David Wu
Attorney Docket No:	C-40,121-AB		

For: FABRICATED ARTICLES MADE FROM ETHYLENE POLYMER BLENDS

RECEIVED
SEP 21 1995
GROUP 1500

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

Sir:

RESPONSE AFTER FINAL REJECTION

The following is responsive to Examiner's Action (Paper No. 11) dated April 18, 1995. Attached herewith is a petition for a three-month extension of time to extend the period for response to October 18, 1995. Also attached herewith is an Declaration under 37 CFR 1.132 by Ronald P. Markovich, a co-inventor of the above-identified application.

IN THE SPECIFICATION

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

-- Determination of Critical Shear Stress

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." Gross melt fracture occurs at unsteady flow conditions and ranges in detail from regular (alternating rough and smooth, helical, etc.) to random distortions. For commercial acceptability, (e.g., in blown film products), surface defects should be minimal, if not absent. The critical shear rate at onset of surface melt fracture (OSMF) and onset of gross melt fracture (OGMF) will be used herein based on the changes of surface roughness and configurations of the extrudates extruded by a GER. Preferably, the critical shear stress at the OGMF and the critical shear stress at the OSMF for the substantially linear ethylene polymers [described] used herein is greater than about 4 x 10^6 dyne/cm^2 and greater than about 2.8 x 10^6 dyne/cm^2, respectively. --

Don't enter, AW 9/29/95

IN THE CLAIMS

Please amend the following claims:

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

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

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

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

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

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

(iv) no linear fraction, [and]

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

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

(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 (SCH) greater than or equal to about 1.3.

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

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

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

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

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

(iv) no linear polymer fraction, [and]

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

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

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 greater than or equal to about 1.3.

Please add the following new claims:

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

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

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

(i) a density from about 0.89 grams/cubic centimeter (g/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 linear fraction,

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

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

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

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

32. An ethylene polymer composition comprising

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

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

(i) a density from about 0.89 grams/cubic centimeter (g/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 linear fraction,

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

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

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

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

REMARKS

Support for the amendment to the specification can be found in the parent application USSN 07/776,130 (now USP 5,272,236) at page 7, lines 27-34 bridging to page 8, lines 1-27. The parent application was explicitly incorporated in to the present application by reference at page 1, lines 2-8. The amendment to the otherwise verbatim text of the parent application directs the incorporated description to the use of substantially linear ethylene polymers rather than a description of the novelty of such polymers.

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

New Claim 31 is based on the description at page 13, lines 3-6 in the specification, original Claim 1, current Claim 2 and parent application 07/776,130 at page 8, lines 23-27. New Claim 32 is based on the description at page 13, lines 3-6 in the specification, original Claim 17, current Claim 18 and parent application 07/776,130 at page 8, lines 23-27.

Applicants do not believe that the amendments to the specification or claims add any new matter. Applicants respectfully request entry of the amendments and reconsideration of Claims 1-8 and 17-23 in view of the following remarks.

Examiner's Rejections

Claims 1-8 and 17-23 remain rejected under 35 USC § 102(b) as anticipated by WO '414 or, in the alternative, under 35 USC § 103 as obvious in view of WO '414. In particular, the PTO alleges a slope of chain hardening (SCH) of greater than 1.3 is an inherent property of the '013 component polymer of WO '414 and if the distinction of the present invention rests on long chain branching, then a long chain branching

limitation must be set forth in the claims. Further, the PTO alleges that Applicants' position respecting inventive compositions having significantly higher dart impact resistance is not supported by truly representative comparative experiments and the declaration by Chum is conclusory and, as such, does not cure cited deficiencies respecting comparative experiments and demonstration of unexpected results.

Applicants' Response

The § 102(b) Rejection

Applicants believe, standing alone, the term "substantially linear ethylene interpolymer" sufficiently and completely distinguishes the present invention over the WO '414 reference. The term clearly means a homogeneously branched ethylene interpolymer having long chain branches. *See*, the description at page 4, lines 27-31 and at page 6, lines 12-30. As such, Applicants believe a long chain branching limitation is already incorporated into the base claims of the present invention.

Moreover, to the extent the term was sufficient to justify a restriction requirement imposed by the PTO as between claims directed to homogeneously branched substantially linear ethylene interpolymers and those directed to homogeneously branched linear ethylene interpolymers (*see*, paper 4 mailed November 15, 1993), the term easily provides sufficient distinction over the WO '414 reference whether or not the PTO is persuaded a long chain branching limitation is intrinsic to the term.

Further, to the extent that Table 1 of the original specification clearly indicates that a slope of strain hardening of greater than 1.3 is not an inherent property of substantially linear ethylene interpolymers whatever they are (that is, the SCH limitation is met by particularly selected substantially linear ethylene interpolymers and not others), it is a fortiori that the characteristic is not inherent as to homogeneously branched polymers in general and homogeneously branched linear ethylene polymers in particular. Certainly substantially linear ethylene polymers are a species of and/or representative of homogeneously branched ethylene polymers.

For each of these three reasons, Applicants believe the 102(b) rejection is traversed and should be withdrawn.

Although the Applicants believe the above reasoning sufficiently traverses the PTO's rejection under 35 USC § 102(b), to make clearer that the term "substantially linear ethylene interpolymer" necessarily includes a long chain branching limitation, the base claims have been amended to incorporate a critical shear stress melt fracture requirement. Improved resistance to melt fracture is believed to be a manifestation of long chain branching and is characteristic of substantially linear ethylene polymers.

Comparative data provided by affidavit by Ronald P. Markovich specifically indicates that homogeneously branched linear ethylene interpolymer compositions representative of the '013 component polymer in WO '414 have significantly lower critical shear stresses at the onset of melt fracture relative to comparable substantially linear ethylene interpolymers. *See*, Table 1 of Markovich Affidavit. Applicants believe these data clearly show a high critical shear stress characteristic is not at all an inherent property of homogeneously branched linear ethylene polymers and easily distinguishes the substantially linear ethylene interpolymers used in the present invention from WO '414 component polymers. However, like the existing term "homogeneously branched," Applicants believe incorporation of the critical shear stress melt fracture limitation merely constitutes amplification of the term "substantially linear ethylene interpolymer."

The § 103 Rejection

Applicants believe that since the PTO predicated its § 103 rejection entirely on alleged similarities between the present inventive composition and the WO '414 composition, the § 103 rejection is traversed by the same reasoning applicable to the § 102(b) rejection and, likewise, the § 103 rejection should be withdrawn.

Moreover, Applicants believe the § 103 rejection should be withdrawn because there is no nexus between the WO '414 reference and the present invention. Applicants originally disclosed that their compositions have significantly higher impact and toughness properties relative to heterogeneously branched single polymer compositions as well as relative to blend compositions consisting entirely of heterogeneously branched component polymers. The WO '414 reference relied on by the PTO pertains to homogeneous blend components wherein each component polymer also has a narrow molecular weight distribution. *See*, WO '414 at page 3, lines 29-37 bridging to page 4, line 1. In addition to requiring the exclusive use of homogeneous component polymers, as another essential requirement, the WO '414 reference specifically teaches that the blend must be free of component polymers having both a relative high density and a relatively high average molecular weight, otherwise poor properties would result. *See*, WO '414 at page 4, lines 2-8 and page 11, lines 14-25.

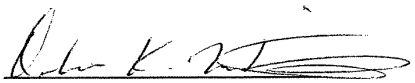
Unlike the WO '414 composition, no density/molecular weight restriction exists for the present inventive compositions. In particular, the WO '414 teachings in no way render obvious higher performing compositions comprising at least one lower density substantially linear ethylene interpolymer and at least one higher density heterogeneously branched ethylene polymer, wherein there is no average molecular weight (melt index) limitation as to the higher density heterogeneously branched ethylene polymer. As such, the WO '414 reference does not provide a nexus that

would lead one skilled in the art to expect a blend composition of a homogeneous component polymer with a particularly selected heterogeneous component polymer would perform equivalent to or better than a blend of two homogeneous component polymers with density/average molecular weight restrictions. A nexus would be only provided (but it is not) if a person skilled in the art assumed and understood that SCH in some way related to polymer homogeneity, wherein the SCH limitation as to the heterogeneously branched ethylene polymer taught by Applicants renders the heterogeneous polymer essentially homogeneous. Such an assumption is not likely and provides an absurd result as it defies all known polymer science. If anything, the recited SCH limitation insures the B component is heterogeneously rather than homogeneously. Moreover, such an assumption still does not address or account for the density/average molecular weight restriction taught by WO '414. In sum, Applicants believe the WO '414 compositions and its restrictions (even in hindsight) are so completely different from the present composition that there could not be any suggestion of the latter. Hence, although such is well short of and is not the standard for § 103 obviousness, the WO '414 reference with its divergent teachings does not even rise to the level of "obvious to try."

Furthermore, specific comparative experiments by Ronald P. Markovich indicate that blend compositions representative of those of the WO '414 reference are in fact inferior to the present composition at least respecting impact performance. *See*, Table 2 Markovich Affidavit.

For all of the above reasons, Applicants believe the rejections under 35 USC § 102(b) and 35 USC § 103 have been traversed and should be withdrawn. Applicants also believe all of the PTO rejections and objections have been traversed and Claims 1-8, 17-23, 31 and 32 are all in a condition of allowance. Applicants respectfully request reconsideration of the pending claims and a notice of allowance of the same.

Respectfully submitted,



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

Freeport, Texas 77541
OKM/okm

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants:	Pak-Wing Steve Chum, et al.		
Serial No.:	08/378,998	Art Unit:	1505
Filed:	January 27, 1995	Examiner:	David Wu
Attorney Docket No:	C-40,121-AB		

For: FABRICATED ARTICLES MADE FROM ETHYLENE POLYMER BLENDS

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

Sir:

DECLARATION UNDER 37 CFR § 1.132

Ronald P. Markovich declares and states:

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

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

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

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

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

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

THAT, he performed comparative testing to determine whether compositions representative of the '013 component polymer in WO '414 have any significant long chain branching characteristics as indicated by relatively high critical shear stresses at onset of gross melt fracture;

THAT, he had to blend together (at 75.9%/24.1% by weight and 74.4%/25.6% by weight) two commercially available homogeneously branched linear ethylene interpolymers (supplied by Exxon Chemical Company under the designation Exact 3027 and 3022, respectively) in order to approximate the melt index and density disclosed in WO '414 for the '013 component polymer and the resulting experimental compositions are designated Comparative Examples AB1 and AB2, respectively, in the attached Table 1;

THAT, he had three different substantially linear ethylene interpolymers made at the Polyolefins Research Miniplant in order to represent the '013 component polymer with long chain branching and that these interpolymers are designated Component Examples A, B, and C in the attached Table 1;

THAT, he had Component Examples A, B and C and Comparative Examples AB1 and AB2 tested by gas extrusion rheometry according to the procedure and requirements described in USSN 07/776,130 at page 7, lines 27-34 bridging to page 8, lines 1-4 to determine the critical shear stress at onset of gross melt fracture for each;

THAT, he performed comparative experiments to determine the performance attributes of his inventive blend compositions relative to blend compositions representative of those disclosed in WO '414;

THAT, to approximate the Banbury and roll mill melt blending procedure described in WO '414 at page 20, lines 4-12, he employed a Haake torque mixer and melt blended various component polymers together with 1000 ppm Irganox 1076 antioxidant and 1000 ppm Irgafos 168 thermal stabilizer at 183°C and 50 rpms for 10 minutes to prepare 200-400 grams each of Inventive Blend Example AD1, BD1, CD1, AD2, BD2 and CD2, and Comparative Blend Example X1 and X2 as listed in the attached Table 2;

THAT, for bulk property comparisons, he compression molded Blend Examples according procedures described in WO '414 at page 20, lines 13-18;

THAT, the preferred test method for compression molded samples having a target thickness of 0.005 inch is ASTM D-882 rather than ASTM D-638 as reported in WO '414 at page 21, Note f of Table 2, in that ASTM D-638 is preferred for target thicknesses greater than 0.04 inch;

THAT, for the Inventive Blend Examples and the two Comparative Blend Examples, he performed tensile break strength determinations according ASTM D-882, intrinsic tear determinations according to ASTM D-1922 and Dynatup total energy impact determinations according to ASTM D-3763-86;

THAT, relative to substantially linear ethylene interpolymers, experimental compositions representative of the '013 component polymer of WO '414 have comparatively low critical shear stresses at onset of gross melt fracture which is indicative of low or, more probably, no long chain branching;

THAT, relative to inventive compositions, experimental blend compositions representative of the blend compositions of WO '414 have equivalent to inferior tensile break strength and intrinsic tear properties, as well as dramatically inferior impact properties;

THAT, specific comparative test results (which also included rheological property comparisons) indicate that the component polymers of WO '414 are completely different from substantially linear ethylene interpolymers in regards to molecular structure and the blend compositions of WO '414 are completely different from the Inventive Blend compositions in regards to at least impact resistance properties; and

THAT, the impact properties of our inventive compositions of the above-identified application are unexpected and surprising in that they show substantially higher impact resistance even at slightly higher densities relative to blend compositions representative of WO '414, whereas one skilled in the art would ordinarily expect compositions having higher densities to show inferior impact properties relative to comparative compositions having lower densities.

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

Date 9/18/95

Ronald P. Markovich

Ronald P. Markovich

Table 1

Sample Designation	A Component Example A	B Component Example B	C Component Example C	AB1 Comparative Component AB1	AB2 Comparative Component AB2	Exact 3027 Comparative Resin	Exact 3022 Comparative Resin
Polymer Type	Substantially Linear Ethylene/ Octene Copolymer	Substantially Linear Ethylene/ Butene Copolymer	Substantially Linear Ethylene/ Octene Copolymer	Homogeneously Branched Linear Ethylene/ Butene Copolymer	Homogeneously Branched Linear Ethylene/ Butene Copolymer	Homogeneously Branched Linear Ethylene/ Butene Copolymer	Homogeneously Branched Linear Ethylene/ Butene Copolymer
Density (g/cc)	0.906	0.9052	0.90575	0.9031	0.9033	0.9015	0.9065
I2 (g/10 min @ 190°C)	4.01	4.23	3.99	3.83	3.93	3.26	8.48
I10 / I2	8.22	7.88	5.82	5.90	5.69	5.65	5.49
I10 (g/10 min @ 190°C)	32.96	33.32	23.21	22.6	22.38	18.42	46.57
Mw by GPC	68200	67100	77400	79100	80700	85800	65100
Mw/Mn by GPC	2.23	2.12	1.89	2.15	2.17	2.00	2.00
Shear Stress @ OSGMF (dyn/cm^2)	> 3.88 x 106	> 4.31 x 106	> 4.31 x 106	> 3.45 x 106	> 3.45 x 106	ND	ND
Shear Stress @ OSGMF (dyn/cm^2)	< 4.09 x 106	< 4.48 x 106	< 4.48 x 106	< 3.66 x 106	< 3.66 x 106	ND	ND

Note 1: Comparative Resin AB1 is a blend containing of 75.87% Exact 3027 and 24.13% Exact 3022.
Note 2: Comparative Resin AB2 is a blend containing of 74.44% Exact 3027 and 25.56% Exact 3022.
ND = not determined

Table 2

Sample Designation	AD1 Inventive Blend Example	BD1 Inventive Blend Example	CD1 Inventive Blend Example	X1 Comparative Blend Example	AD2 Inventive Blend Example	BD2 Inventive Blend Example	CD2 Inventive Blend Example	X2 Comparative Blend Example
Blend Component								
A	38.46%				72.35%			
B		38.14%				71.75%		
C			38.46%				72.35%	
EXACT 3027				28.95%				53.90%
EXACT 3022				9.21%				18.50%
HDPE 04352N	61.54%	61.86%	61.54%	61.84%	27.65%	28.25%	27.65%	27.60%
I2 (g/10 min @ 190°C)	4.11	4.25	4.18	4.13	4.08	4.10	4.04	4.09
I10 / I2	7.31	6.96	6.29	6.19	7.67	7.64	5.98	5.84
I10 (g/10 min @ 190°C)	30.06	29.59	26.29	25.57	31.29	31.34	24.15	23.87
Mw by GPC	74900	74800	77200	83400	71700	73800	77200	80500
Mw/Mn by GPC	2.56	2.53	2.58	2.52	2.47	2.33	2.20	2.27
Strain @ Yield	15.0	15.0	14.9	15.0	14.9	15.0	14.8	15.0
Break Strength	1835	2070	1921	1801	3187	2253	3268	2729
Break Energy	385	57	509	108	1130	781	991	990
Intrinsic Tear	160	102	221	110	279	107	377	142
Dynatup (30 Mil Plaque)								
Total Energy	4.03	3.14	4.31	1.35	4.41	3.08	5.59	1.84

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant(s): Pak-Wing Steve Chum et al.
Serial No.: 08/378,998 Group Art Unit: 1505
Filed: January 27, 1995 Examiner: David Wu
For: FABRICATED ARTICLES MADE FROM ETHYLENE POLYMER BLENDS

RECEIVED
SEP 21 1995
GROUP 1500

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

Sir:

Transmitted herewith is an amendment requiring an additional fee in the above-identified application.

The fee has been estimated as shown below.

CLAIMS AS AMENDED

(1)	(2) Claims remaining after amendment	(3)	(4) Highest number previously paid for	(5) Present Extra	(6) Rate	(7) Add'l Fee
Total Claims	* 17	Minus	** 20	0	$22	$0
Independent Claims	* 4	Minus	*** 3	1	$76	$76
First Presentation of Multiple Dependent Claims					$240	$0
			Total additional fee for this amendment:			$76

*If the entry in Column 2 is less than the entry in Column 4, write "0" in Column 5.
**If the "Highest Number Previously Paid For" in this space is less than 20, write "20" in this space.
***If the "Highest Number Previously Paid For" in this space is less than 3, write "3" in this space.

Please charge the above fee to our Account No. 04-1512. If this estimate is incorrect, please charge or credit our account accordingly. Three copies of this sheet are enclosed.

Respectfully submitted,

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

Dated: September 20, 1995

OKM/mfg

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

SERIAL NUMBER	FILING DATE	FIRST NAMED APPLICANT	ATTORNEY DOCKET NO.
08/378,998	01/27/95	CHUM	P C-40.121-AB

15M2/0929

THE DOW CHEMICAL COMPANY
PATENT DEPARTMENT B 1211
2301 NORTH BRAZOSPORT BLVD
FREEPORT TX 77541

EXAMINER	
WU, D	
ART UNIT	PAPER NUMBER
1505	14

DATE MAILED: 09/29/95

Below is a communication from the EXAMINER in charge of this application

COMMISSIONER OF PATENTS AND TRADEMARKS

ADVISORY ACTION

☐ THE PERIOD FOR RESPONSE:

a) ☒ is extended to run 6 months or continues to run _____ from the date of the final rejection

b) ☐ expires three months from the date of the final rejection or as of the mailing date of this Advisory Action, whichever is later. In no event however, will the statutory period for the response expire later than six months from the date of the final rejection.

Any extension of time must be obtained by filing a petition under 37 CFR 1.136(a), the proposed response and the appropriate fee. The date on which the response, the petition , and the fee have been filed is the date of the response and also the date for the purposes of determining the period of extension and the corresponding amount of the fee. Any extension fee pursuant to 37 CFR 1.17 will be calculated from the date of the originally set shortened statutory period for response or as set forth in b) above.

☐ Appellant's Brief is due in accordance with 37 CFR 1.192(a).

☒ Applicant's response to the final rejection, filed 9-21-95 has been considered with the following effect, but it is not deemed to place the application in condition for allowance:

1. ☐ The proposed amendments to the claim and /or specification will not be entered and the final rejection stands because:

   a. ☐ There is no convincing showing under 37 CFR 1.116(b) why the proposed amendment is necessary and was not earlier presented.

   b. ☒ They raise new issues that would require further consideration and/or search. (See Note).

   c. ☐ They raise the issue of new matter. (See Note).

   d. ☐ They are not deemed to place the application in better form for appeal by materially reducing or simplifying the issues for appeal.

   e. ☐ They present additional claims without cancelling a corresponding number of finally rejected claims.

   NOTE: The recitation "a critical shear stress at onset of gross melt fracture of greater than about 4×10^6 dyne/cm^2" in claims 1 and 17 raise a new issue that would require further consideration and/or search.

2. ☐ Newly proposed or amended claims _____ would be allowed if submitted in a separately filed amendment cancelling the non-allowable claims.

3. ☒ Upon the filing an appeal, the proposed amendment ☐ will be entered ☒ will not be entered and the status of the claims will be as follows:

   Claims allowed: None
   Claims objected to: None
   Claims rejected: 1-8 and 17-23

   However;

   ☐ Applicant's response has overcome the following rejection(s): _____

4. ☒ The affidavit, ~~exhibit~~ or request for reconsideration has been considered but does not overcome the rejection because the polymer blends of comparative Examples AB1 and AB2 are not truly representative blends of WO 96/03464, see p. 26 of Example 1 of the reference.

5. ☐ The affidavit or exhibit will not be considered because applicant has not shown good and sufficent reasons why it was not earlier presented.

☐ The proposed drawing correction ☐ has ☐ has not been approved by the examiner.

☐ Other

David W. Wu

DAVID W. WU
PRIMARY EXAMINER
GROUP 1500

PTOL-303 (REV. 5-89)

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

SERIAL NUMBER	FILING DATE	FIRST NAMED APPLICANT	ATTORNEY DOCKETT NO.

EXAMINER	
ART UNIT	PAPER NUMBER
	15

DATE MAILED:

EXAMINER INTERVIEW SUMMARY RECORD

All participants (applicant, applicant's representative, PTO personnel):

(1) Mr. Osborne K. McKinney (3) _____

(2) David Wu (4) _____

Date of interview 10-5-95

Type: ☐ Telephonic ☒ Personal (copy is given to ☐ applicant ☐ applicant's representative).

Exhibit shown or demonstration conducted: ☐ Yes ☐ No. If yes, brief description: _____

Agreement ☐ was reached with respect to some or all of the claims in question. ☐ was not reached.

Claims discussed: 1

Identification of prior art discussed: _____

Description of the general nature of what was agreed to if an agreement was reached, or any other comments: Applicant has to submit a Declaration to prove the polymer blend of WO '414 is necessarily different from the claimed polymer (i.e. 50-50% blend).

(A fuller description, if necessary, and a copy of the amendments, if available, which the examiner agreed would render the claims allowable must be attached. Also, where no copy of the amendments which would render the claims allowable is available, a summary thereof must be attached.)

☐ 1. It is not necessary for applicant to provide a separate record of the substance of the interview.

Unless the paragraph below has been checked to indicate to the contrary, A FORMAL WRITTEN RESPONSE TO THE LAST OFFICE ACTION IS NOT WAIVED AND MUST INCLUDE THE SUBSTANCE OF THE INTERVIEW (e.g., items 1-7 on the reverse side of this form). If a response to the last Office action has already been filed, then applicant is given one month from this interview date to provide a statement of the substance of the interview.

☐ 2. Since the examiner's interview summary above (including any attachments) reflects a complete response to each of the objections, rejections and requirements that may be present in the last Office action, and since the claims are now allowable, this completed form is considered to fulfill the response requirements of the last Office action. Applicant is not relieved from providing a separate record of the substance of the interview unless box 1 above is also checked.

David Wu
Examiner's Signature

PTOL-413 (REV. 2 -93)

ORIGINAL FOR INSERTION IN RIGHT HAND FLAP OF FILE WRAPPER

☆ U.S. GOVERNMENT PRINTING OFFICE: 1995–394-958

PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants:	Pak-Wing Steve Chum, et al.		
Serial No.:	08/378,998	Art Unit:	1505
Filed:	January 27, 1995	Examiner:	David Wu
Attorney Docket No:	C-40,121-AB		

For: FABRICATED ARTICLES MADE FROM ETHYLENE POLYMER BLENDS

CERTIFICATE OF FACSIMILE TRANSMISSION

I HEREBY CERTIFY THAT THIS PAPER IS BEING FACSIMILE TRANSMITTED TO THE PATENT AND TRADEMARK OFFICE ON THE DATE SHOWN BELOW.

Stacy Lanier

Stacy Lanier
SIGNATURE OF PERSON SIGNING CERTIFICATE

10-18-95
DATE OF SIGNATURE

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

Sir:

SECOND RESPONSE AFTER FINAL REJECTION

The following is responsive to the interview held on October 5, 1995 between applicant's representative, Osborne K. McKinney, and Primary Examiner Wu. Attached herewith is a second Declaration under 37 CFR 1.132 from Ronald P. Markovich, a co-inventor of the above-identified application.

IN THE CLAIMS

Please amend the following claims:

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

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

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

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

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

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

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

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

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

(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 (SCH) greater than or equal to about 1.3.

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

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

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

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

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

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

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

[(vi) a critical shear stress at onset of gross melt fracture of greater than about 4 x 10^6 dyne/cm^2; 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 greater than or equal to about 1.3.

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

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

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

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

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

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

(iv) no [linear] high density fraction,

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

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

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

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

32. (Amended) 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 [linear] high density fraction,

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

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

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

(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.

REMARKS

Claims 1, 17, 31 and 32 were amended to exclude the critical shear stress limitation objected to by the Examiner. Also, the claims were amended as to the parameter (iv) to correct a transcription error. The term "high density" fraction refers to substantially linear ethylene polymer while the term "linear fraction" or "linear polymer fraction" refers to heterogeneously branched ethylene polymer. See specification at page 5, lines 23-27 and page 14, lines 6-10.

Applicants do not believe the amendments to the claims add any new matter. Applicants respectfully request entry of the amendments and reconsideration of Claims 1-8, 17-23, 31 and 32 in view of the following remarks.

Examiner's Rejections

According to the Advisory Action and Examiner Interview Summary Record, Claims 1-8 and 17-23 remain rejected under 35 USC § 102(b) as anticipated by WO '414 or, in the alternative, under 35 USC § 103 as obvious in view of WO '414 because the critical shear stress limitation presents a new issue and Applicants have not provided truly representative comparisons to the blend compositions of WO '414.

Applicants' Response

Applicants gratefully acknowledge and are very appreciative of the interview conducted between their representative and Examiner Wu.

As discussed during the interview, Applicants have amended the claims to exclude a critical shear stress limitation. As explicitly indicated in Response A at pages 7 and 8, the limitation is considered ancillary in view of the clear definition of the term "substantially linear ethylene interpolymer" and the restriction requirement imposed by the Examiner. Exclusion of the limitation is believed to traverse the Examiner's new issue objection.

As agreed to during the interview, Applicants submit herewith by declaration additional data regarding the performance of their inventive compositions relative to compositions representative of those disclosed in WO '414. Applicants believe the comparative compositions reported in the declaration are truly representative of the

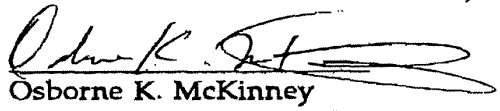
blend compositions of WO '414. Although the PTO specifically emphasized 50/50 blends as to Example 1 of WO '414, the reference also discloses a 75/25 blend in Example 2.

The declaration by Ronald P. Markovich reports on 50/50 blends, 72/28 blends and 38/62 blends. Although the 50/50 blends are complete as to toughness properties, they are incomplete as to impact properties. However, the 72/28 blends evaluated by Markovich as thought to be truly representative of the Example 2 composition of WO '414 and these blends are complete as to both toughness and impact properties.

As declared in his declaration, the results obtained by Ronald P. Markovich indicate that blend compositions representative of both Examples 1 and 2 of the WO '414 reference are in fact inferior to the present inventive compositions in regards to toughness and that blend compositions representative of Examples 2 of the WO '414 reference are in fact inferior to the present inventive compositions in regards to impact performance.

Because the critical shear rate limitation has been excluded and inventive compositions show surprising superior impact properties over the relevant art compositions, Applicants believe all rejections and objections have been traversed and Claims 1-8, 17-23, 31 and 32 are all in a condition of allowance. Applicants respectfully request reconsideration of the pending claims and a notice of allowance of the same.

Respectfully submitted,



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

Freeport, Texas 77541
OKM/okm

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants:	Pak-Wing Steve Chum, et al.		
Serial No.:	08/378,998	Art Unit:	1505
Filed:	January 27, 1995	Examiner:	David Wu
Attorney Docket No:	C-40,121-AB		
For:	FABRICATED ARTICLES MADE FROM ETHYLENE POLYMER BLENDS		

CERTIFICATE OF FACSIMILE TRANSMISSION

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Stacy Lanier

Stacy Lanier

SIGNATURE OF PERSON SIGNING CERTIFICATE

10-18-95

DATE OF SIGNATURE

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

Sir:

SECOND MARKOVICH DECLARATION UNDER 37 CFR § 1.132

Ronald P. Markovich declares and states:

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

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

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

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

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

THAT, he is an inventor as to the above-identified patent application and is therefore familiar with the patent application, the Examiner's Advisory Action thereto, the Examiner Interview Summary Record thereto and the WO '414 reference on which the Examiner relies;

THAT, he performed comparative testing to determine whether compositions representative of the '013 component polymer in WO '414 have any significant long chain branching characteristics as indicated by relatively high critical shear stresses at onset of gross melt fracture;

THAT, he blended at 75.9%/24.1% by weight, 74.4%/25.6% by weight and 73.75%/26.25% by weight two commercially available homogeneously branched linear ethylene interpolymers (supplied by Exxon Chemical Company under the designation Exact 3027 and 3022, respectively) to approximate the melt index and density disclosed in WO '414 for the '013 component polymer. These blends are representative of the '013 component polymer and comparative to the substantially linear ethylene interpolymer component of his inventive composition and are designated Comparative Examples AB1, AB2 and AB3 in the attached Table 1;

THAT, he used a commercially available substantially linear ethylene polymer, Affinity™ PL 1850, supplied by The Dow Chemical Company, and three different substantially linear ethylene interpolymers which were made at the Polyolefins Research Miniplant as representative of the '013 component polymer and of Component A of his inventive composition. The four substantially linear ethylene polymers are designated Component Examples A, B, C and D in the attached Table 1;

THAT, he had Component Examples A, B, C and D as well as Comparative Examples AB1, AB2 and AB3 and Exact 3027 and Exact 3022 tested by gas extrusion rheometry according to the procedure and requirements described in USSN 07/776,130 at page 7, lines 27-34 bridging to page 8, lines 1-4 to determine the critical shear stress at onset of gross melt fracture for each;

THAT, using a commercially available high density polyethylene resin, HDPE 04352N supplied by The Dow Chemical Company, he performed comparative experiments to determine the performance attributes of his inventive blend compositions relative to blend compositions representative of Examples 1 and 2 as disclosed in WO '414;

THAT, to approximate the Banbury and roll mill melt blending procedure described in WO '414 at page 20, lines 4-12, he employed a Haake torque mixer and melt blended various component polymers together with 1000 ppm Irganox 1076 antioxidant and 1000 ppm Irgafos 168 thermal stabilizer at 183°C and 50 rpms for 10 minutes to prepare 200-400 grams each of Inventive Blend Example

AD1, BD1, CD1, AD2, BD2, CD2, AD3, CD3 and ED3 as well as Comparative Blend Example X1, X2, X3 and X4 as listed in the attached Table 2;

THAT, for bulk property comparisons, he compression molded Blend Examples according procedures described in WO '414 at page 20, lines 13-18;

THAT, the preferred test method for compression molded samples having a target thickness of 0.005 inch is ASTM D-882 rather than ASTM D-638 as reported in WO '414 at page 21, Note f of Table 2, in that ASTM D-638 is preferred for target thicknesses greater than 0.04 inch;

THAT, for the nine Inventive Blend Examples and the four Comparative Blend Examples, he performed tensile break strength determinations according ASTM D-882 and intrinsic tear determinations according to ASTM D-1922 and for six Inventive Blend Examples and two Comparative Blend Examples he performed Dynatup total energy impact determinations according to ASTM D-3763-86;

THAT, relative to substantially linear ethylene interpolymers, experimental compositions representative of the '013 component polymer of WO '414 have comparatively low critical shear stresses at onset of gross melt fracture which is indicative of low or, more probably, no long chain branching;

THAT, relative to inventive compositions, blend compositions representative of WO '414 compositions generally have equivalent to inferior tensile break strength and intrinsic tear properties, and preferred inventive compositions have dramatically superior tensile break strength and intrinsic tear properties (toughness) relative to WO '414 compositions;

THAT, although not all impact data (i.e., 50/50 blends) are not currently available due to test difficulties and timing, available impact data clearly indicate that invention compositions have dramatically superior impact performance relative to blends representative of Example 2 of WO '414 (i.e., 75/25 blends);

THAT, specific comparative test results (which also included rheological property comparisons) indicate that the component polymers of WO '414 are completely different from substantially linear ethylene interpolymers in regards to molecular structure and the blend compositions of WO '414 are completely different from the Inventive Blend compositions in regards to toughness and impact resistance properties; and

THAT, the impact properties of our inventive compositions of the above-identified application are unexpected and surprising in that they show substantially higher impact resistance even at slightly higher densities relative to blend compositions representative of WO '414, whereas one skilled in the art would ordinarily expect compositions having higher densities to show inferior impact properties relative to comparative compositions having lower densities.

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

Date 10/18/95

Ronald P. Markovich

Ronald P. Markovich

409 238 0878 P.012/013
DOW CHEMICAL
OCT-18-1995 15:04

Table 1

Sample Designation	A Component Example A	B Component Example B	C Component Example C	D Component Example D	AB1 Comparative Component AB1	AB2 Comparative Component AB2	AB3 Comparative Component AB3	Exact 3027 Comparative Resin	Exact 3022 Comparative Resin
Polymer Type	Substantially Linear Ethylene/ Octene Copolymer	Substantially Linear Ethylene/ Butene Copolymer	Substantially Linear Ethylene/ Octene Copolymer	Substantially Linear Ethylene/ Octene Copolymer	Homogeneously Branched Linear Ethylene/ Butene Copolymer	Homogeneously Branched Linear Ethylene/ Butene Copolymer	Homogeneously Branched Linear Ethylene/ Butene Copolymer	Homogeneously Branched Linear Ethylene/ Butene Copolymer	Homogeneously Branched Linear Ethylene/ Butene Copolymer
Density (g/cc)	0.906	0.9052	0.90575	0.9032	0.9031	0.9033	0.9034	0.9015	0.9065
I2 (g/10 min @ 190°C)	4.01	4.23	3.99	2.70	3.83	3.93	4.19	3.26	8.48
I10 / I2	8.22	7.88	5.82	7.80	5.90	5.69	5.65	5.65	5.49
I10 (g/10 min @ 190°C)	32.96	33.32	23.21	21.05	22.6	22.38	23.64	18.42	46.57
Mw by GPC	68200	67100	77400	72300	79100	80700	77500	85800	65100
Mw/Mn by GPC	2.23	2.12	1.89	2.15	2.15	2.17	2.06	2.00	2.00
Shear Stress @ OSGMF (dyn/cm^2)	> 3.88 x 10^6	> 4.31 x 10^6	> 4.31 x 10^6	gross melt fracture not observed up to 4.41 x 10^6	> 3.45 x 10^6	> 3.45 x 10^6	> 3.45 x 10^6	> 3.45 x 10^6	> 3.23 x 10^6
Shear Stress @ OSGMF (dyn/cm^2)	< 4.09 x 10^6	< 4.48 x 10^6	< 4.48 x 10^6	gross melt fracture not observed	< 3.66 x 10^6	< 3.66 x 10^6	< 3.66 x 10^6	< 3.66 x 10^6	< 3.45 x 10^6

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

Table 2

Sample Designation	AD1 Inventive Blend Example	BD1 Inventive Blend Example	CD1 Inventive Blend Example	X1 Comparative Blend Example	AD2 Inventive Blend Example	BD2 Inventive Blend Example	CD2 Inventive Blend Example	X2 Comparative Blend Example	AD3 Inventive Blend Example	CD3 Inventive Blend Example	ED3 Inventive Blend Example	X3 Comparative Blend Example	X4 Comparative Blend Example
Blend Component													
A	38.48%				72.35%				50.00%				
B		38.14%				71.75%				50.00%			
C			38.48%				72.35%				50.00%		
D				28.95%				53.90%				36.88%	50.00%
EXACT 3027				9.21%				18.50%				13.13%	
EXACT 3022				61.84%				27.60%				50.00%	50.00%
HDPE 04352N	61.54%	61.86%	61.54%		27.65%	28.25%	27.65%		50.00%	50.00%	50.00%		
I2 (g/10 min @ 190°C)	4.11	4.25	4.18	4.13	4.08	4.10	4.04	4.09	4.04	4.07	3.43	4.17	3.74
I10 / I2	7.31	6.98	6.29	6.19	7.67	7.84	5.98	5.84	7.42	6.20	7.33	5.58	6.09
I10 (g/10 min @ 190°C)	30.06	29.59	26.29	25.57	31.29	31.34	24.15	23.87	29.96	25.23	25.13	23.27	22.76
Mw by GPC	74900	74800	77200	83400	71700	73800	77200	80500	71600	78700	78100	80600	79700
Mw/Mn by GPC	2.56	2.53	2.58	2.52	2.47	2.33	2.20	2.27	2.46	2.44	2.46	2.54	2.42
Strain @ Yield	15.0	15.0	14.9	15.0	14.9	15.0	14.8	15.0	15.0	15.1	15.0	14.9	15.0
Break Strength	1835	2070	1921	1801	3187	2253	3268	2729	2188	3655	3050	1652	1539
Break Energy	385	57	509	108	1130	781	991	990	981	1329	1168	249	214
Intrinsic Tear	160	102	221	110	279	107	377	142	224	264	269	116	34
Dynatup (30 Mil Plaque)													
Total Energy	4.03	3.14	4.31	1.35	4.41	3.08	5.59	1.84	NA	NA	NA	NA	NA

NA = not available

RPM/SPC

10/18/95

COVER SHEET FOR FACSIMILE TRANSMISSION FROM THE DOW CHEMICAL COMPANY FREEPORT, TEXAS 77541

TO: Examiner Wu
Fax 703-305-5408

DATE OF TRANSMISSION: October 18, 1995

DOW DOCKET NUMBER: C-40,121-AB

APPLICATION SERIAL NUMBER: 08/378,998

GROUP ART UNIT: 1505

NUMBER OF PAGES OF TRANSMISSION INCLUDING THIS COVER SHEET: 13

NAME OF CONTACT PERSON: Stacy Lanier

TELEPHONE NUMBER FOR CONTACT: (409) 238-7259

PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants:	Pak-Wing Steve Chum, et al.		
Serial No.:	08/378,998	Art Unit:	1505
Filed:	January 27, 1995	Examiner:	David Wu
Attorney Docket No:	C-40,121-AB		

For: FABRICATED ARTICLES MADE FROM ETHYLENE POLYMER BLENDS

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Margaret Greene

SIGNATURE OF PERSON SIGNING CERTIFICATE

10/25/95

DATE OF SIGNATURE

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

Sir:

THIRD RESPONSE AFTER FINAL REJECTION

The following is responsive to the telephone interview held on October 18, 1995 between Applicant's representative, Osborne K. McKinney, and Primary Examiner Wu and also provides a summary record of that interview. Attached herewith are three tables which are intended to summarize the performance data originally presented in Table 2 of the second Declaration under 37 CFR 1.132 from Ronald P. Markovich, a co-inventor of the above-identified application. The second Markovich Declaration was submitted as an attachment to the Second Response After Final Rejection which itself was faxed to the PTO on October 18, 1995.

IN THE CLAIMS

Please amend the following claims:

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

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

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

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

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

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

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

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

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

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

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

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

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

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

(v) a single melting peak as measured using differential scanning calorimetry; 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 greater than or equal to about 1.3.

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

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

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

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

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

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

(iv) no linear [high density] fraction,

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

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

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

32. (Twice amended) 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 linear [high density] fraction,

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

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

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

REMARKS

Claims 1, 17, 31 and 32 were amended to revert back to a "no linear fraction" limitation as responsive to Examiner objection to the "no high density fraction" limitation. Although a "no high density fraction" recitation would be clearer, Applicant believe in the context of TREF analysis and short chain branching distribution, the linear fraction recitation is sufficiently clear. Also, relative to original Claim 17, Claim 17 was amended hereinabove for conformity with Claim 1 by excluding the term "polymer" from the original "no linear polymer fraction" recitation.

Applicants do not believe the amendments to the claims add any new matter. Applicants respectfully request entry of the amendments and reconsideration of Claims 1-8, 17-23, 31 and 32 in view of the following remarks.

Examiner's Rejections

Claims 1-8 and 17-23 remain rejected under 35 USC § 102(b) as anticipated by WO '414 or, in the alternative, under 35 USC § 103 as obvious in view of WO '414 because the no high density fraction limitation presents a new issue and Examiner was unable to confirm whether Applicants have provided truly representative comparisons to the blend compositions of WO '414.

Summary Record

Applicants are, once again, very grateful to Examiner Wu for the telephone interview held on October 18, 1995 between himself and their representative, Osborne K. McKinney.

During the interview, Examiner Wu acknowledged receipt of the Second Response After Final Rejection and the second Markovich Declaration, however, Examiner Wu indicated he was not able to locate the PTO file of the present application.

Examiner Wu objected to the amendments to the claims as pertaining to the no high density fraction recitation. Examiner Wu viewed such amendments as presenting a new issue since no such recitation existed for original claims. McKinney

stated the amendment was necessary because of transcription errors but agreed to exclude the high density fraction recitations.

Applicants' representative Osborne K. McKinney summarized the Second Response After Final Rejection by stating that all of the data agreed to during the personal interview held on October 5, 1995 were not available. That is, impact performance comparative results for 50/50 blend examples (representative of Example 1 of the WO '414 reference) were unavailable due to test difficulties and the short duration of time available. However, McKinney specifically indicated that the Applicants believed that sufficient data were available as proof of the distinction of the inventive examples and, in particular, that data were entirely complete as to and truly representative of Example 2 of the WO '414 reference.

As responsive to these remarks, Examiner Wu indicated that he was not entirely clear as to the conclusions supported by Table 2 of the second Markovich Declaration because of confusing samples designations. McKinney then explained the sample designations and that Table 1 of the second Markovich Declaration pertained to component polymer comparisons and that Table 2 pertained to blend example comparisons. McKinney also indicated that Dynatup total energy determinations are well known as impact performance measurements for molded samples and that tear and tensile break strength performance can be referred to collectively as toughness properties. Finally, McKinney stated that the Applicants believed Table 2 of the second Markovich Declaration clearly demonstrated that inventive examples have similar to dramatically superior tough properties and superior to dramatically superior impact resistance.

Nevertheless, Examiner Wu was unwilling to indicate any agreement as to allowance of the claims because the file for the application was not immediate available and he had another prior commitment.

Applicants' Response

To further aid the Examiner in evaluating the data presented in Table 2 of the second Markovich Declaration, three summary tables are attached wherein performance conclusions are provided based calculated differences between comparative examples and inventive examples. Applicants believe these tables like the first and second Markovich Declarations, prove their inventive compositions are superior to truly representative comparative compositions, especially in regards to impact performance as originally claimed.

Applicants believe that, as of the conclusion of the phone interview held on October 18, 1995, all of the Examiner's rejections and objections had been traversed and the claims were in a condition for allowance. However, Applicants also believe Examiner Wu responded reasonably and responsibly under the circumstance of that interview. As such, Applicants respectfully request that the PTO use its discretion after expiration of the statutory period, consider the circumstances of the October 18, 1995 phone interview and file a notice of allowance as to the Claims 1-8, 17-23, 31 and 32 of the above-identified application.

Respectfully submitted,



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

October 23, 1995
Freeport, Texas 77541
OKM/okm

Dynatup Total Energy Impact Strength
(From Table 2 of Markovich's Second Declaration)

Weight Percent of Polymer Representative of '013	38%	72%
Inventive Examples		
A	4.03 (AD1)	4.41 (AD2)
B	3.14 (BD1)	3.08 (BD2)
C	4.31 (CD1)	5.59 (CD2)
Comparative Example 1	1.35 (X1)	1.84 (X2)
Calculations	Percent Relative Performance of Inventive Examples (Relative to Comparative Example 1) **133-219 % higher**	Percent Relative Performance of Inventive Examples (Relative to Comparative Example 1) **67-204 % higher**
Performance Conclusions - *Inventive Examples are:*	"dramatically superior"	"superior" to "dramatically superior"

NA = not available.
( ) provides the example designation as set forth in Table 2 of the second Markovich Declaration.
"similar" = within 25%; "superior" = 30-80% higher; "dramatically superior" = more than 90% higher

Intrinsic Tear
(From Table 2 of Markovich's Second Declaration)

Weight Percent of Polymer Representative of '013	38%	50%	72%
Inventive Examples			
A	160 (AD1)	224 (AD3)	279 (AD2)
B	102 (BD1)	NA	107 (BD2)
C	221 (CD1)	264 (CD3)	377 (CD2)
E	NA	269 (ED3)	NA
Comparative Examples			
1	110 (X1)	116 (X3)	142 (X2)
2	NA	34 (X4)	NA
Calculations	Percent Relative Performance of Inventive Examples (Relative to Comparative Example 1) 3% less-101% higher	Percent Relative Performance of Inventive Examples (Relative to Comparative Example 1) 93-132 % higher (Relative to Comparative Example 2) 559-891% higher	Percent Relative Performance of Inventive Examples (Relative to Comparative Example 1) 25% less-165% higher
Performance Conclusions - *Inventive Examples are:*	"similar" to "dramatically superior"	"dramatically superior"	"similar" to "dramatically superior"

NA = not available.
( ) provides the example designation as set forth in Table 2 of the second Markovich Declaration.
"similar" = within 25%; "superior" = 30-80% higher; "dramatically superior" = more than 90% higher

Tensile Break Strength
(From Table 2 of Markovich's Second Declaration)

Weight Percent of Polymer Representative of '013	38%	50%	72%
Inventive Examples			
A	1835 (AD1)	2188 (AD3)	3187 (AD2)
B	2070 (BD1)	NA	2253 (BD2)
C	1921 (CD1)	3655 (CD3)	3268 (CD2)
E	NA	3050 (ED3)	NA
Comparative Examples			
1	1801 (X1)	1652 (X3)	2729 (X2)
2	NA	1539 (X4)	NA
Calculations	Percent Relative Performance of Inventive Examples (Relative to Comparative Example 1) 2%-15% higher	Percent Relative Performance of Inventive Examples (Relative to Comparative Example 1) 32-85 % higher (Relative to Comparative Example 2) 42-137% higher	Percent Relative Performance of Inventive Examples (Relative to Comparative Example 1) 18% less-20% higher
Performance Conclusions - *Inventive Examples are*:	"similar"	"superior" to "dramatically superior"	"similar"

NA = not available.
( ) provides the example designation as set forth in Table 2 of the second Markovich Declaration.
"similar" = within 25%; "superior" = 30-80% higher; "dramatically superior" = more than 90% higher

COVER SHEET FOR FACSIMILE TRANSMISSION FROM THE DOW CHEMICAL COMPANY FREEPORT, TEXAS 77541

TO: Examiner Wu
Fax: 703-305-5408

DATE OF TRANSMISSION: October 23, 1995

DOW DOCKET NUMBER: C-40,121-AB

APPLICATION SERIAL NUMBER: 08/378,998

GROUP ART UNIT: 1505

NUMBER OF PAGES OF TRANSMISSION INCLUDING THIS COVER SHEET: 11

NAME OF CONTACT PERSON: Margaret Greene

TELEPHONE NUMBER FOR CONTACT: (409) 238-2265

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

SERIAL NUMBER	FILING DATE	FIRST NAMED APPLICANT	ATTORNEY DOCKET NO.
08/378,998	01/27/95	CHUM P	C-40,121-AB

EXAMINER	
WU, D	
ART UNIT	PAPER NUMBER
1505	17

15M2/1026

THE DOW CHEMICAL COMPANY
PATENT DEPARTMENT B 1211
2301 NORTH BRAZOSPORT BLVD
FREEPORT TX 77541

DATE MAILED: 10/26/95

Below is a communication from the EXAMINER in charge of this application

COMMISSIONER OF PATENTS AND TRADEMARKS

ADVISORY ACTION

☐ THE PERIOD FOR RESPONSE:

a) ☒ is extended to run 6 months or continues to run _____ from the date of the final rejection

b) ☐ expires three months from the date of the final rejection or as of the mailing date of this Advisory Action, whichever is later. In no event however, will the statutory period for the response expire later than six months from the date of the final rejection.

Any extension of time must be obtained by filing a petition under 37 CFR 1.136(a), the proposed response and the appropriate fee. The date on which the response, the petition , and the fee have been filed is the date of the response and also the date for the purposes of determining the period of extension and the corresponding amount of the fee. Any extension fee pursuant to 37 CFR 1.17 will be calculated from the date of the originally set shortened statutory period for response or as set forth in b) above.

☐ Appellant's Brief is due in accordance with 37 CFR 1.192(a).

☒ Applicant's response to the final rejection, filed 10-18-95 has been considered with the following effect, but it is not deemed to place the application in condition for allowance:

1. ☐ The proposed amendments to the claim and /or specification will not be entered and the final rejection stands because:

   a. ☒ There is no convincing showing under 37 CFR 1.116(b) why the proposed amendment is necessary and was not earlier presented.

   b. ☒ They raise new issues that would require further consideration and/or search. (See Note).

   c. ☐ They raise the issue of new matter. (See Note).

   d. ☐ They are not deemed to place the application in better form for appeal by materially reducing or simplifying the issues for appeal.

   e. ☐ They present additional claims without cancelling a corresponding number of finally rejected claims.

   NOTE: The recitation "high density" in claims 1, 17, and 31-32 raises a new issue. In addition, in line 12 of claims 1 and 31, line 11 of claim 32, "10 g/min" should be --- 10 gm/10min ---.

2. ☐ Newly proposed or amended claims _____ would be allowed if submitted in a separately filed amendment cancelling the non-allowable claims.

3. ☒ Upon the filing an appeal, the proposed amendment ☐ will be entered ☒ will not be entered and the status of the claims will be as follows:

   Claims allowed: None
   Claims objected to: None
   Claims rejected: 1-8 and 7-23

   However;

   ☐ Applicant's response has overcome the following rejection(s): _____

4. ☒ The affidavit, ~~exhibit or~~ request for reconsideration has been considered but does not overcome the rejection because in the 2nd Markovich Declaration, there is no impact properties comparison for 50/50 blends ; as to 72/28 blend, the toughness property of comparative run is not necessarily inferior to that of the inventive run, e.g. X2 v. 802 and X, v. 801.

5. ☐ The affidavit or exhibit will not be considered because applicant has not shown good and sufficent reasons why it was not earlier presented.

☐ The proposed drawing correction ☐ has ☐ has not been approved by the examiner.

☐ Other

David Wu

DAVID W. WU
PRIMARY EXAMINER
GROUP 1500

PTOL-303 (REV. 5-89)

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

SERIAL NUMBER	FILING DATE	FIRST NAMED APPLICANT	ATTORNEY DOCKET NO.
08/378,998	01/27/95	CHUM P	C-40,121-AB

15M2/1026

THE DOW CHEMICAL COMPANY
PATENT DEPARTMENT B 1211
2301 NORTH BRAZOSPORT BLVD
FREEPORT TX 77541

EXAMINER	
WU, D	
ART UNIT	PAPER NUMBER
1505	18

DATE MAILED: 10/26/95

Below is a communication from the EXAMINER in charge of this application

COMMISSIONER OF PATENTS AND TRADEMARKS

ADVISORY ACTION

☐ THE PERIOD FOR RESPONSE:

a) ☒ is extended to run 6 months or continues to run _____ from the date of the final rejection

b) ☐ expires three months from the date of the final rejection or as of the mailing date of this Advisory Action, whichever is later. In no event however, will the statutory period for the response expire later than six months from the date of the final rejection.

Any extension of time must be obtained by filing a petition under 37 CFR 1.136(a), the proposed response and the appropriate fee. The date on which the response, the petition , and the fee have been filed is the date of the response and also the date for the purposes of determining the period of extension and the corresponding amount of the fee. Any extension fee pursuant to 37 CFR 1.17 will be calculated from the date of the originally set shortened statutory period for response or as set forth in b) above.

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1. ☐ The proposed amendments to the claim and /or specification will not be entered and the final rejection stands because:

   a. ☒ There is no convincing showing under 37 CFR 1.116(b) why the proposed amendment is necessary and was not earlier presented.

   b. ☒ They raise new issues that would require further consideration and/or search. (See Note).

   c. ☐ They raise the issue of new matter. (See Note).

   d. ☐ They are not deemed to place the application in better form for appeal by materially reducing or simplifying the issues for appeal.

   e. ☐ They present additional claims without cancelling a corresponding number of finally rejected claims.

   NOTE: The recitation "high density" in claims 1, 17, and 31-32 raises a new issue. In addition, in line 12 of claims 1 and 31, line 11 of claim 32, "10 g/min" should be --- 10 gm/10min ---.

2. ☐ Newly proposed or amended claims _____ would be allowed if submitted in a separately filed amendment cancelling the non-allowable claims.

3. ☒ Upon the filing an appeal, the proposed amendment ☐ will be entered ☒ will not be entered and the status of the claims will be as follows:

   Claims allowed: None
   Claims objected to: None
   Claims rejected: 1-8 and 17-23

   However;

   ☐ Applicant's response has overcome the following rejection(s): _____

4. ☒ The affidavit, ~~exhibit or~~ request for reconsideration has been considered but does not overcome the rejection because in the 2nd Markevich Declaration, there is no impact properties comparison for 50/50 blends ; as to 72/28 blend, the toughness property of comparative run is not necessarily inferior to that of the inventive run, e.g. X2 v. B02 and X1 v. B01.

5. ☐ The affidavit or exhibit will not be considered because applicant has not shown good and sufficent reasons why it was not earlier presented.

☐ The proposed drawing correction ☐ has ☐ has not been approved by the examiner.

☐ Other

David Wu
DAVID W. WU
PRIMARY EXAMINER
GROUP 1500

PTOL-303 (REV. 5-89)

#22

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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(List continued on next page.)

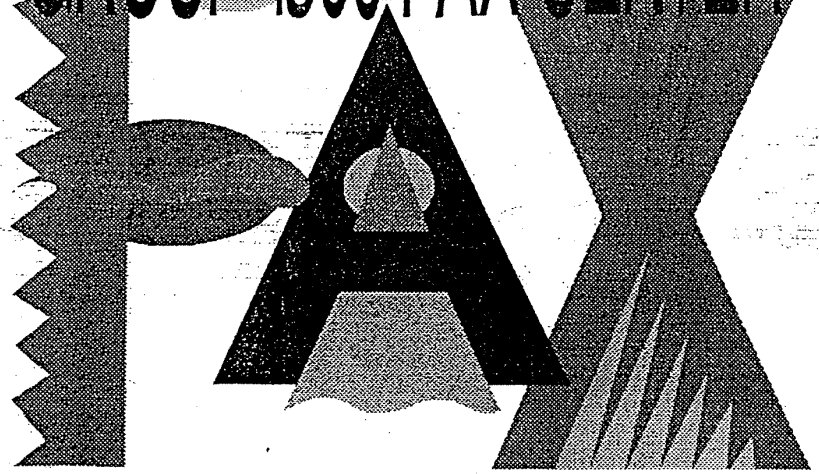
Primary Examiner—David W. Wu

[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

GROUP 1500 FAX CENTER



To: Mr. Osborne K. McKinney

From: David Wu

Faxed
11/7/95
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Date: 11-7-95

Fax #: 409-238-0878

Total pages including cover: 2

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1505

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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant(s): Pak-Wing Steve Chum et al.

Serial No.: 08/378,998 Group Art Unit: 1505

Filed: January 27, 1995 Examiner: D. Wu

For: FABRICATED ARTICLES MADE FROM ETHYLENE POLYMER BLENDS

RECEIVED
NOV 3 1995

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

October 18, 1995

DATE OF DEPOSIT Stephen P. Wapp

Stacy Lanier

PRINT OR TYPE NAME OF PERSON SIGNING CERTIFICATE

Stacy Lanier Stephen P. Wapp

SIGNATURE OF PERSON SIGNING CERTIFICATE

10-18-95

DATE OF SIGNATURE

#19

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

Sir:

SUPPLEMENTAL INFORMATION DISCLOSURE STATEMENT

Pursuant to Applicant's duty of disclosure under 37 CFR §1.56, the Examiner's attention is directed to the information identified in the attached Form PTO-1449.

No item of information contained herein was cited in a communication from a foreign patent office in a counterpart foreign application or, to the knowledge of the undersigned after making reasonable inquiry, was known to any individual designated in 37 CFR §1.56(c) more than three (3) months prior to the filing date hereof.

A copy of all cited patents and printed publications is enclosed. The Examiner is requested to review each reference and formulate his own understanding thereof.

Respectfully submitted,

Osborne K. McKinney
Registration No. P-40,084
Address: Bldg. B-1211
Freeport, Texas 77541
Phone: 409-238-7889

Dated: October 18, 1995

OKM/alb

Sheet 1 of 1

FORM PTO 1449 (modified)	Atty. Docket No. C-40,121-AB	Serial No. 08/378,998
LIST OF REFERENCES CITED BY APPLICANT	Applicant: Pak-Wing Steve Chum et al.	
	Filing Date: 01-27-95	Group: 1505

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Examiner Initial		Document Number	Date	Name	Class	Sub-class	Filing Date If Appropriate
	AA	5,374,700	12-20-94	Tsutsui et al.	526	348.3	
	AB						
	AC						
	AD						
	AE						
	AF						
	AG						
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FOREIGN PATENT DOCUMENTS

		Document Number	Date	Country	Class	Sub-class	Translation	
	BA							
	BB							
	BC							
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	BE							

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	C B		
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United States Patent [19]

Tsutsui et al.

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[45] Date of Patent: Dec. 20, 1994

[54] ETHYLENE COPOLYMER

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[21] Appl. No.: 686,599

[22] Filed: Apr. 17, 1991

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May 14, 1990 [JP] Japan 2-123858
Aug. 8, 1990 [JP] Japan 2-211334

[51] Int. Cl.[5] C08F 210/16; C08F 4/602

[52] U.S. Cl. 526/348.3; 526/128; 526/129; 526/160; 526/348; 526/348.2; 526/348.5; 526/348.6; 526/904

[58] Field of Search 526/160, 348, 348.5, 526/348.6, 348.2, 348.3, 904, 128

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Primary Examiner—Fred Teskin
Attorney, Agent, or Firm—Sherman and Shalloway

[57] ABSTRACT

The present invention provides an ethylene copolymer comprising constituent units (a) derived from ethylene and constituent units (b) derived from an α-olefin having 3 to 20 carbon atoms, the ethylene copolymer being characterized in that

(A) the ethylene copolymer has a density (d) of 0.86 to 0.95 g/cm^3;

(B) the ethylene copolymer has a MFR of 0.001 to 50 g/10 min as measured at a temperature of 190° C. and a load of 2.16 kg;

(C) the melt tension (MT) and MFR of the ethylene copolymer satisfy the relation

$$\log MT > -0.66 \log MFR + 0.6; \text{ and}$$

(D) the temperature (T) at which the exothermic curve of the ethylene copolymer measured by a differential scanning calorimeter (DSC) shows the highest peak and the density (d) satisfy the relation

$$T < 400d - 250.$$

2 Claims, 3 Drawing Sheets

FIG. 1

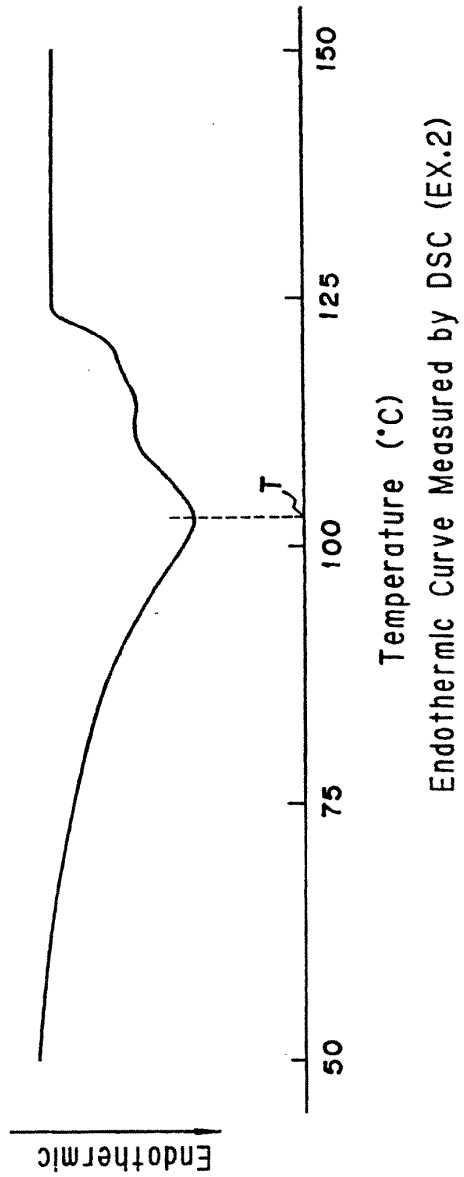

Endothermic
50
75
100
125
150
T
Temperature (°C)
Endothermic Curve Measured by DSC (EX.2)

FIG. 2

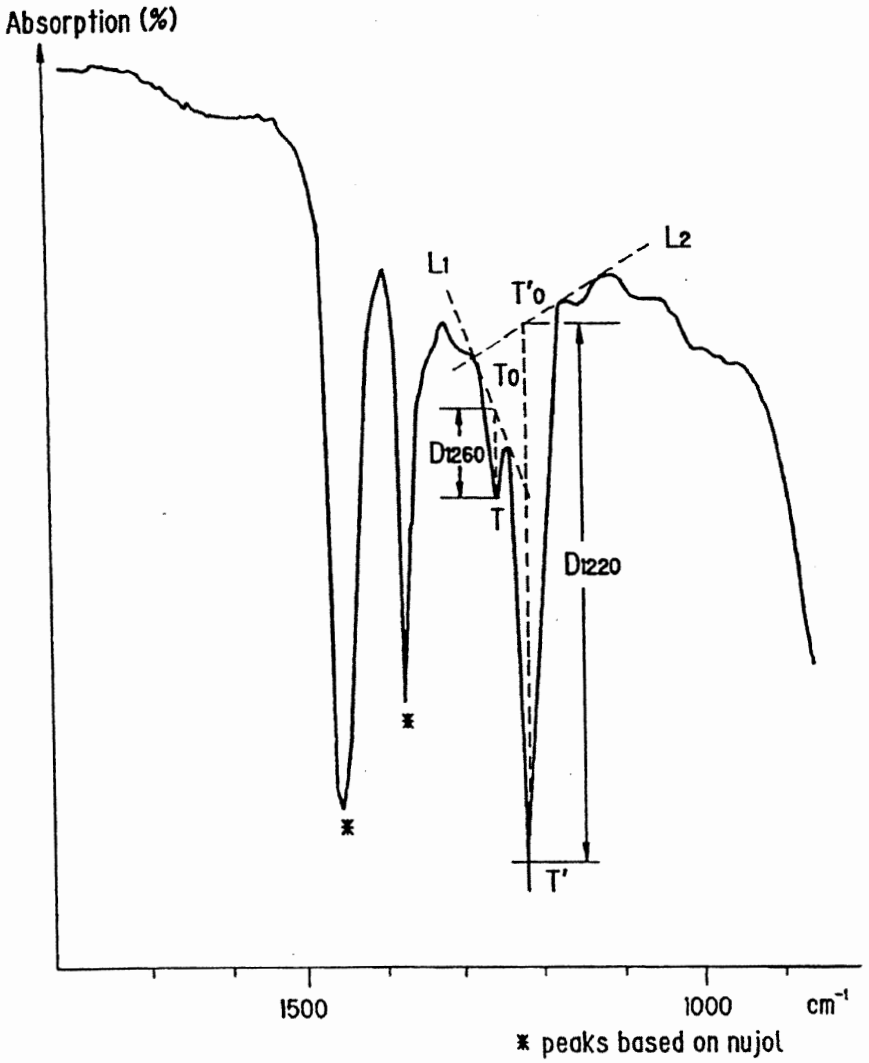
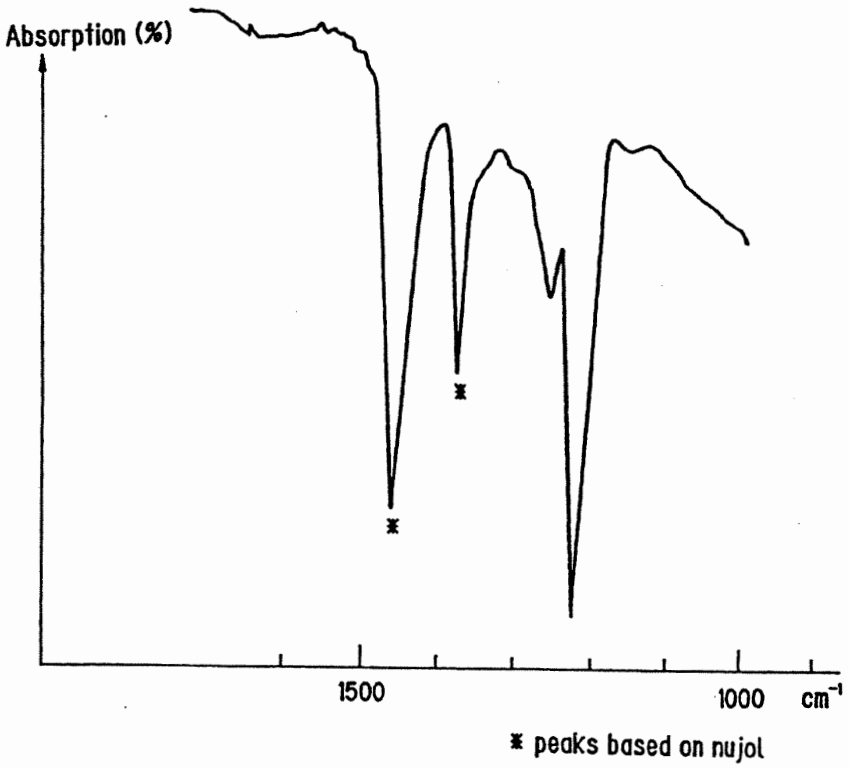

Absorption (%)
L1
L2
T'o
To
D1260
T
D1220
T'
1500
1000
cm-1
* peaks based on nujol

FIG. 3



ETHYLENE COPOLYMER

FIELD OF THE INVENTION

The present invention relates to a novel ethylene copolymer, more particularly to a novel ethylene copolymer having a narrow composition distribution and an excellent melt tension compared with known ethylene copolymers.

Furthermore, the present invention relates to a process for the preparation of an olefin polymer, especially an ethylene polymer, more particularly to a process for the preparation of an ethylene polymer being excellent in melt tension, and, in the case of a copolymer, having a narrow composition distribution.

Still furthermore, the present invention relates to a solid catalyst for olefin polymerization and a process for olefin polymerization using the catalyst, more particularly to a solid catalyst for olefin polymerization applicable to process for suspension polymerization and a process for gas phase polymerization, capable of producing, with high polymerization activities, a sphere olefin polymer excellent in particle properties when applied to these polymerization processes with use of an organoaluminum oxy-compound in a decreased amount, and excellent in melt tension, and a process for olefin polymerization using the catalyst.

BACKGROUND OF THE INVENTION

Ethylene copolymers have heretofore been molded by various molding methods, and used in many fields. The requirement for the characteristics of the ethylene copolymers differ depending on the molding methods ant uses. For example, when an inflation film is molded at a high speed, it is necessary to select an ethylene copolymer having a high melt tension compared with its molecular weight in order to stably conduct high speed molding without fluctuation or tearing of bubbles. An ethylene copolymer is required to have similar characteristics in order to prevent sag or tearing in blow molding, or to suppress width shortage to the minimum range in T-die molding.

A high-pressure low density polyethylene has a high meat tension compared with an ethylene copolymer prepared with a Ziegler type catalyst, and is used as a material for films and hollow containers. The high-pressure low density polyethylene as described above has low mechanical strength such as tensile strength, tear strength and impact strength, and in addition it has also low heat resistance, low stress cracking resistance, etc.

On the other hand, Japanese Patent L-O-P Nos. 90810/1981 and 106806/1985 propose a method for improving the melt tension and blow ratio (die/swell ratio) of ethylene polymers obtained by using Ziegler type catalysts, especially a titanium type catalyst.

The ethylene polymers obtained by using a titanium catalyst, however, especially the low density ethylene polymers generally have problems such as their broad composition distribution and stickiness of their molded articles such as films.

Accordingly, the advent of ethylene polymers having an excellent melt tension and a narrow composition distribution will industrially be of great value.

There has recently been developed a new Ziegler type catalyst for olefin polymerization comprising a zirconium compound and an aluminoxane, said catalyst being capable of producing ethylene/α-olefin copolymers with high polymerization activities. There has also

been proposed a process for the preparation of ethylene/α-olefin copolymers using such a new type catalyst.

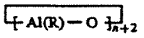
For example, Japanese Patent L-O-P No. 19309/1983 discloses a process for polymerizing ethylene with one or at least two C_3–C_{12} α-olefins at a temperature of −50° to 200° C., in the presence of a catalyst composed of a transition metal compound represented by the formula

(cyclopentadienyl)$_2$Me R Hal

wherein R is cyclopentadienyl, C_1–C_6 alkyl or halogen, Me is a transition metal and Hal is halogen, and a linear aluminoxane represented by the formula

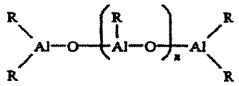
$Al_2OR_4[Al(R)—O]_n$

wherein R is methyl or ethyl, and n is a number of 4 to 20, or a cyclic aluminoxane represented by the formula

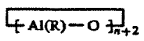


wherein R and n are as defined above.

Japanese Patent L-O-P No. 19309/1983 discloses an invention relating to processes for preparing a linear aluminoxane represented by the formula

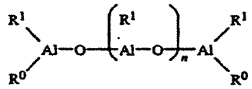


wherein n is a number of 2 to 40, and R is C_1–C_8 alkyl, and a cyclic aluminoxane represented by the formula



wherein n and R are as defined above. The same Patent Publication also discloses a process for the polymerization of olefin using a catalyst prepared by mixing, for example, methylaluminoxane prepared by the above-mentioned process and a bis(cyclopentadienyl) compound of titanium or zirconium.

Japanese Patent L-O-P No. 35005/1985 discloses a process for preparing an olefin polymerization catalyst, wherein the process comprises reacting an aluminoxane represented by the formula

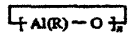


wherein R^1 is C_1–C_{10} alkyl, and R^O is R^1 or R^O represents —O— by linkage, with a magnesium compound at first, then chlorinating the reaction product, and treating with a compound of Ti, V, Zr or Cr.

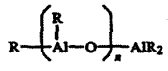
Japanese Patent L-O-P No. 35006/1985 discloses a catalyst composed of mono- di- or tricyclopentadienyl-transition metals (a) (transition metals being at least two different metals) or their derivatives and an alumoxane

(aluminoxane) in combination. Example 1 of this Patent publication discloses that ethylene and propylene are polymerized to form a polyethylene in the presence of a catalyst composed of bis(pentamethylcyclopentadienyl)zirconiumdimethyl and an aluminoxane. In Example 2 of this Patent publication, ethylene and propylene are polymerized to form a polymer blend of a polyethylene and an ethylene/propylene copolymer in the presence of a catalyst composed of bis(pentamethylcyclopentadienyl)zirconiumdichloride, bis(methylcyclopentadienyl)zirconium dichloride and an alumoxane.

Japanese Patent L-O-P No. 35007/1985 discloses a process wherein ethylene alone is polymerized, or ethylene and an α-olefin of not less than 3 carbon atoms are copolymerized in the presence of metallocene, and a cyclic aluminoxane represented by the formula



wherein R is an alkyl group of 1 to 5 carbon atoms, and n is an integer of 1 to about 20, or a linear aluminoxane represented by the formula



wherein R and n are as defined above.

Japanese Patent L-O-P No. 35008/1985 discloses a process for the preparation of a polyethylene or a copolymer of ethylene and a C_3–C_{10} α-olefin, wherein a catalyst system comprising not less than two types of metallocene and an alumoxane is used.

Though the catalysts formed from a transition metal compound and an aluminoxane proposed by the prior art are excellent in polymerization activities, especially ethylene polymerization activities compared with those catalysts having been known prior to the appearance of these catalysts and formed from a transition metal compound and an organolauminum compound, most of the catalysts are soluble in the reaction system, and in most cases the processes for the preparation are limited to a solution polymerization system. In addition, the catalysts have such a problem that the productivity of a polymer is lowered due to a marked increase in the viscosity of the polymer-containing reaction solution when the manufacture of a polymer having a high molecular weight is tried, that the polymer obtained by after-treatment of polymerization has a low bulk specific gravity, and that the preparation of a sphere polymer having excellent particle properties is difficult.

On the other hand, polymerization of olefin has been tried in a suspension polymerization system or a gas phase polymerization system by using catalysts in which at least one of the transition metal compound component and the aluminoxane component described above is supported on a porous inorganic oxide carrier such as silica, alumina and silica-alumina.

For example, Japanese Patent L-O-P Nos. 35006/1985, 35007/1985 and 35008/1985 described above disclose that there can be used catalysts in which a transition metal compound and an aluminoxane are supported on silica, alumina, silica-alumina, etc.

Furthermore, Japanese Patent L-O-P Nos. 106808/1985 and 106809/1985 disclose a process for the preparation of a composition composed of an ethylene polymer and a filler, which process comprises polymerizing ethylene or copolymerizing ethylene and α-olefin in the presence of a product prepared by contacting a highly activated catalyst component comprising a hydrocarbon-soluble titanium compound and/or a zirconium compound with a filler, an organoaluminum compound and a filler having an affinity for polyolefin.

Japanese Patent L-O-P No. 31404/1986 discloses a process for polymerizing ethylene or copolymerizing ethylene and an α-olefin in the presence of a catalyst mixture composed of a transition metal compound and a product obtained by the reaction of trialkylaluminum and water in the presence of silicon dioxide or aluminum oxide.

Furthermore, Japanese Patent L-O-P No. 276805/1986 discloses that olefin is polymerized in the presence of a catalyst composed of a zirconium compound and a reaction mixture obtained by reacting an aluminoxane with trialkylaluminum at first, and further by reacting the resultant reaction mixture with such an inorganic oxide having a hydroxide group on the surface as silica.

Still furthermore, Japanese Patent L-O-P Nos. 108610/1986 and 296008/1986 discloses a process for polymerizing olefin in the presence of a catalyst in which a transition metal compound such as metallocene and an aluminoxane are supported on a carrier such as an inorganic oxide.

However, during the polymerization or copolymerization of olefin in a suspension or gas phase by using such a solid catalyst component supported on a carrier as described in the above-mentioned Patent publns., the catalyst component considerably lowers the polymerization activities compared with the above-described solution polymerization, and the resulting polymers do not have a satisfactory bulk density.

OBJECT OF THE INVENTION

The present invention is intended to solve such problems associated with the prior art technique as described above, and an object of the invention is to provide an ethylene copolymer being excellent in melt tension and having a narrow composition distribution.

Another object of the present invention is to provide a process for the preparation of ethylene polymers being excellent in melt tension, and, in the case of a copolymer, having a narrow composition distribution.

A still further object of the invention is to provide solid catalysts for olefin polymerization capable of manufacturing with high activities sphere olefin polymers excellent in particle properties and melt tension even when they are applied to suspension polymerization and gas phase polymerization with an organoaluminum oxy-compound used not in a large quantity, and to carry out olefin polymerization by using such catalysts having good properties.

SUMMARY OF THE INVENTION.

The ethylene copolymer according to the present invention is an ethylene copolymer comprising constituent units (a) derived from ethylene and constituent units (b) derived from an (α-olefin having 3 to 20 carbon atoms, and is characterized in that:

(A) the ethylene copolymer has a density (d) of 0.86 to 0.95 g/cm^3;

(B) the ethylene copolymer has a MFR of 0.001 to 50 g/10 min as measured at a temperature of 190° C. and a load of 2.16 kg;

(C) the melt tension (MT) and MFR of the ethylene copolymer satisfy the relation

$$\log MT > -0.66 \log MFR + 0.6; \text{ and}$$

(D) the temperature (T) at which the endothermic curve of the ethylene copolymer measured by a differential scanning calorimeter (DSC) shows the highest peak and the density (d) satisfy the relation

$$T < 400d - 250.$$

Furthermore, a first process for the preparation of an olefin polymer according to the present invention comprises polymerizing olefin in the presence of a solid catalyst formed from

(A) a compound of a transition metal in Group IVB of a periodic table, having at least two groups each having a cyclopentadienyl skeleton, said at least two groups being crosslinked through a group containing carbon and/or silicon, and

(B) an organoaluminum oxy-compound, and under the condition that the produced polymer exists in a solid state in the polymerization system, to form an olefin polymer satisfying the following conditions:

a) the olefin polymer has a MFR of 0.001 to 100 g/10 min at a temperature of 190° C. and a load of 2.16 kg; and

b) the melt tension (MT) and MFR of the olefin polymer satisfy the relation

$$\log MT > -0.66 \log MFR + 0.6.$$

A first prepolymerized polyolefin-containing solid catalyst (hereinafter refer to prepolymerized solid catalyst) for olefin polymerization according to the present invention is characterized in that the solid catalyst is formed by prepolymerizing olefin in a suspension or a gas phase in the presence of a catalyst comprising

[A] a fine particle carrier,

[B] a transition metal compound (designated as a non-bridge type transition metal compound hereinafter) comprising ligands having a cyclopentadienyl skeleton, the cyclopentadienyl skeletons being not bonded mutually,

[C] a transition metal compound (designated as a bridge type metal compound) comprising at least two ligands each having a cyclopentadienyl skeleton, said at least two ligands being bonded together through an alkylene group, a substituted alkylene group, a silylene group or a substituted silylene group, and

[D] an organoaluminum oxy-compound.

A second olefin polymerization catalyst according to the present invention is characterized in that the olefin polymerization catalyst is formed from the above-described components [A], [B], [C] and [D], and [E] an organoaluminum compound.

Furthermore, a second process for the preparation of olefin polymer according to the present invention comprises polymerizing or copolymerizing olefin in the presence of the solid catalyst as described above.

BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 shows an endothermic curve obtained by measuring heat absorption of an ethylene copolymer (prepared in Example 2) of the invention using a DSC (differential scanning calorimeter).

FIG. 2 is an example of an IR spectrum of an organoaluminum oxy-compound of the invention.

FIG. 3 is an example of an IR spectrum of a known benzene-soluble organoaluminum oxy-compound.

DETAILED DESCRIPTION OF THE INVENTION

First, the ethylene copolymer according to the present invention is concretely illustrated below.

The ethylene copolymer according to the invention is a random copolymer of ethylene with an α-olefin having 3 to 20 carbon atoms. The ethylene copolymer has a density (d) of 0.86 to 0.95 g/cm^3, preferably 0.87 to 0.94 g/cm^3, more preferably 0.88 to 0.93 g/cm^3.

The density is determined by means of a density gradient tube using the strand, which has been obtained at the time of MFR measurement at 190° C. under a load of 2.16 kg, and which is heat treated by heating at 120° C. for 1 hour and slowly cooling to room temperature over a period of 1 hour.

The ethylene copolymer as described above desirably comprises constituent units (a) derived from ethylene in an amount of 55 to 99% by weight, preferably 65 to 98% by weight, more preferably 70 to 96% by weight, constituent units (b) derived from an α-olefin having 3 to 20 carbon atoms in an amount of 1 to 45% by weight, preferably 2 to 35% by weight, more preferably 4 to 30% by weight.

The composition of the copolymer is usually determined by ^{13}C-NMR spectrum analysis of a sample prepared by uniformly dissolving 200 mg of the copolymer in 1 ml of hexachlorobutadiene in a sample tube having a diameter of 10 mm under the following conditions: a measuring temperature of 120° C., a measuring frequency of 25.05 MHz, a spectrum width of 1500 Hz, a pulse repetition period of 4.2 sec and a pulse width of 6 μsec.

Examples of the α-olefin having 3 to 20 carbon atoms include propylene, 1-butene, 1-pentene, 1-hexene, 4-methyl-1-pentene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene and 1-eicosene.

The ethylene copolymer according to the present invention desirably has a MFR of 0.001 to 50 g/10 min, preferably 0.01 to 20 9/10 min.

The determination of the MFR is carried out in accordance with ASTM D1238-65T, under the conditions of a temperature at 190° C. and a load at 2.16 kg.

Furthermore, the melt tension (MT) and MFR of the ethylene copolymer of the invention satisfy the following relation:

$$\log MT > -0.66 \log MFR + 0.6, \text{ preferably}$$

$$\log MT > -0.66 \log MFR + 0.7, \text{ more preferably}$$

$$\log MT > -0.66 \log MFR + 0.8.$$

As described above, the ethylene copolymer of the invention is excellent in melt tension (MT), and has good moldability.

In addition, the melt tension (MT) is determined by measuring the stress of a molten copolymer while the molten copolymer is being stretched at a constant rate. That is, a produced copolymer powder or a polymer obtained by once dissolving the copolymer powder in

decane, and pouring the solution into a methanol/acetone (1/1) solution in an amount 5 times as much as that of decane to be precipitated is used as a sample to be measured. The measurement is carried out by extruding the sample at a resin temperature of 190° C., an extrusion rate of 10 mm/min and a take-up rate of 10 to 20 m/min using a MT measuring apparatus (manufactured by Toyo Seiki Seisakusho K. K.) having a nozzle diameter of 2.09 mm and a nozzle length of 8 mm. During the measurement of melt tension, the ethylene copolymer is premixed with 0.1% by weight of 2,6-di-tert-butyl-p-cresol as a crosslinking stabilizer.

Furthermore, in the ethylene copolymer of the invention, the temperature (T) at which its endothermic curve measured by a differential scanning calorimeter (DSC) shows the highest peak, and its density (d) satisfy the following relation:

$T < 400d - 250$, preferably

$T < 450d - 297$, more preferably

$T < 500d - 344$, particularly preferably

$T < 550d - 391$.

In addition, measurement by DSC was carried out using a DSC-7 type apparatus manufactured by Perkin Elmer Co., Ltd. The temperature (T) at which the endothermic curve shows the maximum peak is sought from an endothermic curve obtained by filling about 5 mg of a sample in an aluminum pan, heating to 200° C. at a rate of 10° C./min, holding the sample at 200° C. for 5 minutes, lowering the temperature to room temperature at a rate of 20° C./min, and then heating at a rate of 10° C./min.

In the ethylene copolymer of the invention, it is desirable that the quantity fraction (W) of a n-decane-soluble component and the density of the copolymer at 23° C. satisfy the following relation:

$\log W < -50d + 46.5$, preferably

$\log W < -50d + 46.4$, more preferably

$\log W < -50d + 46.3$.

It may be concluded from the relation between the temperature (T) and density (d), and the relation between the quantity fraction (W) of a n-decane-soluble component and density (d) that the ethylene copolymer of the present invention has a narrow composition distribution.

Moreover, the n-decane-soluble component quantity is obtained by a procedure described below.

Measurement of the n-decane-soluble component quantity (polymer having a smaller soluble component quantity has a narrower composition distribution) is carried out by adding 3 g of the copolymer to 450 ml of n-decane, dissolving the copolymer at 145° C., cooling the solution to 23° C., removing a n-decane-insoluble component by filtering, and recovering a n-decane-soluble component from the filtrate.

The ethylene copolymer according to the present invention having characteristics as described above can be prepared, for example, by copolymerizing ethylene with an α-olefin having 3 to 20 carbon atoms in the presence of a catalyst formed from

(i) a catalyst component obtained by the reaction of a bidentate compound in which two groups selected from negatively ionized indenyl groups or substituents thereof are bonded together through a group containing carbon and/or silicon such as a lower alkylene group and a halide of a transition metal in Group IVB of the periodic table, (the catalyst component is the substantially same as a transition metal compound comprising at least two ligands each having a cyclopentadienyl skelton, said at least two ligands being bonded together through a group containing carbon and/or silicon such as a lower alkylene group)

(ii) an organoaluminum oxy-compound,

(iii) an organoaluminum compound, and

(iv) a carrier, so that the thus obtained copolymer has a density of 0.86 to 0.95 g/cm^3.

In the catalyst component (i) in the invention, the bidentate compound (i—1) having two groups selected from negatively ionized indenyl groups or their substituents, which are bonded together through a group containing carbon and/or silicon such as a lower alkylene group, is represented by the formula

$$MR^1—R^2—R^3M$$

wherein R^1 and R^3 are each an indenyl anion, a substituted indenyl anion or a partially hydrogenated anion of either of these anions, R^1 and R^3 may be the same or different, R^2 is a lower alkylene group, and M is an alkali metal cation. Concrete examples of the bidentate compound (i—1) include ethylenebisindenylidilithium, ethylenebisindenylidisodium ethylenebis (4,5,6,7-tetrahydro-1-indenyl)dilithium, ethylenebis(4-methyl-1-indenyl)dilithium, ethylenebis(5-methyl-1-indenyl)dilithium, ethylenebis(6-methyl-1-indenyl)dilithium and ethylenebis(7-methyl-1-indenyl)dilithium.

Concrete examples of the halide (i-2) of a transition metal in Group IVB of the perodic table include zirconium tetrachloride, hafnium tetrachloride, titanium tetrachloride and titanium tetrabromide.

The catalyst component (i) of the invention is prepared by mixing and contacting such a bidentate compound as described above with such a transition metal compound and halide as described above in an organic solvent such as ether, tetrahydrofuran, benzene, toluene and methylene dichloride. During the preparation, the mixing molecular ratio ($MR^1—R^2—R^3M$/transition metal) of the bidentate compound (i-1) to the halide (i2) of a transition metal is 0.5 to 2, preferably 0.75 to 1.25, and the concentration of the transition metal is usually 0.03 to 0.5 mol/l, preferably 0.05 to 0.3 mol/l.

Next, the organoaluminum oxy-compound (ii) is explained below.

The organoaluminum oxy-compound (ii) may be a known aluminoxane or the benzene-insoluble organoaluminum oxy-compound having been discovered by the present inventors.

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

(1) a procedure for recovering an aluminoxane as its hydrocarbon solution which comprises adding an organoaluminum compound such as trialkylaluminum to a suspension in a hydrocarbon medium of a compound containing adsorbed water, or a salt containing water of crystallization such as magnesium chloride hydrate, copper sulfate hydrate, aluminum sulfate hydrate, nickel sulfate hydrate and cerous chloride hydrate, and reacting the organoaluminum compound; and

(2) a procedure for recovering an aluminoxane as its hydrocarbon solution which comprises reacting water, ice or steam directly with an organoaluminum compound such as trialkylaluminum in a solvent such as benzene, toluene, ethyl ether and tetrahydrofuran.

Moreover, the aluminoxane may contain a small amount of an organometal component. Furthermore, the solvent or unreacted organoaluminum compound may be removed from the above-mentioned recovered aluminoxane-containing solution, by distillation, and the aluminoxane may be redissolved in a solvent.

Concrete examples of the organoaluminum compound used for the preparation of the aluminoxane include

trialkylaluminum such as trimethylaluminum, triethylaluminum, tripropylaluminum, triisopropylaluminum, tri-n-butylaluminum, triisobutylaluminum, tri-sec-butylaluminum, tri-tert-butylaluminum, tripentylaluminum, trihexylaluminum, trioctylaluminum, tridecylaluminum, tricyclohexylaluminum and 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 these compounds, trialkylaluminum is particularly preferable.

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 $z \geqq 2x$.

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

Solvents used for the solutions of the aluminoxane include aromatic hydrocarbons such as benzene, toluene, xylene, cumene and cymene; aliphatic hydrocrbons 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; and halogenated compounds derived from the above-mentioned aromatic hydrocarbons, aliphatic hydrocarbons and alicyclic hydrocarbons, especially chlorinated and brominated hydrocarbons.

In addition, there may also be used ethers such as ethyl ether and tetrahydrofuran. Of these solvents as exemplified above, aromatic hydrocarbons are particularly preferred.

The benzene-insoluble organoaluminum oxy-compounds used in the invention contain an Al component soluble in benzene at 60° C. in an amount of not greater than 10%, preferably not greater than 5%, particularly preferably not greater 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, mixing the resulting suspension at 60° C. for 6 hours with stirring, filtering the resulting mixture with a G-5 glass filter equipped with a jacket kept at 60° C., washing 4 times the solid portion separated on the filter with 50 ml of benzene at 60° C., and measuring the amount (x mmole) of Al atoms present in the whole filtrate.

When the benzene-insoluble organoaluminum oxy-compounds as described above of the present invention are analyzed by infrared spectrophotometry (IR), a ratio (D_{1260}/D_{1220}) of an absorbance (D_{1260}) at about 1260 cm^{-1} to an absorbance (D_{1220}) at about 1220 cm^{-1} is preferably not greater than 0.09, more preferably not greater than 0.08, particularly preferably in the range of 0.04 to 0.07.

Infrared spectrophotometric analysis of the organoaluminum oxy-compounds is carried out in the following manner.

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

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

The IR spectrum of the organoaluminum oxy-compound used in the present invention 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 about 1280 cm^{-1} and a maximum point at about 1240 cm^{-1} is taken as a base line L_1.

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

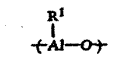
(c) Similarly, a line connecting maximum points at about 1280 cm^{-1} and at about 1180 cm^{-1} is taken as a base line L_2.

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

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

The 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 organoaluminum oxy-compound has a D_{1260}/D_{1220} value of about 0.10 to 0.13, and thus the benzene-insoluble organoaluminum oxy-compound of the present invention obviously differ from the known benzene-soluble organoaluminum oxy-compound on the value of D_{1260}/D_{1220}.

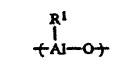
The benzene-insoluble organoaluminum oxy-compounds as described above are estimated to have an alkyloxyaluminum unit represented by the formula



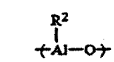
wherein R^1 is a hydrocarbon group of 1 to 12 carbon atoms.

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 [I] of the formula



wherein R^1 is a hydrocarbon group of 1 to 12 carbon atoms, the benzene-insoluble organoaluminum oxy-compounds may contain an oxyaluminum unit [II] represented by the formula



wherein R^2 is a hydrocarbon group of 1 to 12 carbon atoms, an alkoxy 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 in the alkyloxyaluminum unit [I] and R^2 are different from each other. In that case, the organoaluminum oxy-compounds desirably contain the alkyloxyaluminum unit [I] in a proportion of not less than 30 mol %, preferably not less than 50 mol % particularly preferably not less than 70 mol %

The process for preparing the benzene-insoluble organoaluminum oxy-compounds as described above is concretely illustrated below.

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

Examples of the active hydrogen-containing compound 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 particulaly preferred are alcohols.

Water or the active hydrogen containing compound with which the solution of an aluminoxane is brought into contact may be used as a solution or a dispersions in a hydrocarbon solvent such as benzene, toluene and hexane, in an ether solvent such as tetrahydrofuran or in an amine solvent such as triethylamine, or may be used in the form of vapor or solid. The water with which the solution of an aluminoxane is brought into contact may be water of crystallization of a salt such as magnesium chloride, magnesium sulfate, aluminum sulfate, copper sulfate, nickel sulfate, iron sulfate and cerous chloride, or adsorbed water adsorbed to an inorganic compound such as silica, alumina and aluminum hydroxide or a polymer.

Reaction of an aluminoxane in a solution with water or an active hydrogen-containing compound is carried out usually in a solvent, for example, a hydrocarbon solvent. Examples of the solvent used in this case 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 methylcyclohexane;
- petroleum fractions such as gasoline, kerosene and gas oil; or halogenated compounds of the above-mentioned aromatic hydrocarbons, aliphatic hydrocarbons and alicyclic 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 based on 1 g atom of Al present in the solution of an aluminoxane. The 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 the 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 an aluminoxane may be brought into contact with water or the active hydrogen-containing compound, for example, by the following procedures.

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

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

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

(4) A procedure which comprises mixing the solution of an aluminoxane with a suspension of an adsorbed 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 is adsorbed, in hydrocarbon, thereby bringing the aluminoxane into contact with the adsorbed water or water of crystallization.

The solution of an aluminoxane may contain other components so long as they do not exert adverse effects on the reaction of the aluminoxane with water or the active hydrogen-containing compound.

The above-mentioned reaction of an aluminoxane in a solution with water or the active hydrogen-containing compound is carried out at a temperature of usually −50 to 150° C., preferably 0° to 120° C., more preferably 20° to 100° C. The reaction time employed is usually 0.5 to 300 hours, preferably about 1 to 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 such

an organoaluminum as described above with water. In this case, water is used in such an amount that the organoaluminum atoms dissolved in the reaction system are not greater than 20% based on the total organoaluminum atoms.

Water with which the organoaluminum compound is brought into contact may be used as a solution or dispersion in a hydrocarbon solvent such as benzene, toluene and hexane, an ether solvent such as tetrahydrofuran or an amine solvent such as triethylamine, or may be used in the form of steam or ice. The water with which the organoaluminum compound is brought into contact may be water of crystallization of a salt such as magnesium chloride, magnesium sulfate, aluminum sulfate, copper sulfate, nickel sulfate, iron sulfate and cerous chloride, or adsorbed water adsorbed to an inorganic compound such as silica, alumina and aluminum hydroxide or a polymer.

Reaction of the organoaluminum compound with water is carried out usually in a solvent, for example, a hydrocarbon solvent. Examples of the solvent used in this case 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 methylcyclohexane;
- petroleum fractions such as gasoline, kerosene and gas oil; or halogenated compounds such as halides of the above-mentioned aromatic hydrocarbons, aliphatic hydrocarbons and alicyclic hydrocarbons, particularly, chlorides and bromides; and ethers such as ethyl ether and tetrahydrofuran. Of these solvents as exemplified above, particularly preferred are aromatic hydrocarbons.

The concentration of the 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 the 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 atoms dissolved in the reaction system are not greater than 20%, preferably not greater than 10%, more preferably 0 to 5% based on the total organoaluminum atoms.

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

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

(2) A procedure which comprises blowing steam into the hydrocarbon solution of the organoaluminum, etc., thereby bringing the organoaluminum into contact with the steam.

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

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

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

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

Next, the organoaluminum compound (iii) of the invention is illustrated below.

Examples of the organoaluminum compound (iii) used herein include an organoaluminum compound represented by the formula

$$R^6_nAlX_{3-n}$$

wherein R^6 is a hydrocarbon group of 1 to 12 carbon atoms, X is halogen or hydrogen, and n is 1 to 3.

In the above formula, R^6 is a hydrocarbon group of 1 to 12 carbon atoms, for example, an alkyl group, a cycloalkyl group or an aryl group. Concrete examples of R^6 include methyl, ethyl, n-propyl, isopropyl, isobutyl, pentyl, hexyl, octyl, cyclopentyl, cyclohexyl, phenyl and tolyl.

Concrete examples of such organoaluminum compounds include

- trialkylaluminum such as trimethylaluminum, triethylaluminum, triisopropylaluminum, triisobutylaluminum, trioctylaluminum and tri-2-ethylhexylaluminum;
- alkenylaluminum such as isoprenylaluminum;
- dialkylaluminum halides such as dimethylaluminum chloride, diethylaluminum chloride, diisopropylaluminum chloride, diisobutylaluminum chloride and dimethylaluminum bromide;
- alkylaluminum sesquihalides such as methylaluminum sesquichloride, ethylaluminum sesquichloride, isopropylaluminum sesquichloride, butylaluminum sesquichloride and ethylaluminum sesquibromide;
- alkylaluminum dihalides such as methylaluminum dichloride, ethylaluminum dichloride, isopropylaluminum dichloride and ethylaluminum dibromide; and
- alkylaluminum hydrides such as diethylaluminum hydride and diisobutylaluminum hydride.

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 to 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.

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

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

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

(4) Compounds of the formula $R^6_nAl(NR^{10}_2)_{3-n}$ such as Me_2AlNEt_2, $Et_2AlNHMe$, $Me_2AlNHEt$, $Et_2AlN(SiMe_3)_2$, $(iso\text{-}Bu)_2AlN(SiMe_3)_2$.

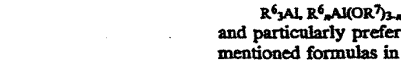
(5) Compounds of the formula $R^6_nAl(SiR^{11}_3)_{3-n}$ such as $(iso\text{-}Bu)_2AlSiMe_3$.

(6) Compounds of the formula

such as



Of the organoaluminum compounds as exemplified above, preferred are those having the formulas



and particularly preferred are those having the above-mentioned formulas in which R^6 is isoalkyl and n is 2. These organoaluminum compounds may also be used in combination of two or more.

The carrier used as a carrier of the catalyst component (iv) of the invention is a solid inorganic or organic compound in granules or fine particles having a particle size of 10 to 300 μm, preferably 20 to 200 μm. Of these carriers, porous oxides are preferable as inorganic carriers. Concrete examples of the oxide carriers include SiO_2, Al_2O_3, MgO, ZrO_2, TiO_2, B_2O_3, CaO, ZnO, BaO, ThO_2, or a mixture of these compounds such as SiO_2—MgO, SiO_2—Al_2O_3, SiO_2—TiO_2, SiO_2—V_2O_5, SiO_2—Cr_2O_3 and SiO_2—TiO_2—MgO. Of these carriers, preferred are those comprising at least one compound selected from the group consisting of SiO_2 and Al_2O_3 as a major component.

Furthermore, the above-mentioned inorganic oxide or oxides may also contain a small amount of a carbonate, a sulfate, a nitrate and an oxide such as Na_2CO_3, K_2CO_3, $CaCO_3$, $MgCO_3$, Na_2SO_4, $Al_2(SO_4)_3$, $BASO_4$, KNO_3, $Mg(NO_3)_2$, $Al(NO_3)_3$, Na_2O, K_2O and LiO_2.

Though the porous inorganic carriers have different properties among them depending on the types and preparation methods thereof, the carriers preferably used in the invention have a specific surface area of 50 to 1000 m^2/g, preferably 100 to 700 m^2/g, a pore volume of desirably 0.3 to 2.5 cm^2/g. The carriers are prepared if necessary by firing at a temperature of 150° to 1000° C., preferably 200° to 800° C.

Moreover, there can be mentioned organic compounds in solid granules or fine solid particles each having a particle size of 10 to 300 μm as carriers which can be used in the present invention. Examples of these organic compounds include (co)polymers containing as the main component constituent units derived from an α-olefin of 2 to 14 carbon atoms, such as ethylene, propylene, 1-butene and 4-methyl-1-pentene, or polymers or copolymers containing as the main component constituent units derived from vinylcyclohexane or styrene.

In the present invention, it is desirable that catalyst formed by prepolymerizing olefin on the catalyst components (i), (ii), (iii) and (iv) as described above should be used during the preparation of the ethylene copolymers.

Before the prepolymerization, the catalyst component (i), the catalyst components (i) and (ii), on the catalyst components (i), (ii) and (iii) may be supported on the catalyst component (iv), a carrier, or the catalyst components may only be arbitrarily contacted together and mixed, and used for the prepolymerization.

A sphere olefin copolymer excellent in particle shape can be manufactured if the catalyst component (i) is used, during the prepolymerization, with the transition metal compound (vi) comprising ligangs which have each a cyclopentadienyl skeleton and which are not bonded together.

Concrete examples of the transition metal compound (vi) comprising ligands which have a cyclopentadienyl skeleton and which are not bonded together include

bis(cyclopentadienyl)zirconium dichloride,
bis(methylcyclopentadienyl)zirconium dichloride,
bis(dimethylcyclopentadienyl)zirconium dichloride,
bis(ethylcyclopentadienyl)zirconium dichloride,
bis(n-butylcyclopentadienyl)zirconium dichloride, and
bis(indenyl)zirconium dichloride.

The proportion for use of the transition metal compound (vi) to the catalyst component (i) is 0 to 50 mol %, preferably 5 to 40 mol %, more preferably 10 to 30 mol % based on the total amount of the components (i) and (vi) defined as 100 mol %.

During the prepolymerization, the olefin polymer (v) is formed in an amount, based on 1 g of the carrier, of 0.05 to 100 g, preferably 0.1 to 50 g, more preferably 0.2 to 30 g.

Examples of the olefin include ethylene and an α-olefin having 3 to 20 carbon atoms, for example, propylene, 1-butene, 1-pentene, 4-methyl-1-pentene, 1-hexene, 1-octene, 1-decene, 1-dodecene and 1-tetradecene. Of these, ethylene is preferable.

The prepolymerization is carried out without a solvent or in an inactive hydrocarbon solvent. In the prepolymerization process, there are used the organoaluminum compound in an amount of 0.2 to 20 mmoles, preferably 0.5 to 10 mmoles, the organoaluminum oxy-compound in an amount of 1 to 50 mg atoms, preferably 2 to 20 mg atoms in terms of Al, and the catalyst component (i) in an amount of 0.02 to 2 mg atoms, preferably 0.05 to 1 mg atom in terms of the transition metal, all the amounts being based on 1 g of the carrier.

Furthermore, a desirable molecular ratio of the orgnaoaluminum compound (iii) in terms of Al atom to the organoaluminum oxy-compound (ii) in terms of Al atom [Al (iii)/Al (ii)] is usually 0.02 to 3, preferably 0.05 to 1.5 A molecular ratio of the organoaluminum oxy-compound (ii) in terms of Al atom to the catalyst component (i) in terms of transition metal atom (M) [Al (ii)/M] is usually 5 to 250, preferably 10 to 150. When the prepolymerization is conducted in an inactive hydrocarbon solvent, the concentration of the catalyst component (i) in terms of the transition metal is usually 0.1 to 10 mg atom/liter, preferably 0.5 to 5 mg atom/liter.

The prepolymerization is carried out at a temperature of −20° to 70° C., preferably −10° to 60° C., more preferably 0 to 50° C.

The prepolymerization may be carried out either batchwise or continuously, and under reduced pressure,

normal pressure or applied pressure. Though a molecular weight modifier such as hydrogen may be allowed to be present during prepolymerization, its amount is desirably restricted so that there can be prepared a prepolymer having an intrinsic viscosity [η] of not less than 0.2 dl/g, preferably 0.5 to 10 dl/g as measured in decalin at 135° C.

In the thus obtained prepolymerization catalyst, the catalyst component (i) is supported in an amount in terms of transition metal atom, based on 1 g of the carrier, of 0.1 to 50 rag, preferably 0.3 to 30 mg, more preferably 0.5 to 20 mg. The molecular ratio of the catalyst components (ii) and (iii) in terms of Al atom to the catalyst component (i) in terms of the transition metal (M) (Al/M) is 5 to 200, preferably 10 to 150, more preferably 15 to 100.

The ethylene copolymers according to the present invention are obtained by copolymerizing ethylene with such an α-olefin having 3 to 20 carbon atoms as propylene, 1-butene, 1-pentene, 1-hexene, 4-methyl-1-pentene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene and 1-eicosene.

In the present invention, olefin is usually polymerized in a gas phase or liquid phase, for example, in slurry. In the slurry polymerization, an inactive hydrocarbon or the olefin itself may be used as a solvent.

Concrete examples of the hydrocarbon solvent include aliphatic hydrocarbons such as butane, isobutane, pentane, hexane, octane, decane, dodecane, hexadecane and octadecane; alicyclic hydrocarbons such as cyclopentane, methylcyclopentane, cyclohexane and cyclooctane; aromatic hydrocarbons such as benzene, toluene and xylene; and petroleum fractions such as gasoline, kerosene and gas oil. Of these hydrocarbons, preferred are aliphatic hydrocarbons, alicyclic hydrocarbons and petroleum fractions.

In the present invention, the slurry polymerization is conducted at a temperature of usually −50° to 100° C., preferably 0° to 90° C.

In the present invention, the gas phase polymerization is carried out at a temperature of usually 0° to 120° C., preferably 20° to 100° C.

In the slurry polymerization or gas phase polymerization of the invention, the concentration of the transition metal compound is usually 10^{-8} to 10^{-2} g atom/liter, preferably 10^{-7} to 10^{-3} g atom/liter in terms of the transition metal.

Furthermore, in the polymerization of the invention, an aluminum oxy-compound or an aluminum compound similar to those used in the catalyst components (ii) and (iii) may be added. During the polymerization, the ratio of the aluminum compound in terms of Al atom to the transition metal atom (M) (Al/M) is 5 to 300, preferably 10 to 200, more preferably 15 to 150.

The polymerization is carried out usually at a normal pressure to 100 kg/cm^2, preferably under a pressure condition of 2 to 50 kg/cm^2. The polymerization can be carried out either batchwise, semicontinuously or continuously.

Furthermore, the polymerization may also be carried out in not less than 2 steps having reaction conditions different from each other.

The second process for the preparation of an olefin polymer according to the present invention is concretely illustrated below.

The olefin polymer, especially the ethylene polymer prepared by the second process for the preparation of an olefin polymer according to the present invention is an ethylene homopolymer or a random copolymer of ethylene with an α-olefin having 3 to 20 carbon atoms.

The random copolymer of ethylene with an α-olefin having 3 to 20 carbon atoms prepared by the second process for the preparation of an olefin polymer according to the present invention has characteristics as described above.

In the second process for the preparation of an olefin polymer of the invention, there is used a solid catalyst formed from

(A) a compound of a transition metal in Group IVB of the periodic table, having as a ligand at least two groups having a cyclopentadienyl skeleton, said at least two groups being crosslinked through a group containing carbon and/or silicon, and

(B) an organoaluminum oxy-compound, and polymerization of olefin is carried out under the condition that the produced polymer exists in a solid state in the polymerization system.

The transition metal compound (A) used in the second process for the preparation of an olefin polymer according to the present invention is represented by the formula

$$M^1L^1_x$$

wherein M^1 is a transition metal, L^1 is a ligand coordinating to the transition metal, at least two of L^1 are ligands having a cyclopentadienyl skeleton and bonded together through a group containing carbon and/or silicon, L^1 other than the ligand having a cyclopentadienyl skeleton is a hydrocarbon group of 1 to 12 carbon atoms, an alkoxy group, an aryloxy group, halogen or hydrogen, and x is a valence of the transition metal.

In the above-mentioned formula, M^1 is a transition metal, and concrete preferable examples of M^1 include zirconium, titanium, hafnium, chromium and vanadium. Of these, particularly preferred are zirconium and hafnium.

The ligands having a cyclopentadienyl skeleton include, for example, cyclopentadienyl, an alkyl-substituted cyclopentadienyl group such as methylcyclopentadienyl, ethylcyclopentadienyl, n-butylcyclopentadienyl, dimethylcyclopentadienyl and pentamethylcyclopentadienyl, indenyl, 4,5,6,7-tetrahydroindenyl and fluorenyl.

The ligand other than those having a cyclopentadienyl skeleton is a hydrocarbon group having 1 to 12 carbon atoms, an alkoxy group, an aryloxy group, halogen or hydrogen.

The hydrocarbon group having 1 to 12 carbon atoms includes, for example, an alkyl group, a cycloalkyl group, an aryl group and an aralkyl group, and concrete examples of these groups are as follows:

an alkyl group such as methyl, ethyl, propyl, isopropyl and butyl;

a cycloalkyl group such as cyclopentyl and cyclohexyl;

an aryl group such as phenyl and tolyl;

an aralkyl group such as benzyl and neophyl;

an alkoxy group such as methoxy, ethoxy and butoxy;

an aryloxy group such as phenoxy; and

halogen such as fluorine, chlorine, bromine and iodine.

Such a transition metal compound (A) comprising ligands having a cyclopentadienyl skeleton as used in the present invention and having a transition metal with

a valence of four may be represented more concretely by the formula

$$R^2R^3R^4R^5M^1$$

wherein M^1 is zirconium, titanium, hafnium or vanadium, at least two of R^2 R^3 R^4 and R^5 that is R^2 and R^3 are each a group having a cyclopentadienyl skeleton, said two groups, each having a cyclopentadienyl skeleton, being bonded together through a group containing carbon and/or silicon such as an alkylene group (e.g., ethylene and propylene), a substituted alkylene group such as isopropylidene and diphenylmethylene, a silylene group, and a substituted silylene group such as dimethylsilylene, R^4 and R^5 are each a group having a cyclopentadienyl skeleton, an alkyl group, a cycloalkyl group, an aryl group, an aralkyl group, an alkoxy group, an aryloxy group, halogen or hydrogen.

Listed below are concrete examples of the transition metal compound (A) having at least two ligands containing a cyclopentadienyl skeleton, said at least two ligands having a cyclopentadienyl skeleton being bonded together through an alkylene group, a substituted alkylene group, a silylene group or a substituted silylene group.

Ethylenebis(indenyl)dimethylzirconium,
Ethylenebis(indenyl)diethylzirconium,
Ethylenebis(indenyl)diphenylzirconium monochloride,
Ethylenebis(indenyl)methylzirconium monochloride,
Ethylenebis(indenyl)ethylzirconium monochloride,
Ethylenebis(indenyl)methylzirconium monobromide,
Ethylenebis(indenyl)zirconium dichloride,
Ethylenebis(indenyl)zirconium dibromide,
Ethylenebis(4,5,6,7-tetrahydro-1-indenyl)dimethylzirconium,
Ethylenebis(4,5,6,7-tetrahydro-1-indenyl)methylzirconium 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(cyclopentadienylfluorenyl)zirconium dichloride,
Isopropylidene(cyclopentadienyl-2,7-di-tert-butylfluorenyl)zirconium dichloride,
Isopropylidene(cyclopentadienylmethylcyclopentadienyl)zirconium dichloride,
Dimethylsilylenenbis(cyclopentadienyl)zirconium dichloride,
Dimethylsilylenebis(methylcyclopentadienyl)zirconium dichloride,
Dimethylsilylenenbis(dimethylcyclopentadienyl)zirconium dichloride,
Dimethylsilylenenbis(trimethylcyclopentadienyl)zirconium dichloride, and
Dimethylsilylenebis(indenyl)zirconium dichloride.

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

In the second process for the preparation of an olefin polymer according to the present invention, a compound similar to the organoaluminum oxy-compound (ii) is used as the organoaluminum oxy-compound (B).

Moreover, in the second process for the preparation of an olefin polymer according to the present invention, an organoaluminum compound (C) may also be used if necessary in addition to the transition metal compound (A) and the organoaluminum oxy-compound (B) as described above during the manufacture of olefin polymer.

A compound similar to the organoaluminum compound (iii) is used for such the organoaluminum compound (C).

The catalyst component used in the second process for the preparation of an olefin polymer according to the present invention is in a solid state, and such a solid catalyst component can be prepared, for example, by supporting the catalyst component (A) on a carrier (D) or a solid organoaluminum oxy-compound.

A carrier similar to that described above can be used as the carrier (D).

In the preparation of an ethylene polymer by the second process for the preparation of an olefin polymer according to the present invention, it is desirable that there should be used a catalyst formed by prepolymerizing olefin on catalyst components comprising the catalyst components (A) and (B), and if necessary the catalyst component (C) and/or the catalyst component (D), all these catalyst components having been described above.

Before the prepolymerization, the catalyst component (A), the catalyst components (A) and (B) or the catalyst components (A), (B) and (C) may be presupported on a carrier, or these catalyst components may only be arbitrarily contacted and mixed.

When a transition metal compound (E) containing ligands each having a cyclopentadienyl skeleton, said ligands being not bonded together, is used with the catalyst component (A) during contacting and mixing, a sphere olefin copolymer excellent in particle properties can be prepared.

The transition metal compound (E) used if necessary in the present invention is a compound similar to the above-described transition metal compound (vi) containing ligands each having a cyclopentadienyl skeleton, said ligands being not bonded together, and is illustrated more in detail below. The transition metal compound (E) is represented by the formula

$$M^2L^2_x$$

wherein M^2 is a transition metal, L^2 is a ligand coordinating to the transition metal, at least one of L^2 is a ligand having a cyclopentadienyl skeleton, L^2 other than the ligand having a cyclopentadienyl skeleton is a hydrocarbon group of 1 to 20 carbon atoms, an alkoxy group, an aryloxy group, halogen or hydrogen, and x is a valence of the transition metal.

In the above-mentioned formula, M^2 is a transition metal, and concrete preferable examples of M^2 include zirconium, titanium, hafnium, chromium and vanadium.

Of these, particularly preferred are zirconium and hafnium.

Examples of the ligand having a cyclopentadienyl skeleton include a cyclopentadienyl group an alkyl-substituted cyclopentadienyl group such as a methylcyclopentadienyl group, an ethylcyclopentadienyl group, a n-butylcyclopentadienyl group, a dimethylcyclopentadienyl group and a pentamethylcyclopentadienyl group, an indenyl group and a fluorenyl group.

At least one, preferably two ligands each having a cycloalkadienyl skeleton as mentioned above coordinate to the transition metal M^2.

The ligand other than those having a cycloalkadienyl skeleton is a hydrocarbon group of 1 to 12 carbon atoms, an alkoxy group, an aryloxy group, halogen or hydrogen.

The hydrocarbon group having 1 to 12 carbon atoms includes, for example, an alkyl group, a cycloalkyl group, an aryl group and an aralkyl group, and concrete examples of these groups are listed below.

The alkyl group includes methyl, ethyl, propyl, isopropyl and butyl.

The cycloalkyl group includes cyclopentyl and cyclohexyl.

The aryl group includes phenyl and tolyl.

The aralkyl group includes benzyl and neophyl.

The alkoxy group includes methoxy, ethoxy and butoxy.

The aryloxy group includes phenoxy.

The halogen includes fluorine, chlorine, bromine and iodine.

Such a transition metal compound (E) containing ligands each having a cyclopentadienyl skeleton, which is not bonded to other cyclopentadienyl skeletons, as used in the present invention and having a transition metal with a valence of 4 may be represented more concretely by the formula

$$R^{2'}kR^{3'}lR^{4'}mR^{5'}nM^2$$

wherein M^2 is zirconium, titanium, hafnium or vanadium, $R^{2'}$ is a group having a cyclopentadienyl skeleton, , $R^{3'}$, $R^{4'}$ and $R^{5'}$ are each a group having a cyclopentadienyl skeleton, an alkyl group, a cycloalkyl group, an aryl group, an aralkyl group, an alkoxy group, an aryloxy group, halogen or hydrogen, k is an integer of not less than 1, and $k+l+m+n=4$.

Listed below are concrete examples of the transition metal compound (E) having zirconium as M^2 and ligands each containing a cyclopentadienyl skeleton which is not bonded to other cyclopentadienyl skeletons.

Bis(cyclopentadienyl)zirconium monochloride monohydride,
Bis(cyclopentadienyl)zirconium monobromide monohydride,
Bis(cyclopentadienyl)methylzirconium hydride,
Bis(cyclopentadienyl)ethylzirconium hydride,
Bis(cyclopentadienyl)phenylzirconium hydride,
Bis(cyclopentadienyl)benzylzirconium hydride,
Bis(cyclopentadienyl)neopentylzirconium hydride,
Bis(methylcyclopentadienyl)zirconium monochloride hydride,
Bis(indenyl)zirconium monochloride monohydride,
Bis(cyclopentadienyl)zirconium dichloride,
Bis(cyclopentadienyl)zirconium dibromide,
Bis(cyclopentadienyl)methylzirconium monochloride,
Bis(cyclopentadienyl)ethylzirconium monochloride,
Bis(cyclopentadienyl)cyclohexylzirconium monochloride,
Bis(cyclopentadienyl)phenylzirconium monochloride,
Bis(cyclopentadienyl)benzylzirconium monochloride,
Bis(methylcyclopentadienyl)zirconium dichloride,
Bis(dimethylcyclopentadienyl)zirconium dichloride,
Bis(n-butylcyclopentadienyl)zirconium dichloride,
Bis(indenyl)zirconium dichloride,
Bis(indenyl)zirconium dibromide,
Bis(cyclopentadienyl)zirconiumdimethyl,
Bis(cyclopentadienyl)zirconiumdiphenyl,
Bis(cyclopentadienyl)zirconiumdibenzyl,
Bis(cyclopentadienyl)zirconium methoxychloride,
Bis(cyclopentadienyl)zirconium ethoxychloride,
Bis(methylcyclopentadienyl)zirconium ethoxychloride,
Bis(cyclopentadienyl)zirconium phenoxychloride, and
Bis(fluorenyl)zirconium dichloride.

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

During the prepolymerization, the olefin polymer is formed in an amount, based on 1 g of the carrier, of 0.05 to 100 g, preferably 0.1 to 50 g, more preferably 0.2 to 30 g.

Examples of the olefin include ethylene and an α-olefin having 3 to 20 carbon atoms, for example, propylene, 1-butene, 1-pentene, 4-methyl-1-pentene, 1-hexene, 1-octene, 1-decene, 1-dodecene and 1-tetradecene. Of these, ethylene is preferable.

The prepolymerization is carried out without a solvent or in an inactive hydrocarbon solvent. During the prepolymerization, there are used the organoaluminum compound in an amount of 0.2 to 20 mmoles, preferably 0.5 to 10 mmoles, the organoaluminum oxy-compound in an amount of 1 to 50 mg atoms, preferably 2 to 20 mg atoms in terms of Al, and the catalyst component (A) in an amount of 0.02 to 2 mg atoms, preferably 0.05 to 1 mg atom in terms of the transition metal, all the amounts being based on 1 g of the carrier.

Furthermore, a desirable molecular ratio [Al(C-)/Al(B)] of the orgnaoaluminum compound in terms of Al atom [Al(C)] to the organoaluminum oxy-compound in terms of Al atom [Al(B)] is usually 0.02 to 3, preferably 0.05 to 1.5. A desirable molecular ratio [Al(B)/M] of the organoaluminum oxy-compound in terms of Al atom [Al(B)] to the catalyst component (A) in terms of transition metal atom (M) is usually 5 to 250, preferably 10 to 150. When the prepolymerization is carried out in an inactive hydrocarbon solvent, the concentration of the catalyst component (A) in terms of the transition metal atom is usually 0.1 to 10 mg atom/l, preferably 0.5 to 5 mg atom/l.

The prepolymerization is carried out at a temperature of −20° to 70° C., preferably −10° to 60° C., more preferably 0° to 50° C.

The prepolymerization may be carried out either batchwise or continuously, and under reduced pressure, normal pressure or applied pressure. Though a molecular weight modifier such as hydrogen may be allowed to be present during prepolymerization, its amount is desirably restricted so that there can be prepared a prepolymer having an intrinsic viscosity [η] of not less than 0.2 dl/g, preferably 0.5 to 10 dl/g as measured in decalin at 135° C.