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HIGH ACTIVITY POLYETHYLENE CATALYSTS

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(71) Applicant(s)
MOBIL OIL CORPORATION

(72) Inventor(s)
ROBERT OLDS HAGERTY; PER KRISTIAN HUSBY; YURY VIKTOROVICH KISSIN; ROBERT IVAN MINK; THOMAS EDWARD NOWLIN

(74) Attorney or Agent
PHILLIPS ORMONDE & FITZPATRICK , 367 Collins Street, MELBOURNE VIC 3000

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(57) Claim

1. A catalyst composition for co-polymerizing ethylene and an alpha-olefin of 3 to 10 carbon atoms, comprising a solid supported catalyst precursor and a cocatalyst wherein the precursor comprises:

a) silica, wherein the silica has 0.4 to 0.9 mmol of OH groups per gram of silica;

b) a dialkylmagnesium compound, $R_mMgR'_n$, wherein each of R and R' is an alkyl group of 4 to 10 carbon atoms, and wherein m plus n equal the valence of magnesium, wherein the dialkyl-magnesium compound is present in an amount to provide a Mg:OH molar ratio of 1.0 to 1.8;

c) tetraalkyl orthosilicate, in an amount to provide a tetraalkyl orthosilicate:Mg molar ratio of 0.50 to 0.80, wherein the alkyl group contains 2 to 6 carbon atoms;

d) titanium tetrachloride in an amount to provide a Ti:Mg molar ratio of 0.7 to 1.4; and wherein the co-catalyst is dimethylaluminum chloride.

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(71) Applicant: MOBIL OIL CORPORATION [US/US]; 3225 Gallows Road, Fairfax, VA 22037 (US).

(72) Inventors: HAGERTY, Robert, Olds; 24 Ross Avenue, Metuchen, NJ 08840 (US). HUSBY, Per, Kristian; 105 DeMott Lane, Somerset, NJ 08873 (US). KISSIN, Yury, Viktorovich; 35 Pine Ridge Drive, East Brunswick, NJ 08816 (US). MINK, Robert, Ivan; 30 A Gates Avenue, Warren, NJ 07059 (US). NOWLIN, Thomas, Edward; 7 Perrine Path, Cranbury, NJ 08512 (US).

(74) Agents: SCHNELLER, Marina, V. et al.; Mobil Oil Corporation, 3225 Gallows Road, Fairfax, VA 22037 (US).

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(57) Abstract

An ethylene polymerization catalyst is prepared by impregnating a porous support, such as silica, with an organomagnesium compound such as a dialkylmagnesium compound, contacting the magnesium-containing support with a silane compound which is free of hydroxyl groups, such as tetraalkoxysilanes, e.g. tetraethyl orthosilicate, and incorporating a transition metal component, such as titanium tetrachloride, in a specific ratio to the magnesium and silane components. Activation of this catalyst precursor with dimethylaluminum chloride as a cocatalyst results in a catalyst system which is effective for the production of ethylene copolymers with multimodal molecular weight distributions.

HIGH ACTIVITY POLYETHYLENE CATALYSTS

This invention is a catalyst composition for (co)polymerizing ethylene and an alpha-olefin of 3 to 10 carbon atoms, comprising a solid supported catalyst precursor and dimethylaluminum chloride as a co-catalyst. The supported catalyst precursor comprises:

a) silica, wherein the silica has 0.4 to 0.9 mmol of OH groups per gram of silica;

b) a dialkylmagnesium compound, $R_mMgR'_n$, wherein each of R and R' is an alkyl group of 4 to 10 carbon atoms, and wherein m plus n equal the valence of magnesium, wherein the dialkyl-magnesium compound is present in an amount to provide a Mg:OH molar ratio of 1.0 to 1.8;

c) tetraalkyl orthosilicate, in an amount to provide a tetraalkyl orthosilicate:Mg molar ratio of 0.50 to 0.80, wherein the alkyl group contains 2 to 6 carbon atoms;

d) titanium tetrachloride in an amount to provide a Ti:Mg molar ratio of 0.7 to 1.4.

The invention relates to catalysts for the manufacture of linear polyethylene resins with densities between 0.918 and 0.945 g/cc and with a relatively narrow molecular weight distribution (MWD) and with multimodal and/or bimodal MWD. Such resins with excellent bubble stability can be processed on high-stalk extrusion equipment at high rates and produce film with much improved toughness relative to the film made of polyethylene resins with a relatively broad MWD. The present invention relates to a method for copolymerizing ethylene and alpha-olefins, a catalyst for such a copolymerization and a method for producing such a catalyst.

All commercial polyethylene resins used in high-stalk extrusion equipment have a relatively broad MWD as indicated by MFR values of 80-200.

In contrast, polyethylene resins with a relatively narrow MWD have not been suitable for high-stalk film extrusion equipment. Polyethylene resins with a relatively narrow MWD produced with catalysts of the invention can be processed with such equipment, because unexpectedly the resins contain a significant fraction of polymer molecules with very high molecular weights. Moreover, such resins exhibit excellent film properties such as impact strength and tear resistance.

One of the measures of MWD of a LLDPE or MDPE resin is its melt flow ratio (MFR), which is the ratio of the high-load melt index (HLMI or I_{21}) to the melt index (MI or I_2) for a given resin: MFR = I_{21}/I_2. The MFR value is an approximate indication of MWD of a polymer: the higher the MFR value, the broader the MWD. Common polyethylene resins for film applications usually have relatively low MFR values, e.g., of 15 to 30.

It ~~is an object of the present invention~~ would be desirable to provide a high-activity catalyst for copolymerization of ethylene and alpha-olefins yielding products with a multimodal, relatively narrow MWD as indicated by MFR values in the 28-70 range. It ~~is an additional object of the present invention~~ would also be disirable to provide a catalytic process for copolymerizing ethylene with alpha-olefins which yields products with a bimodal MWD at high productivity.

Figure 1 is a GPC chromatogram (gel permeation chromatography) of a resin produced with a catalyst system of the invention; it is a plot of weight fraction vs. molecular weight.

Figure 2 is a GPC of a resin produced in accordance with the Comparative Example.

The catalyst systems described herein exhibit unique catalytic effects in olefin polymerization. When used in copolymerization of ethylene and alpha-olefins, the catalysts produce products with bimodal and trimodal MWDs, in a single reactor. The phrase "a resin with a bimodal

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molecular weight distribution" means herein that the resins produced by the catalyst systems of the invention contain a relatively lower molecular weight (LMW) component and the second component of a relatively higher molecular weight (HMW) than that of the first component. The phrase "a resin with a trimodal molecular weight distribution", as used herein, means that the resins produced by the catalyst systems of the invention contain three components which differ from each other in molecular weight: a first, relatively LMW component, a second component of an intermediate molecular weight, and the third component which has the highest molecular weight of the three components. The amount of the HMW component in the bimodal or trimodal products, can range from 5 to 50 weight percent.

The resins so produced exhibit the MFR values in the range of 25 to 80, preferably 30 to 75, and most preferably, 35 to 70.

The films, fabricated from the resins exhibit superior dart impact properties and machine-direction (MD) tear properties. Dart impact is measured by ASTM D-1709, Method A(F_{50}) with a 38.1-mm dart, and a drop height of 0.66 meters. MD tear is measured by ASTM D-1922. For example, the 1.0 mil films produced with catalysts of this invention exhibit dart drop strength in the range from 100 g to greater than 800 g and usually higher than 400 grams; in particular, dart drops are in the range of 400 to 1500, and preferably 800 to 1500.

Such resins can be used in high stalk film extrusion processes. This is entirely unexpected for LLDPE products produced with titanium-based catalysts and with densities less than 0.94, because LLDPE resins produced with conventional titanium-based catalysts cannot be processed on high-stalk extrusion equipment.

The unique catalyst compositions of the invention comprise a solid supported catalyst precursor and DMAC

(dimethylaluminum chloride) as an activator (cocatalyst).

Catalysts produced according to aspects of the present invention may be described in terms of the manner in which they can be made. Suitable carrier materials include solid, porous carrier materials such as silica, alumina and combinations thereof. Such carrier materials may be amorphous or crystalline in form. These carriers may be in the form of particles having a particle size of from 0.1 micron to 250 microns, preferably from 10 to 200 microns, and most preferably from 10 to 80 microns. Preferably, the carrier is in the form of spherical particles, e.g., spray-dried silica.

The carrier material must be porous. The internal porosity of these carriers may be larger than 0.2 cm^3/g. The specific surface area of these carriers is at least 3 m^2/g, preferably at least 50 m^2/g, and more preferably from, e.g., 150 to 1500 m^2/g.

It is desirable to remove physically bound water from the carrier material prior to contacting it with water-reactive magnesium compounds. This water removal may be accomplished by heating the carrier material. A suitable range of temperatures is from 100°C to 800°C, preferably from 150°C to 650°C.

Hydroxyl groups such as silanol (Si-OH) groups may be present in the carrier, when it is contacted with the magnesium compounds. These OH groups may be present at 0.3 mmoles or more per gram of carrier. Although, in general, from 0.5 to 5 mmol of OH groups per gram of carrier may be present, a preferred range is from 0.3 to 0.9 mmol of OH groups per gram of carrier. Excess OH groups present in the carrier may be removed by heating the carrier for a sufficient time at a sufficient temperature. For example, a relatively small number of OH groups may be removed by heating at from 150°C to 250°C, whereas a relatively large number of OH groups may be removed by heating at at least 500 to 800°C, most preferably, from 550°C to 650°C. The

duration of heating may be from 4 to 16 hours. In a most preferred embodiment, the carrier is silica which, prior to the use thereof in the first catalyst synthesis step, has been dehydrated by fluidizing it with nitrogen or air and heating at least 600°C for 4 - 16 hours to achieve a surface hydroxyl group concentration of 0.7 millimoles per gram (mmol/g). The surface hydroxyl concentration in silica may be determined according to J.B. Peri and A.L. Hensley, Jr., J. Phys. Chem., 72 (8), 2926 (1968). Internal porosity of carriers can be determined by a technique termed BET-technique, described by S. Brunauer, P. Emmett and E. Teller in Journal of the American Chemical Society, 60, pp. 209-319 (1938). Specific surface areas of carriers can also be measured in accordance with the above-mentioned BET-technique, with use of the standardized method as described in British Standards BS 4359, Volume 1, (1969).

The silica of the most preferred embodiment is a high surface area, amorphous silica (surface area = 300 m^2/g; pore volume of 1.65 cm^3/g), and it is a material marketed under the tradenames of Davison 952 or Davison 955 by the Davison Chemical Division of W. R. Grace and Company. When such silica has been dehydrated by fluidizing with nitrogen or air and heating at 600°C for 4 - 16 hours, the surface hydroxyl concentration is 0.72 mmol/g.

While heating is a preferred means of removing OH groups inherently present in a carrier such as silica, other removal means are also possible such as chemical means. For example, a desired fraction of OH groups may be reacted with a chemical agent such as a hydroxyl-reactive organs aluminum compound, e.g., triethylaluminum.

Other examples of suitable carrier materials are described in the Graff, U.S. Patent No. 4,173,547. Note particularly the passage extending from column 3, line 62 to column 5, line 44 of this Graff patent.

molar ratio of the organomagnesium compound to the hydroxyl groups will vary and must be determined on a case-by-case basis to assure that only so much of the organomagnesium compound is added to the solution as will be deposited onto the support without leaving any excess of the organomagnesium compound in the solution. Furthermore, it is believed that the molar amount of the organomagnesium compound deposited onto the support is greater than the molar content of the hydroxyl groups on the support. Thus, the molar ratios given below are intended only as an approximate guideline and the exact amount of the organomagnesium compound in this embodiment must be controlled by the functional limitation discussed above, i.e., it must not be greater than that which can be deposited onto the support. If greater than that amount is added to the solvent, the excess may react with the reagents added subsequently, thereby forming a precipitate outside of the support which is detrimental in the synthesis of our catalyst and must be avoided. The amount of the organomagnesium compound which is not greater than that deposited onto the support can be determined in any conventional manner, e.g., by adding the organomagnesium compound to the slurry of the carrier in the solvent, while stirring the slurry, until the excess of the organomagnesium compound is detected in the solvent.

For example, for the silica carrier heated at 600°C, the amount of the organomagnesium compound added to the slurry is such that the molar ratio of Mg to the hydroxyl groups (OH) on the solid carrier is 1:1 to 4:1, preferably 1.1:1 to 2.8:1, more preferably 1.2:1 to 1.8:1 and most preferably 1.4:1. The reaction between the carrier and the organomagnesium compound is carried out at 35-75°C for 10 minutes to 10 hours.

It is also possible to add such an amount of the organomagesium compound which is in excess of that which will be deposited onto the support, and then remove, e.g.,

by filtration and washing, any excess of the organomagnesium compound. However, this alternative is less desirable than the most preferred embodiment described above.

It is noted that if the organomagnesium compound is only sparingly soluble, e.g., to the extent of even 1 percent or less, the organomagnesium compound which is consumed by reactive sites on the carrier will be replaced by further dissolution of undissolved organomagnesium compound by a mass-action effect.

The second step in the production of the catalyst composition of the invention is the addition to the aforementioned slurry of a silane compound which is free of hydroxy groups, $(R^1O)_xSiR^2_y$, wherein x is 1, 2, 3, or 4 and y is 4-x; R^1 is a hydrocarbyl group of 1 to 10 carbon atoms; and R^2 is a halogen atom, preferably chlorine, or a hydrocarbyl group of 1 to 10 carbon atoms, or a hydrogen atom. The preferred species of silane compound are those defined by $Si(OR)_4$ wherein R is a C_1-C_{10} hydrocarbyl group, preferably a hydrocarbyl group of 2 to 6 carbon atoms. Hydrocarbyl groups include alkyl, aryl, arylalkyl, alkenyl and arylalkenyl, containing 1 to 10 carbon atoms. Specific silane compounds which can be used in accordance with the invention include tetramethoxysilane, tetraethoxysilane, tetraisopropoxysilane, tetrapropoxysilane, tetrabutoxysilane, tetraphenoxysilane, tetrakis(2-methoxyethoxy)silane, tetrakis(2-ethylhexoxy)silane, and tetraalkyloxysilane.

Before the introduction of the silane compound, the slurry of the carrier material and of the organomagnesium compound in the solvent is maintained at temperatures of 40 to 65°C. The amount of the silane compound added to the slurry is such that the molar ratio of the silane compound to Mg on the solid carrier is 0.40 to 1.00, preferably 0.50 to 0.80, more preferably 0.55 to 0.75 and most preferably

0.66. The reaction is carried out for 10 minutes to 10 hours.

Finally, the slurry is contacted with at least one transition metal compound soluble in the non-polar solvent. Suitable transition metal compounds used herein are compounds of metals of Groups 4-10 adopted by IUPAC of the Periodic Chart of the Elements, as published by the Fisher Scientific Company, providing that such compounds are soluble in the non-polar solvents. The preferred transition metal compounds are titanium compounds, preferably tetravalent titanium compounds. The most preferred titanium compound is titanium tetrachloride. Mixtures of transition metal compounds may also be used and generally no restrictions are imposed on the transition metal compounds which may be included. Any transition metal compound that may be used alone may also be used in conjunction with other transition metal compounds.

This synthesis step is conducted at 25 to 75°C, preferably at 30 to 65°C, and most preferably at 45 to 60°C for 10 min. to 10 hours. In a preferred embodiment, the amount of the transition metal compound added is not greater than that which can be deposited onto the carrier. The exact molar ratio of the transition metal to Mg and of the transition metal to the hydroxyl groups of the carrier will therefore vary (depending, e.g., on the carrier drying temperature) and must be determined on a case-by-case basis. For example, for the silica carrier heated at 200 to 850°C, the amount of the transition metal compound is such that the molar ratio of the transition metal, derived from the transition metal compound, to the hydroxyl groups of the carrier is 1 to 2.0, preferably 1.3 to 2.0. The amount of the transition metal compound is also such that the molar ratio of transition metal to Mg is 0.33 to 1.5, preferably 0.5 to 1.

In accordance with preferred embodiments of the invention, the proportions of the components of the

catalyst precursor of the invention satisfy the following rule:

the ratio $K = \frac{[Ti]}{[Mg] + 4[Si]}$ must be

less than 0.4 and, preferably, be in the 0.23 to 0.31 range. Outside of this range of K values (from 0.23 to 0.31), the toughness of the LLDPE resins, catalyzed by the catalysts of the invention and the strength of the films fabricated therefrom decline. The "[Ti]", "[Mg]" and "[Si]" in the formula refer to the concentrations of titanium (provided by the transition metal compound, e.g. $TiCl_4$); magnesium (provided by the organomagnesium compound) and silicon (provided by the silane compound). The concentration of each is presented in units of mmol/gram silica.

The slurry of the supported catalyst precursor formed from the four components described above is dried of the solvent at 25 to 75°C for 1 - 10 hours. Then it is activated with dimethylaluminum chloride as a cocatalyst.

The catalyst precursor may be activated in situ by adding the cocatalyst and the solid catalyst precursor separately to the polymerization medium. It is also possible to combine the catalyst precursor and the cocatalyst before introduction into the polymerization medium, e.g., for up to 2 hours at a temperature from -40 to 80°C.

A suitable activating amount of the cocatalyst may be used. The number of moles of the cocatalyst per gram atom of titanium in the catalyst may be from 1 to 500 and is preferably greater than 5.

Ethylene and alpha-olefins may be copolymerized with the catalyst systems prepared according to aspects of the present invention by any suitable process. Such processes include polymerizations carried out in suspension, in solution or in the gas phase. Gas phase polymerizations

are preferred such as those taking place in stirred bed reactors and, especially, fluidized bed reactors. The ethylene copolymers prepared in accordance with the present invention may be copolymers of ethylene with one or more C_3-C_{10} alpha-olefins. Thus, copolymers having two monomeric units are possible as well as terpolymers having three monomeric units. Particular examples of such polymers include ethylene/propylene copolymers, ethylene/1-butene copolymers, ethylene/1-hexene copolymers, ethylene/4-methyl-1-pentene copolymers, ethylene/1-butene/1-hexene terpolymers, ethylene/propylene/1-hexene terpolymers and ethylene/propylene/1-butene terpolymers. The most preferred polymers are copolymers of ethylene with 1-hexene, 1-butene or 4-methyl-1-pentene.

The ethylene copolymers produced in accordance with the present invention preferably contain at least 80 percent by weight of ethylene units, and most preferably contain from 90 to 95 weight percent of ethylene units.

The molecular weight of the copolymers may be controlled in a known manner, preferably by using hydrogen. With the catalysts produced according to aspects of the present invention, molecular weight may be suitably controlled with hydrogen when the polymerization is carried out at relatively low temperatures, e.g., from 30 to 105°C. This control of molecular weight may be evidenced by a measurable positive change of the melt index (I_2).

The catalyst systems prepared according to aspects of the present invention are particularly useful for the production of linear low density and medium density ethylene polymers. Such polymers may have a density of 0.945 g/cc.

The molecular weight distributions of the ethylene copolymers prepared in the presence of the catalysts of the present invention, may be characterized by the values of their melt flow ratios, MFR. MFR is defined herein as the ratio of the high load melt index (HLMI or I_{21}) divided by

the melt index (I_2), i.e., MFR = I_{21}/I_2. Low MFR values indicate polymers with relatively narrow MWDs.

The MWD of the polymers prepared in the presence of the catalysts of the present invention, as expressed by the MFR values, varies from 28 to 80 for LLDPE and MDPE products having a density of 0.920 to 0.945 g/cc. As is known to those skilled in the art, such MFR values are indicative of a relatively narrow MWD.

The physical and mechanical properties of the films made from the resins polymerized with the catalyst systems of this invention are better than those of the resins polymerized with trialkylaluminum compounds such as triethylaluminum, as cocatalysts.

The following Examples further illustrate the essential features of the invention. However, it will be apparent to those skilled in the art that the specific reactants and reaction conditions used in the Examples do not limit the scope of the invention.

The properties of the polymers produced in the Examples were determined by the following test methods:

Density	ASTM D-1505 - A plaque is made and conditioned for one hour at 100°C to approach equilibrium crystallinity. Measurement for density is then made in a density gradient column; reported as g/cc.
Melt Index (MI), I_2	ASTM D-1238 - Condition E - Measured at 190°C - reported as grams per 10 minutes.
High Load Melt (HLMI), Index I_{21}	ASTM D-1238 - Condition F - Measured at 10.5 times the weight used in the melt index test above.
Melt Flow Ratio (MFR)=	I_{21}/I_2

Comonomer Content	Comonomer contents of ethylene copolymers measured by the infrared spectroscopic method, as described in the article of T. E. Nowlin, Y. V. Kissin and K. P. Wagner HIGH ACTIVITY ZIEGLER-NATTA CATALYST FOR THE PREPARATION OF ETHYLENE COPOLYMERS, Journal of Polymer Science: Part A: Polymer Chemistry, Volume 26, pages 755-764 (1988).
Dart Impact	ASTM D1709 Free Falling DART Method (F50)
Tear Strength	ASTM D-1922

Example 1

Catalyst precursor (E): 6.00 gram of silica calcined at 600°C for 6 hours was weighed into a 300 ml pear-flask, containing a magnetic stirring bar, followed by ca. 100 cm^3 of dry heptane. The flask was placed into a 55°C oil bath. Next, dibutylmagnesium (6.00 mmol) was added to the silica/heptane slurry. The contents of the flask were stirred for 62 minutes. Then, tetraethyl orthosilicate (3.96 mmol) was added to the flask and the contents were stirred for 128 minutes. Finally, titanium tetrachloride (6.00 mmol) was added to the flask and stirring was continuetd for 57 minutes. The solvent was removed from the flask with a nitrogen purge and 3.4 grams of a free-flowing powder of catalyst precursor E was obtained.

The catalyst precursor of the Example was evaluated with DMAC as cocatalyst in order to determine the effect of the catalyst precursor type on the fraction of the HMW component in the polymer. Typical slurry polymerization conditions in these experiment, are as follows: A 1.6-liter stainless steel autoclave, at 53°C, was filled with 0.750 liter of dry heptane, 0.120 liter of dry 1-hexene and 3.0 mmol of DMAC while under a slow nitrogen purge. The stirring rate was set at 900 rpm, the internal temperature was increased to ca. 85°C, and the internal pressure was raised from .55 to 4.065 Bars with hydrogen. Ethylene was

introduced to maintain the total pressure at 14.8 Bars. Next, 0.0192 gram of catalyst precursor D was introduced into the reactor with ethylene over-pressure and the temperature was maintained at 85°C continued for 60 minutes. Then the ethylene supply was stopped and the reactor was allowed to cool to room temperature. A yield of polyethylene was obtained. A yield of polyethylene was obtained. High-load flow index (HLMI) of this polymer was measured the Melt Flow Ratio was determined. The polymer contained 1.40 mol.% of 1-hexene. The laboratory slurry polymerization data is summarized in Table I. The GPC chromatogram of a polymer prepared with a catalyst of the invention appears in in Figure 1.

TABLE I

Laboratory Slurry Polymerization Data

Activity g/g/h	FI 21	MFR I_{21}/I_2	1-Hexene mol%	HMW Component (wt%)
1570	8.1	33.5	1.70	9.2

Table II summarizes some gas-phase fluidized bed product data for Catalyst system E.

TABLE II

Pilot Plant Polymerization Data

Catalyst Precursor	HME Component (wt%)	Bubble Stability of a film
E	12.7	Good

Example 2

A 1.6 liter stainless-steel autoclave equipped with a magnet stirrer was filled with heptane (500 ml) and 1-hexene (250 ml) under a slow nitrogen purge at 50°C and then 3.0 mmol of DMAC was added. The reactor vent was closed, the stirring was increased to 1000 rpm, and the temperature was increased to 85°C. The internal pressure

was raised 2.62 bars psi with hydrogen and then ethylene was introduced to maintain the total pressure at 16.80 bars psig. After that, the temperature was decreased to 80°C, 18.0 mg of catalyst precursor as produced in Example 1 was introduced into the reactor with ethylene over-pressure, and the temperature was increased and held at 85°C. The polymerization reaction was carried out for 1 h and then the ethylene supply was stopped. The reactor was allowed to cool to ambient temperature and the polyethylene was collected and dried in the air.

Example 3

Same as Example 2 except the polymerization reaction was carried out at 90°C.

Example 4

Same as Example 2 except the polymerization reaction was carried out at 93°C.

Example 5

A 1.6 liter stainless-steel autoclave equipped with a magnet stirrer was filled with heptane (750 ml) and 1-hexene (150 ml) under a slow nitrogen purge at 50°C and then 3.0 mmol of DMAC was added. The reactor vent was closed, the stirring was increased to 1000 rpm, and the temperature was increased to 93°C. The internal pressure was raised 9.032 bars psi with hydrogen and then ethylene was introduced to maintain the total pressure at 18.66 bars psig. After that, the temperature was decreased to 80°C, 22.5 mg of catalyst precursor was introduced into the reactor with ethylene over-pressure, and the temperature was increased and held at 93°C. The polymerization reaction was carried out for 1 h and then the ethylene supply was stopped. The reactor was allowed to cool to ambient temperature and the polyethylene was collected and dried in the air.

Example 6

Same as Example 3 except the internal pressure was raised 73 psi with hydrogen and ethylene was introduced to maintain the total pressure at 13.9 bars psig.

Example 7

A 1.6 liter stainless-steel autoclave equipped with a magnet stirrer was filled with heptane (750 ml) and 1-hexene (160 ml) under a slow nitrogen purge at 50°C and then 3.0 mmol of DMAC was added. The reactor vent was closed, the stirring was increased to 1000 rpm, and the temperature was increased to 93°C. Ethylene was introduced to maintain the total pressure at 8.20 bars psig (no hydrogen was added). After that, the temperature was decreased to 80°C, 29.9 mg of catalyst precursor of Example 1 was introduced into the reactor with ethylene over-pressure, and the temperature was increased and held at 93°C. The polymerization reaction was carried out for 1 h and then the ethylene supply was stopped. The reactor was allowed to cool to ambient temperature and the polyethylene was collected and dried in the air.

Example	Productivity g/g-h	Flow Index	MFR	Mole % hexene	*T_m °C
2	1780	1.4	---	2.5	124.9
3	2440	2.0	---	2.6	124.6
4	3070	3.7	---	3.7	124.0
5	1630	22.9	34.5	3.2	125.6
6	1690	8.6	39.8	3.0	125.2
7	1505	0.5	---	3.3	121.4

T_m melting point of the copolymer

Comparative Example

The following describes the preparation of the catalyst precursor of Satoshi et al. in Example 14 of European Patent Application 0 261 808.

The catalyst precursor was synthesized as follows. N-butylethylmangesium (26.8 mmol) in heptane was added to calcined silica (5.00 g) at ambient temperature. The slurry was stirred at ambient temperature for 77 minutes. The supernatant was removed by decantation and the suspension was washed with heptane (3 times 100 ml) and then heptane (25 ml) was added. To this slurry at ambient temperature was added a solution of 20 ml tetraethyl orthosilicate (89.7 mmol) and 30 ml heptane over a period of 31 minutes. The flask was warmed to 50°C and then placed into an oil bath (53°C). Total heating time was 115 minutes. Then, at ambient temperature, the supernatant was removed by decantation and the white solid was washed with heptane (5 times 100 ml). To this solid was added 50 ml toluene and 20 ml $TiCl_4$ (182 mmol). The flask was then placed into an oil bath (90°C). After stirring 123 minutes at this temperature, the flask was removed from the oil bath and was allowed to cool to ambient temperature. The supernatant was removed by decantation and the solid was washed with heptane (5 times 100 ml). The solid was then dried yielding 8.11 grams of a light pink-brown free-flowing powder.

Ethylene/1-hexene copolymers were prepared in our 1.6 liter slurry reactor using the catalyst precursor of Satoshi et al. and the cocatalyst triethylaluminum (TEAL).

A 1.6 liter stainless-steel autoclave equipped with a magnet stirrer was filled with heptane (750 ml) and 1-hexene (150 ml) under a slow nitrogen purge at 50°C and then 3.0 mmol of TEAL (trimethylaluminum chloride) was added. The reactor vent was closed, the stirring was increased to 1000 rpm, and the temperature was increased to 85°C. The internal pressure was raised 0.89 bar psi with

hydrogen and then ethylene was introduced to maintain the total pressure at 8.46 bars psig. After that, the temperature was decreased to 75°C, 10.8 mg of catalyst precursor of Satoshi et al. was introduced into the reactor with ethylene over-pressure, and the temperature was increased and held at 85°C. The polymerization reaction was carried out for 1 h and then the ethylene supply was stopped. The reactor was allowed to cool to ambient temperature and the polyethylene was collected and dried in the air.

Productivity g/g-h	Flow Index	MFR	Mole % hexene	T_m °C
9,660	18.1	35.6	2.5	129.1

The GPC (gel permeation chromatography) chromatograms show that the resin prepared with the CIS-S/DMAC system contains a higher molecular weight component (Cf. Figure 1) which is absent in the resin prepared with the catalyst precursor of Satoshi et al. and TEAL (Cf. Figure 2).

Thus it is apparent that there has been provided, in accordance with the invention, a catalyst system composition, that fully satisfies the objects, aims, and advantages set forth above. While the invention has been described in conjunction with specific embodiments thereof, it is evident that many alternatives, modifications, and variations will be apparent to those skilled in the art in light of the foregoing description. Accordingly, it is intended to embrace all such alternatives, modifications, and variations as fall within the spirit and broad scope of the appended claims.

Throughout the description and claims of this specification, the word "comprise" and variations of the word, such as "comprising and "comprises", is not intended to exclude other additives, components or process steps.

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THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A catalyst composition for co-polymerizing ethylene and an alpha-olefin of 3 to 10 carbon atoms, comprising a solid supported catalyst precursor and a cocatalyst wherein the precursor comprises:

a) silica, wherein the silica has 0.4 to 0.9 mmol of OH groups per gram of silica;

b) a dialkylmagnesium compound, $R_mMgR'_n$, wherein each of R and R' is an alkyl group of 4 to 10 carbon atoms, and wherein m plus n equal the valence of magnesium, wherein the dialkyl-magnesium compound is present in an amount to provide a Mg:OH molar ratio of 1.0 to 1.8;

c) tetraalkyl orthosilicate, in an amount to provide a tetraalkyl orthosilicate:Mg molar ratio of 0.50 to 0.80, wherein the alkyl group contains 2 to 6 carbon atoms;

d) titanium tetrachloride in an amount to provide a Ti:Mg molar ratio of 0.7 to 1.4; and wherein the co-catalyst is dimethylaluminum chloride.

2. The catalyst composition of Claim 1, wherein the solid catalyst precursor is characterized by the K value, which is defined as

$$K = \frac{[Ti]}{[Mg] + 4[Si],}$$

wherein [Ti] is the molar titanium content provided by $TiCl_4$, [Mg] is the molar magnesium content provided by said dialkylmagnesium compound; [Si] is the molar silicon content concentration provided by said tetraalkyl orthosilicate, and K is less than 0.4.

3. The catalyst composition of claim 2, wherein the K value is in the range of 0.23 to 0.31.

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4. The catalyst composition of any one of claims 1-3, wherein the precursor is formed by the steps comprising:

(a) providing a slurry of silica in a non-polar solvent, wherein the silica has 0.4 to 0.9 mmol of OH groups per gram of silica;

(b) contacting said silica with said dialkylmagnesium compound in an amount to provide a Mg:OH molar ratio of 1.0 to 1.8.

(c) adding to said step (b) product tetraalkyl orthosilicate in which the alkyl group contains 2 to 6 carbon atoms, in an amount to provide a tetraalkyl orthosilicate:Mg molar ratio of 0.50 to 0.80;

(d) contacting said step (c) product with titanium tetrachloride in an amount to provide a Ti:Mg molar ratio of 0.7 to 1.4.

5. The catalyst composition of any one of Claims 1-4, wherein the tetraalkyl orthosilicate is tetraethyl orthosilicate or tetrabutyl orthosilicate.

6. The catalyst composition of Claim 5, wherein the tetraalkyl orthosilicate is tetraethyl orthosilicate.

7. The catalyst composition of Claim 4 wherein steps (a) - (d) are undertaken at a temperature in the range of 40 to 65°C.

8. A catalyst composition substantially as hereinbefore described with reference to any one of examples 1-7.

DATED: 12 March, 1998

PHILLIPS ORMONDE & FITZPATRICK

Attorneys for:

MOBIL OIL CORPORATION

AUSTRALIAN PATENT OFFICE

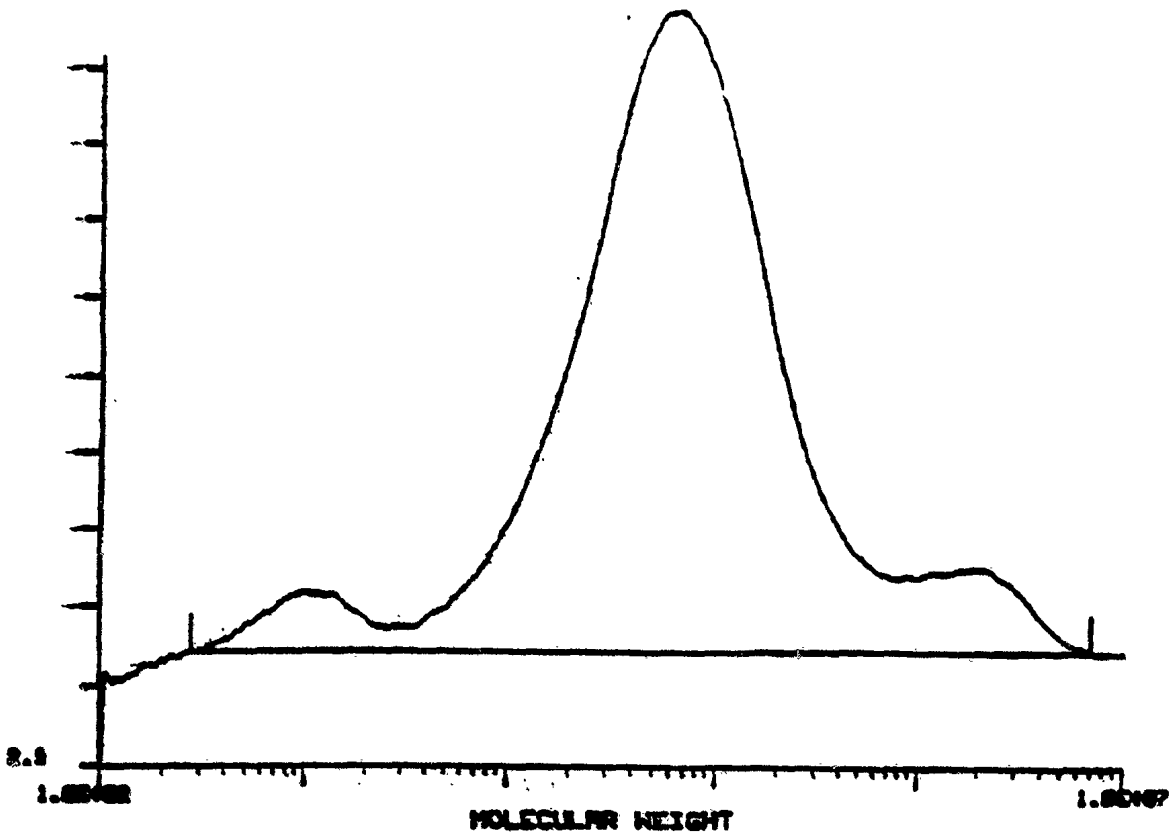

FIGURE 1

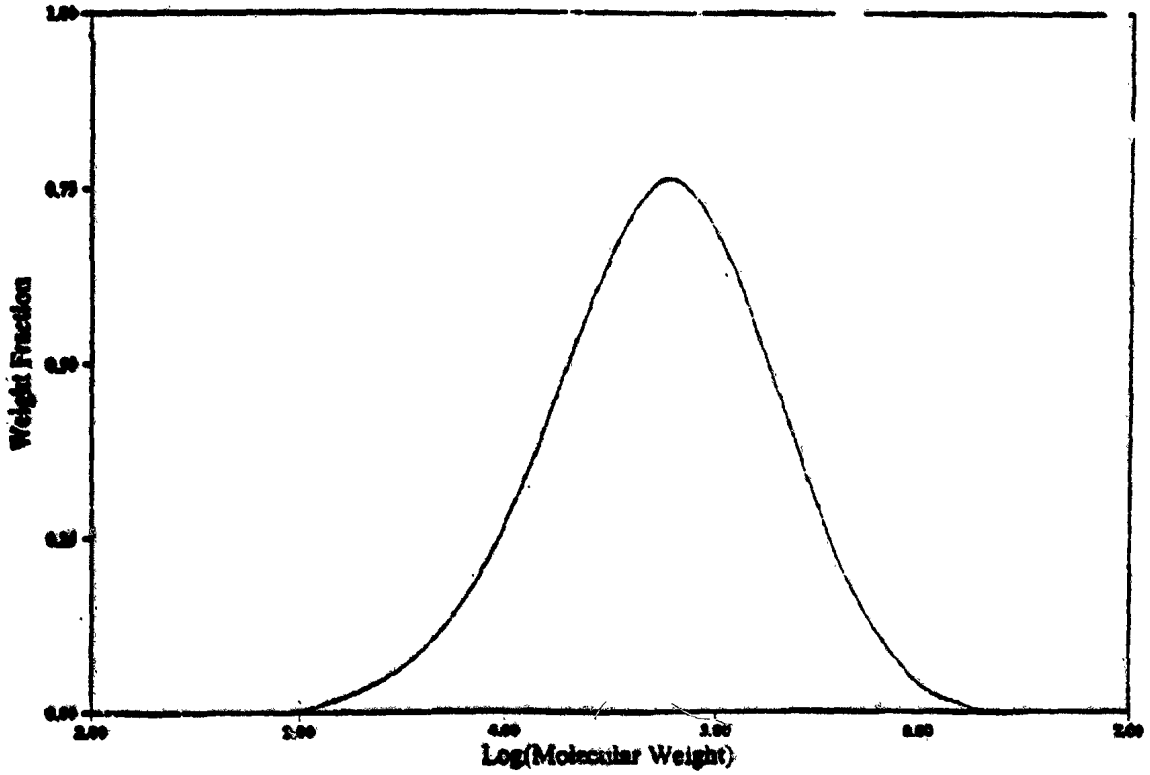

FIGURE 2

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US95/07090

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : B01J 31/12
US CL :502/120,125

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 502/120,125

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

None

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS
Search terms: silica, surface OH or hydroxyl, dialkylmagnesium, orthosilicate, silicon, titanium/

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US, A, 4,362,648 (DIETZ ET AL) 07 December 1982, see the whole document.	1-5,7
A	US, A, 4,719,193 (LEVINE ET AL) 12 January 1988, see the whole document.	1-5,7
A	US, A, 5,139,986 (COOK ET AL) 18 August 1992, see the whole document.	1-5,7
Y	EP, A, 0,261,808 (TOA NENRYO KOGYO KABUSHIKI KAISHA), see page 3, line 6 to page 6, line 56.	1-5,7

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be part of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E"	earlier document published on or after the international filing date	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&"	document member of the same patent family
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search	Date of mailing of the international search report
08 JULY 1995	21 SEP 1995
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230	Authorized officer P. ACHUTAMURTHY Telephone No. (703) 308-0196

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

INTERNATIONAL SEARCH REPORT

In...national application No.
PCT/US95/07090

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

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

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

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☒ Claims Nos.: 6
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

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

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

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

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

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

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

Remark on Protest

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

☐ No protest accompanied the payment of additional search fees.