

ROBUST SPRAY-DRIED ZIEGLER-NATTA PROCATALYST AND POLYMERIZATION PROCESS EMPLOYING SAME

CROSS REFERENCE STATEMENT

5 This application claims the benefit of U.S. Provisional Application No. 60/600,082, filed August 9, 2004.

BACKGROUND OF THE INVENTION

10 This invention relates to procatalyst compositions, processes for making such compositions, and methods for using such compositions to make polymers. More particularly, the present invention relates to novel Ziegler-Natta procatalyst compositions which in combination with a cocatalyst form catalyst compositions for use in polymerization of olefins.

15 The properties of polymers substantially depend upon the properties of the catalysts used in their preparation. In particular, the choice of the shape, size, size distribution, and other morphological properties of supported catalysts is important to ensure operability and commercial success. This is particularly important in gas phase and slurry polymerizations. A successful catalyst composition should be based on a procatalyst particle having good mechanical properties including resistance to wear, abrasion and shattering during the polymerization process, thereby imparting good bulk density and uniformity to the resulting polymer product. Equally important are
20 procatalyst compositions that produce such polymer products in high catalyst efficiency.

25 Spray-drying is a well known technique for preparing solid Ziegler-Natta polymerization procatalysts. In spray-drying, liquid droplets containing dissolved and/or suspended materials are ejected into a chamber under drying conditions to remove solvent or diluent leaving behind a solid residue. The resulting particle size and shape is related to the characteristics of the droplets formed in the spraying process. Structural reorganization of the particle can be influenced by changes in volume and size of the droplets. Depending on conditions of the spray drying process, either large, small, or aggregated particles can be obtained. The conditions may also produce particles that are compositionally uniform or contain voids or pores. The use of inert fillers in forming spray-dried particles can help control shape and composition of the resulting particles.

30 Numerous spray-dried olefin polymerization procatalysts containing magnesium and titanium and production processes for making and utilizing them have been reported. Examples include US-A's 6,187,866; 5,567,665; 5,589,539; 5,290,745; 5,122,494; 4,990,479; 4,728,705; 4,508,842; 4,482,687; 4,302,565, and 4,293,673. Generally, such compositions have been produced in the form of substantially spheroidal shaped solid procatalyst particles having average particle
35 diameters from 1 to 100 μm , depending on the intended end use. Porosity and cohesive strength of the particles can be adjusted by the use of fillers, such as silica, and binders, such as polymeric additives. Generally, solid rather than hollow particles are desired due to greater structural integrity

of the resulting particles. Disadvantageously however, solid particles tend to have lower productivities or efficiencies due to the fact that interior regions of the procatalyst particle are not able to effectively come into contact with the cocatalyst or monomer or to otherwise participate in the polymerization process as readily as surface regions of the particle. Among the foregoing list, 5 US-A- 5,589,539, disclosed particles having a narrow span, such that $(D_{90} - D_{10}) / D_{50} < 1.2$. Although possessing improved two stage resin production having fewer gels, the presence of polymer fines and static electricity generation using the foregoing procatalysts remains a problem.

Despite the advance in the art obtained by the foregoing disclosures, there still remains a need to produce Ziegler-Natta procatalysts having improved performance properties. Procatalyst 10 compositions having increased resistance to shattering and generation of polymer fines are highly desired. Generation of polymer fines is undesirable due to buildup in the polymerization equipment, thereby causing problems with bed level control and entrainment in the cycle gas leading to equipment failure, impaired operability, and reduced efficiency. High levels of fines can also cause problems in downstream handling of the polymer once it exits the polymerization system. Fines can 15 cause poor flow in purge bins, plug filters in bins, and present safety problems. The above problems make elimination or reduction of polymer fines important to commercial operation, especially of a gas-phase polymerization process.

Moreover, it has now been discovered that both catalyst fines and polymer fines are an important component in the accumulation of static charge inside of a gas-phase, fluidized bed 20 reactor. Excess accumulation of static leads to poor reactor performance due to polymer attraction to the solid surfaces of the reactor, where due to reduced heat transfer, the particles ultimately fuse together destroying the desired particle form and coating reactor surfaces.

In a multiple series reactor system, where the composition of the polymers produced in the separate reactors is widely variable, the presence of polymer fines is particularly harmful to 25 continuous and smooth operation. This is due to the extreme importance of precise bed level control, in as much as the product properties of the final polymer are strongly influenced by the relative amount of polymer produced in each reactor. If the bed weights are not precisely known, it is extremely difficult to properly control the final product properties.

With respect to the preparation of polyethylene and other ethylene/ α -olefin copolymers, it is 30 preferred to produce polymer in the separate reactors with both large molecular weight differences and relatively large differences in incorporated comonomer. To produce final polymers with the best physical properties, it is preferred to have one of the reactors produce a polymer with high molecular weight and incorporating a majority of any comonomer present. In the second reactor, a low molecular weight portion of the polymer is formed which may also have comonomer 35 incorporated, but normally in an amount less than that incorporated in the high molecular weight portion. When the high molecular weight component is produced first, polymer fines can become a significant problem, especially when the flow index (I21, ASTM D-1238, condition 190/21.6) of the

resulting polymer is in the range from 0.1 to 2.0 g/10min, and the incorporated comonomer content is less than 5 weight percent, especially less than 4.5 wt weight percent.

Depending on the order of production of the different polymers in the multiple reactor system (that is production of high molecular weight polymer first and lower molecular weight polymer second or vice versa), the fines will tend to have significantly different polymer properties than the bulk of the polymer granules. This is believed to be due to the fact that the fines also tend to be the youngest particles in the reactor and hence they do not achieve conformation to the final product properties before transiting to the second reactor in series.

This in turn leads to further problems in compounding the polymer into pellets for end-use. In particular, the fines are normally of significantly different molecular weight or branching composition compared to the remainder or bulk polymer. Although the particles of both the bulk material and the fines will melt at roughly the same temperature, mixing is hampered unless the products have a similar isoviscous temperature (that is the temperature at which the melt viscosity of the two products is essentially the same). These polymer fines, which tend to be of significantly different molecular weight and isoviscous temperature than the remainder of the polymer, are not readily homogeneously mixed with the bulk phase, but rather form segregated regions in the resulting polymer pellet and can lead to gels or other defects in blown films or other extruded articles made therefrom.

Thus, generation of polymer fines is a problem, especially for gas phase olefin polymerization processes and, in particular, for staged or series reactor systems in which precise control of polymer composition is only achieved by precise control of the relative amount of polymer produced in the multiple reactors.

Accordingly, it is desirable to minimize polymer fines in an olefin polymerization process. One factor in reducing such polymer fines is by eliminating or reducing those procatalyst particles that are susceptible to the production of polymer fines due to fractioning or abrasion. To that end, one object of the invention is to provide an improved supported procatalyst composition with greater mechanical strength that results in reduced polymer fines while, at the same time, possessing good polymerization response and efficiency. Another object of the invention is to provide an improved supported procatalyst particle that contains reduced quantities of small sized particles.

SUMMARY OF THE INVENTION

The aforementioned needs and objects are fulfilled by one or more aspects of the invention disclosed herein. In one aspect, the invention comprises substantially spheroidal shaped particles of a magnesium halide containing procatalyst composition, said particles having an average size (D50) of from 10 to 70 μm , preferably 15 to 50 μm , and most preferably from 20 to 35 μm , and characterized by a D95/D5 particle size ratio of less than or equal to 10, preferably less than or equal to 9.75.

In another aspect, the invention comprises the foregoing substantially spheroidal shaped particles of a magnesium halide containing procatalyst composition characterized by an average shell thickness/ particle size ratio (Thickness Ratio) determined by SEM techniques for particles having particle size greater than 30 μm of greater than 0.2, preferably greater than 0.25.

5 In yet another aspect, the invention comprises substantially spheroidal shaped particles of a magnesium halide containing procatalyst composition, said particles having an average size (D_{50}) of from 10 to 70 μm , preferably 15 to 50 μm , and most preferably from 20 to 35 μm , and comprising at least 5 percent, preferably at least 20 percent and most preferably at least 25 percent of particles having substantial internal void volume and a substantially monolithic surface layer (shell)
10 characterized by an average shell thickness/ particle size ratio (Thickness Ratio) determined by SEM techniques for particles having particle size greater than 30 μm of greater than 0.4, preferably greater than 0.45 and a D_{95}/D_5 ratio of less than or equal to 10, preferably less than or equal to 9.75.

In another aspect, the invention relates to a method for making the foregoing procatalyst composition, the steps of the method comprising: a) providing a liquid composition comprising i) a
15 magnesium halide compound, ii) a solvent or diluent, iii) a transition metal compound wherein the transition metal is selected from the metals of Groups 3-10 and Lanthanides of the Periodic Table of the Elements, iv) optionally an internal electron donor, and v) a filler; b) spray-drying the composition to form a spray-dried particle; and c) collecting the resulting solid particles, characterized in that the magnesium halide compound forms a substantially saturated solution in the
20 solvent or diluent.

In yet another aspect of the invention, the procatalyst particles possess improved particle cohesiveness and size distribution. More particularly, the particles are characterized by a significant percentage, preferably at least 50 percent, more preferably at least 60 percent thereof, that are substantially solid, having a Thickness Ratio greater than or equal to 0.4, more preferably greater
25 than or equal to 0.45 and/or characterized by a $D_{95}/D_5 \leq 9.5$. The latter property is characteristic of supported procatalyst particles that are extremely robust and not subject to shattering and fines generation during manufacture and usage.

In still another aspect, the invention relates to a process for making a polymer comprising contacting at least one olefin monomer with the foregoing supported procatalyst compositions or
30 made by the foregoing method, and a cocatalyst under olefin polymerization conditions to form a polymer product.

DETAILED DESCRIPTION

All reference to the Periodic Table of the Elements herein shall refer to the Periodic Table of
35 the Elements, published and copyrighted by CRC Press, Inc., 2003. Also, any reference to a Group or Groups shall be to the Group or Groups as reflected in this Periodic Table of the Elements using the IUPAC system for numbering groups. For purposes of United States patent practice, the

contents of any patent, patent application, or publication referenced herein are hereby incorporated by reference in their entirety (or the equivalent US version thereof is so incorporated by reference) especially with respect to the disclosure of synthetic techniques, raw materials, and general knowledge in the art. Unless stated to the contrary, implicit from the context, or customary in the art, all parts and percents are based on weight.

If appearing herein, the term "comprising" and derivatives thereof is not intended to exclude the presence of any additional component, step or procedure, whether or not the same is disclosed herein. In order to avoid any doubt, all compositions claimed herein through use of the term "comprising" may include any additional additive, adjuvant, or compound, unless stated to the contrary. In contrast, the term, "consisting essentially of" if appearing herein, excludes from the scope of any succeeding recitation any other component, step or procedure, excepting those that are not essential to operability. The term "consisting of", if used, excludes any component, step or procedure not specifically delineated or listed. The term "or", unless stated otherwise, refers to the listed members individually as well as in any combination.

The terms "D₅", "D₁₀", "D₅₀", "D₉₀", and "D₉₅" are employed to indicate the respective percentiles (5, 10, 50, 90 and 95) of log normal particle size distribution determined, for example, by means of an automated particle size analyzer, such as a Coulter™ brand particle analyzer, using dodecane solvent. Thus, particles having a D₅₀ of 12 μm have a median particle size of 12 μm. A D₉₀ of 18 μm indicates that 90 percent of the particles have a particle size of less than 18 μm, and a D₁₀ of 8 μm indicates that 10 percent of the particles have a particle size of less than 8 μm. The width or narrowness of a particle size distribution can be given by its span. The span is defined as (D₉₀-D₁₀)/(D₅₀). A ratio of various percentiles, such as D₉₅/D₅, can be used to define the relative percentile distributions of the particles.

Ziegler-Natta procatalyst compositions can be produced by numerous techniques including physical blending of solid mixtures of magnesium halides with titanium halides or the *in situ* formation of halogenating agents such as by reducing a titanium halide compound with elemental magnesium. Solid phase forming techniques involve the use of ball-mills or other suitable grinding and comminuting equipment. Precipitation techniques may use repeated halogenations with various halogenating agents, preferably TiCl₄ to prepare suitable procatalyst compositions.

Various methods of making procatalyst compositions are known in the art. Included in these methods are those described, inter alia, in: US-A-5,487,938; 5,290,745; 5,247,032; 5,247,031; 5,229,342; 5,153,158; 5,151,399; 5,146,028; 5,106,806; 5,082,907; 5,077,357; 5,066,738; 5,066,737; 5,034,361; 5,028,671; 4,990,479; 4,927,797; 4,829,037; 4,816,433; 4,547,476; 4,540,679; 4,460,701; 4,442,276; and elsewhere. In a preferred method, the preparation involves chlorination of a magnesium compound or mixture of compounds, optionally in the presence of an inert solid material, especially silica, alumina, an aluminosilicate, or similar substance. The resulting

compound or complex comprises at least magnesium, halogen, and transition metal moieties, especially titanium or vanadium moieties.

In one embodiment the procatalyst is formed by halogenation of a precursor by reaction with one or more magnesium, halogen and transition metal sources. Suitable sources for magnesium moieties include magnesium metal, anhydrous magnesium chloride, magnesium alkoxides or aryloxides, or carboxylated magnesium alkoxides or aryloxides. Preferred sources of magnesium moieties are magnesium halides, especially magnesium dichloride, as well as magnesium (C₁₋₄) alkoxides, especially magnesium compounds or complexes containing at least one ethoxy group. Preferred compositions additionally comprise a transition metal compound, especially titanium compounds. Suitable sources of transition metal moieties include the corresponding (C₁₋₈) alkoxides, aryloxides, halides and mixtures thereof. Preferred precursors comprise one or more magnesium (C₁₋₄) alkoxide or halide containing compounds and optionally one or more titanium (C₁₋₄) alkoxides or halides.

Suitable transition metal compounds other than titanium or vanadium include compounds of other Group 3-8 transition metals, especially zirconium, hafnium, niobium, or tantalum. In certain embodiments, other transition metals, such as later transition metals and Lanthanides, or mixtures of transition and/or Lanthanide metals may be suitable as well. Two or more metal compounds may be combined, if desired, in order to produce polymer products reflecting multiple polymerization forming environments. Typically the resulting polymer product has a broadened molecular weight distribution.

Preferred transition metal compounds are titanium compounds corresponding to the formula: $Ti(OR^2)_aX_{4-a}$ wherein R² independently each occurrence is a substituted or unsubstituted hydrocarbyl group having 1 to 25 carbon atoms, preferably methyloxy, ethyloxy, butyloxy, hexyloxy, decyloxy, dodecyloxy, phenyloxy, or naphthyloxy; X is halide, preferably chloride, and a may range from 0 to 4. Mixtures of titanium compounds can be employed if desired.

Most preferred transition metal compounds are titanium halides and haloalkoxides having 1 to 8 carbon atoms per alkoxide group. Examples of such compounds include: TiCl₄, TiBr₄, TiI₄, TiCl₃, Ti(OCH₃)Cl₃, Ti(OC₂H₅)Cl₃, Ti(OC₄H₉)Cl₃, Ti(OC₆H₅)Cl₃, Ti(OC₆H₁₃)Br₃, Ti-(OC₈H₁₇)Cl₃, Ti(OCH₃)₂Br₂, Ti(OC₂H₅)₂Cl₂, Ti(OC₆H₁₃)₂Cl₂, Ti(OC₈H₁₇)₂Br₂, Ti(OCH₃)₃Br, Ti(OC₂H₅)₃Cl, Ti(OC₄H₉)₃Cl, Ti(OC₆H₁₃)₃Br, and Ti(OC₈H₁₇)₃Cl.

The quantity of a transition metal compound or mixture of transition metal compounds used in preparing procatalysts of the invention may vary widely depending on the type of procatalyst desired. In some embodiments, the molar ratio of magnesium to transition metal compound may be as high as 56 and as low as 0.5, depending upon the specific catalyst design. Generally, molar ratios of magnesium to transition metal compound from 3 to 10 are preferred.

Forming a suitable procatalyst composition may be accomplished in any manner. One suitable technique involves mixing of a magnesium halide compound with a transition metal

compound to form a procatalyst precursor. The components are desirably combined at a temperature ranging from -70 to 200 °C. Preferably, the temperature is from 20 to 150 °C, most preferably from 25 to 120 °C, and should be below the boiling point of any solvent or diluent employed. In some embodiments, the magnesium halide solution and the titanium compound may be mixed from 5 minutes to 24 hours. In other embodiments, 30 minutes to 5 hours are sufficient to achieve the desired concentration of magnesium halide. Sufficient mixing is generally attained by the use of mechanical stirring equipment, however ultrasonic sound generators, static mixers, or other suitable devices may be employed to aid in dispersion and mixing, if desired.

A preferred precursor composition for use herein is a mixed magnesium/titanium composition of the formula $Mg_dTi(OR^e)_eX_f$ wherein R^e is an aliphatic or aromatic hydrocarbon radical having 1 to 14 carbon atoms or COR' wherein R' is an aliphatic or aromatic hydrocarbon radical having 1 to 14 carbon atoms; each OR^e group is the same or different; X is independently R' , chlorine, bromine or iodine; d is 0.5 to 5, preferably 2-4, most preferably 3; e is 0-12, preferably 0-10, most preferably 0-4; and f is 1-10, preferably 2-8, most preferably 2-6. The precursors are ideally prepared by halogenation of a magnesium and titanium containing compound or mixture. An especially desirable reaction medium comprises a mixture of an aromatic liquid, especially a chlorinated aromatic compound, most especially chlorobenzene, an alkanol, especially ethanol, and an inorganic chlorinating agent. Suitable inorganic chlorinating agents include chlorine derivatives of silicon, aluminum and titanium, especially titanium tetrachloride or aluminum sesquichloride, most especially titanium tetrachloride.

In certain embodiments, the precursor comprises a composition of the formula: $[Mg(R^1OH)_r]_dTi(OR^e)_eX_f[ED]_q$, wherein R^1OH is a monofunctional, linear or branched alcohol having between one and 25 carbon atoms; ED is an electron donor, especially a compound selected from the group consisting of alkyl esters of aliphatic and aromatic carboxylic acids, aliphatic ethers, cyclic ethers, and aliphatic ketones; q ranges from 0 to 50; r is 0, 1, or 2; and R^e , X , d , e , and f are as previously defined. Procatalyst compositions employed in the manufacture of propylene homopolymers or copolymers generally include an electron donor for purposes of controlling tacticity of the resulting polymer, and may differ in chemical composition from procatalysts used to prepare ethylene homopolymers or copolymers of ethylene and an α -olefin. Other procatalysts include an electron donor, especially a Lewis base, such as aliphatic ethers, especially tetrahydrofuran or aromatic esters or diesters such as p-ethoxyethylbenzoate or diisobutylphthalate, for different purposes such as forming a complex to stabilize the resulting compound. Where one or more additional transition metal compounds are included in the procatalyst composition, the same may be incorporated in the precursor composition (replacing a portion of the titanium compound in the above formula) or added subsequently, even after complete formation of the procatalyst particles, for example by contacting the solid procatalyst with a solution of the transition metal compound and removing the solvent.

Another preferred procatalyst composition for ethylene polymerizations comprises TiCl_3 , formed by the reduction of TiCl_4 with magnesium metal in the presence of an electron donor. The electron donor employed in this embodiment of the invention must be free of substituents containing active hydrogen, such as hydroxyl groups, due to the fact that such functional groups readily react with both magnesium and titanium tetrachloride. The reduction process results in the formation of a mixture of magnesium dichloride and titanium trichloride, in the form or a complex with the electron donor. This reaction can be illustrated by the following equation:

$$2 \text{TiCl}_4(\text{ED})_2 + \text{Mg} \rightarrow 2 \text{TiCl}_3(\text{ED})_3 + \text{MgCl}_2(\text{ED})_{1.5}$$
, where ED is a Lewis base electron donor, preferably tetrahydrofuran.

Because magnesium metal is highly reactive with titanium tetrachloride, it is preferable to employ the metal in the form of coarse granules rather than a powder in order to moderate the reaction rate. Magnesium particles having an average particle size of from 0.25 mm to 10 mm, preferably from 1 mm to 4 mm, are preferably employed. Desirably, one mole of magnesium metal for every two moles of titanium tetrachloride is employed in the reduction.

From 5 mols to 400 mols of electron donor compound are advantageously employed per mol of titanium tetrachloride, preferably 50 mols to 200 mols of electron donor compound per mol of titanium tetrachloride, with most of the excess being removed prior to or during spray-drying or other subsequent particle forming process. Usually the magnesium metal is added to a mixture of titanium tetrachloride dissolved in the electron donor compound. However, it is also possible to add the titanium tetrachloride to a mixture of the magnesium metal in the electron donor compound, or even to add the titanium tetrachloride and magnesium metal to the electron donor compound together. Ordinarily reaction is effected below the boiling point of the electron donor compound, preferably between 20 and 70 °C. An inert atmosphere should be maintained, that is, an atmosphere that is nonreactive under the conditions employed during the reduction.

The reduction of titanium tetrachloride with magnesium metal desirably results in formation of a solution containing one mole of magnesium dichloride for every two moles of titanium trichloride, and which is substantially free of undesirable by-products. Additional magnesium dichloride may be added to the solution to increase the Mg/Ti ratio, if desired. Highly desirably, sufficient magnesium dichloride is added to result in a Mg/Ti molar ratio from 1.5:1 to 15:1, most preferably from 4:1 to 6:1. Additional transition metal compounds such as those defined previously may be added as well. Additional electron donor compounds, especially those which may have reactive functionality towards either Mg metal or TiCl_4 may be added after the reduction is completed as well.

More than one transition metal compound may be included in the procatalyst compositions of the present invention. In particular, a titanium containing compound, especially a titanium/magnesium complex, and a hafnium or vanadium halide compound, such as a hafnium/magnesium/halide complex, or a mixture thereof, are desired for combination in a

procatalyst composition to prepare broadened molecular weight polyethylene products, having a desired high molecular weight "tail", meaning a major quantity of a low molecular weight polymer and a minor quantity of high molecular weight, higher crystallinity polymer. Generally the quantity of hafnium or vanadium compound is present in an amount from 0.1 to 100 percent of the titanium
5 compound. The resulting polymer may have a PDI from 6 to 8 compared to PDI's from 3 to 6 resulting from the use of procatalysts lacking a second transition metal component.

Additional components of the procatalyst composition may include fillers, binding agents, solvents, polymerization modifiers, and the aforementioned electron donor compounds. Typically a liquid mixture in which the magnesium halide (procatalyst) composition is soluble is contacted with
10 the filler, especially finely particulated, substantially spheroidal shaped silica. The term "substantially spheroidal" as used herein means particles having an average aspect ratio from 1.0 to 2.0, where aspect ratio is defined as the ratio of the largest linear dimension of a particle to the smallest linear dimension thereof as determined from Scanning Electron Micrograph (SEM) images. Preferred fillers have an average particle size ranging from 0.01 μm to 12 μm . Larger sized filler
15 particles do not pack as densely as smaller particles leaving inter-particle voids in the resulting dried particles, in which the procatalyst composition and/or binders are inserted. A sufficient amount of procatalyst composition and optional binder should be used to fill any voids between filler particles, resulting in the formation of a relatively dense, tough and shatter resistant shell on the surface of the procatalyst particle. If the shell Thickness Ratio is 0.4 or higher the particles are substantially solid
20 (the theoretical upper limit for Thickness Ratio being 0.5), and such particles are particularly immune to breakage or shattering due to abrasion.

Suitable fillers are inert to the other components of the procatalyst composition, and to the active components employed in any subsequent polymerization. Suitable compounds can be organic or inorganic and include, but are not limited to, silicas, titanium dioxide, zinc oxide, magnesium
25 carbonate, magnesium oxide, carbon, and calcium carbonate. In some embodiments, the filler is fumed hydrophobic silica that imparts relatively high viscosity to the slurry and good strength to the spray-dried particles. In other embodiments, two or more fillers may be used. Suitable fillers for use herein include those sold under the trade designation Gasil™, available from Ineos Corporation, and Cabosil™, available from Cabot Corporation.

30 Fillers for use herein may be porous and, if greater than 1 micrometer in particle size preferably are porous. Porosity of the filler may allow better diffusion of monomer into the interior of the procatalyst particle during polymerization. Preferred porous filler particles have a cumulative pore volume from 0.1 to 2.0 ml/g calculated by the B.E.T. technique according to ASTM Standard D3663-99. These preferred fillers are also characterized by a surface area ranging from 25 m^2/g to
35 200 m^2/g , preferably from 50 m^2/g to 100 m^2/g . Surface area may also be measured using the B.E.T. technique. Certain fillers, such as fumed silicas, fumed aluminas, and fumed titanias are generally

of very small particle size, typically with primary particle sizes less than 0.1 micrometers, although materials in the form of aggregates of the primary particle, may be employed as well.

Whatever the choice of filler, it should be dry, that is, free of absorbed water. Drying of the filler is carried out by heating it at a temperature below the sintering or melting point of the filler material for a suitable period, or the material, for example fumed silica, may, due to its specific manufacturing method, be naturally low in residual moisture content. Typically, temperatures of at least 100°C are used. Lower temperatures may be used where prolonged drying times are acceptable or where the support has a low melting or sintering temperature. Inorganic filler materials are typically dried at a temperature from 200 to 800°C. In addition, the filler material may be optionally treated with from 1 to 8 weight percent of one or more Lewis acids, such as aluminum trialkyl compounds, alkylalumoxanes, or organosilane compounds, to remove polar impurities, including water or hydroxyl groups.

The filler is generally employed in an amount from 1 to 95 percent of the total procatalyst slurry composition weight. The quantity of filler employed is adjusted to produce a slurry of the desired viscosity for good spray drying operation. Preferably, the filler comprises from 50 to 98, preferably from 70 to 98, and most preferably from 75 to 98 percent of the slurry. It has been generally discovered that in order to prepare particles having D95/D5 less than or equal to 10, slurries containing higher quantities of filler and/or precursor composition should be employed. Preferably, the filler comprises from 10 to 98, preferably from 20 to 95, and most preferably from 25 to 90 percent of the dried procatalyst particle weight.

The term "polymerization modifier" as used herein refers to a compound added to the procatalyst composition or to the polymerization mixture in order to modify one or more process or product properties. Examples include selectivity control agents used to modify tacticity and crystallinity of the polymer.

By using a polymerization modifier (PM), one or more process or product properties are beneficially affected. Examples include the ability to prepare copolymers having higher or lower comonomer incorporation at equivalent polymerization conditions or alternatively, preparing equivalent copolymers at higher polymerization temperatures or lower comonomer concentrations in the reaction mixture. Another beneficial feature of the use of a polymerization modifier may be greater selectivity in product formation as determined by narrower or broader molecular weight distribution (Mw/Mn) of homopolymers and copolymer products or a relative lack of formation or reduction in formation of a particular species, such as a polymer fraction having differentiated crystallinity, solubility, tacticity, melting point, melt flow index, or other physical property. A further desirable result of the use of a PM may be improved process properties such as improved monomer conversion efficiency by scavenging impurities that may be present in a polymerization mixture.

The molar quantity of PM employed is generally in the amount from 0.1 to 10 moles per mole of metal complex. The PM may be incorporated in or on the procatalyst composition of the invention or added separately to the polymerization reactor continuously or intermittently during polymerization according to conventional techniques. The PM composition is especially

5 beneficially employed for the foregoing purpose in combination with a procatalyst composition comprising both titanium and hafnium compounds or complexes, especially one comprising substantially spheroidal shaped particles of a magnesium halide containing procatalyst composition, said particles having an average size (D50) of from 10 to 70 μm , preferably 15 to 50 μm , and most preferably from 20 to 35 μm , and characterized by a D95/D5 particle size ratio of less than or equal

10 to 10, preferably less than or equal to 9.75; or a procatalyst comprising substantially spheroidal shaped particles of a magnesium halide composition characterized by an average shell thickness/ particle size ratio (Thickness Ratio) determined by SEM techniques for particles having particle size greater than 30 μm of greater than 0.2, preferably greater than 0.25; or a procatalyst comprising substantially spheroidal shaped particles of a magnesium halide composition having an average size

15 (D50) of from 10 to 70 μm , preferably 15 to 50 μm , and most preferably from 20 to 35 μm , and comprising at least 5 percent, preferably at least 20 percent and most preferably at least 25 percent of particles having substantial internal void volume and a substantially monolithic surface layer (shell) characterized by an average shell thickness/ particle size ratio (Thickness Ratio) determined by SEM techniques for particles having particle size greater than 30 μm of greater than 0.4,

20 preferably greater than 0.45 and a D95/D5 ratio of less than or equal to 10, preferably less than or equal to 9.75.

In another aspect, the invention relates to a method for making the foregoing procatalyst compositions, the steps of the method comprising: a) providing a liquid composition comprising i) a magnesium halide compound, ii) a solvent or diluent, iii) a transition metal compound wherein the

25 transition metal is selected from the metals of Groups 3-10 and Lanthanides of the Periodic Table of the Elements, iv) optionally an internal electron donor, and v) a filler; b) spray-drying the composition to form a spray-dried particle; and c) collecting the resulting solid particles, characterized in that the magnesium halide compound forms a substantially saturated solution in the solvent or diluent and/or the filler comprises from 50 to 98 percent of the slurry.

30 In yet another aspect of the invention, the procatalyst particles possess improved particle cohesiveness and size distribution. More particularly, the particles are characterized by a significant percentage, preferably at least 50 percent, more preferably at least 60 percent thereof, that are substantially solid, having a Thickness Ratio greater than or equal to 0.4, more preferably greater than or equal to 0.45 and/or characterized by a D95/D5 ≤ 9.5 .

35 Exemplary equipment and techniques for spray drying have been previously disclosed in US-A's 6,187,866; 5,567,665; 5,290,745; 5,122,494; 4,990,479; 4,728,705; 4,508,842; 4,482,687; 4,302,565, and 4,293,673, and elsewhere. According to the present invention however, the

conditions used in the spray-drying process are critical to formation of the desired procatalyst particles. Generally, the spray-drying is accomplished by mixing a solution or slurry of the procatalyst or the procatalyst precursor with any filler, binder, selectivity control agent, polymerization modifier, or other component of the composition. The resulting mixture is then heated and atomized by means of a suitable atomizing device to form discrete droplets. Atomization is usually effected by passing the slurry through the atomizer together with an inert drying gas. An atomizing nozzle or a centrifugal high speed disc can be employed to effect atomization. The volumetric flow of drying gas is considerably higher than volumetric flow of the slurry to effect atomization of the slurry and removal of solvent or diluent and other volatile components. The drying gas should be nonreactive under the conditions employed during atomization. Suitable gases include nitrogen and argon. However, any other gas may be used so long as it is nonreactive and performs the desired drying of the procatalyst. Generally, the drying gas is also heated to facilitate rapid removal of electron donor, diluent or solvent and solid particle formation. If the volumetric flow of drying gas is maintained at a very high level, it is possible to employ lower gas temperatures. The pressure of the drying gas is also adjusted to provide a suitable droplet size during atomization. Suitable atomization nozzle pressures are from 1-200 psig (100-1500 kPa), preferably from 10 to 150 psig (170-1100 kPa). In centrifugal atomization, the atomizer wheel diameter is typically from 50 mm to 500 mm. Wheel speed is adjusted to control particle size. Typical wheel speeds are from 8,000 to 24,000 rpm, although higher or lower speed can be used if needed to obtain the desired particle size and composition.

The present inventors have discovered that the concentration of magnesium component of the procatalyst composition in the slurry used to form the droplet in the spray-drying procedure, the quantity of filler, as well as the drying conditions employed in forming particles from the atomized droplets are directly related to the morphology as well as the mechanical and chemical properties of the resulting spray-dried procatalyst composition. In particular, the D95/D5 ratio of the resulting procatalyst particles is reduced by the use of increased concentrations of magnesium compound in the procatalyst slurry used to prepare the particles as well as increased concentrations or amounts of filler, preferably in combination with rapid drying conditions. It is believed that the use of increased concentrations of magnesium compound/ filler during droplet formation results in reduced stress on the particle during subsequent drying leading to a reduction in the D95/D5 ratio of the product. Moreover, formation of smaller sized droplets during atomization is also reduced. The resulting particles are better able to resist crumbling and breakage during formation, handling, and feeding operations resulting in a final activated catalyst particle that is more robust and less likely to fracture during the initial stages of the polymerization reaction. All of these features are believed to contribute to reduced polymer fines generation using the invented compositions.

By the term "substantially saturated" is meant that the magnesium compound, especially a magnesium halide compound, forms a solution in the diluent or solvent that is highly concentrated

and may even exceed the normal solution concentration limits of the diluent or solvent at the temperature of the atomization. Super-saturated solutions of the magnesium compound may arise due to the fact that solubility may decrease as temperature is increased so that upon heating of the slurry, the saturation threshold is exceeded. Due to the presence of fillers and other dissolved or
5 other undissolved materials in the slurry; the use of elevated pressures, extreme mixing and turbulent flow conditions, and the brevity of the exposure to elevated temperatures, precipitation of the magnesium compound, if it occurs at all, is not detrimental to particle properties. Moreover, use of the foregoing concentrated slurry conditions and rapid drying conditions results in the formation of relatively robust, thick shelled, hollow or solid particles, especially in the larger diameter ranges.
10 Such particles are believed to be relatively immune to polymer fines generation and highly efficient, since catalyst material is concentrated on the surface of the particles and not isolated within the interior thereof.

Isolation of material in the interior of generally solid procatalyst particles is thought to be disadvantageous due to the fact that different diffusion velocities of different monomers can affect
15 the monomer concentration available in the interior of the particle compared to the bulk monomer concentration. This in turn results in differences in the polymer formed by catalyst sites located in the interior of the particle as compared to the surface, especially when copolymers are prepared from mixtures of monomers. Moreover, another advantage to procatalyst compositions having a D95/D5 of less than or equal to 10 is that problems due to static electricity build up during conveying and
20 use are reduced. In as much as the particle volume is proportional to the cube of the particle size whereas the surface area is proportional to the square of the particle size, larger sized particles have reduced charge density/ mass ratios as well as reduced charge transfer rates. This results in a reduction of attraction forces for such particles due to static electricity build up.

Not only are larger sized particles less affected by static electricity build up, it is further
25 believed that the generation of static electricity per se is reduced for compositions where the D95/D5 ratio is lower. That is, the presence of both small and large particles leads to generation of bigger static electricity charges due to an increase in particle interactions or collisions, as well as an increase in charge transfer. These two factors are believed to lead to greater static electricity charge density in the resulting particles. Reducing the D95/D5 ratio as provided herein reduces the
30 quantity of static electricity build up on the particles as well as the charge density, thereby reducing any adverse affects resulting therefrom.

Generally, feedstock slurries used to prepare the particles of the invention are from 50-150 percent, preferably from 80-125 percent of the saturation concentration of the magnesium compound, preferably the magnesium halide compound, most preferably magnesium dichloride, in
35 the solvent or diluent at the temperature employed during the atomization. Highly desirably, the feedstock solutions are prepared and maintained prior to atomization at a concentration that is greater than 90 percent of the saturation concentration at that temperature. Solvents or diluents used

in the preparation of the spray dried particles include Lewis base compounds, such as ethers or other electron donors, especially tetrahydrofuran, as well as hydrocarbons, especially toluene, xylene, ethylbenzene, and/or cyclohexane. If an electron donor is desirable for purposes of stabilizing a component of the precursor composition, it may serve as the diluent, normally by using an excess thereof.

When spray dried, such slurries produce discrete particles having the desired physical properties. In some embodiments the spray dried particles have smaller particles encapsulated within an outer shell or attached thereto and at times completely or nearly completely filling the interior of the resulting particles. Generally however, upon drying or removing the diluent or solvent, a portion of the interior volume of such particles is left relatively empty, thereby reducing the density of the resulting particles and improving catalyst efficiency. Although the surface of the particles is referred to as monolithic, it is to be understood that the crust or skin may include pores, ridges, crevices, fissures, or other discontinuities allowing communication with the interior of the particle without departing from the scope of the present invention. Preferably the relatively empty regions of the particle interior constituting the center half of the particle's interior volume comprise no more than 20 percent, more preferably no more than 10 percent, of the particle's mass.

One method for determining the thickness ratio in a collection of particles is to embed the particles in an inert matrix material such as polyethylene. The sample is then polished or sheared to expose a cross-section of representative particles. Any suitable form of microscopy may then be employed to visually determine the average thickness ratio of the particles.

The procatalyst particles are also characterized by their size distribution. In some embodiments, the procatalyst particles have a span less than 2.0, preferably less than 1.8. A narrower span has a smaller percentage of particles that may be too small or too large for a given application. The desirable span varies with the application. Percentile distributions (D_{95}/D_5) of less than 10, and especially less than 9, are an indication of particle cohesiveness since shattering of only a few large particles generates large numbers of small particles.

In the operation of the invention the procatalyst is combined with a cocatalyst to form the active catalyst composition. The activation may occur prior to or simultaneously with, or after contacting with the monomer or monomers to be polymerized. In a preferred embodiment, the procatalyst is partially or fully activated outside the polymerization reactor by contacting the same with a portion of the cocatalyst in an inert liquid hydrocarbon as disclosed in US-A-6,187,866 or US-A-6,617,405. After contacting the procatalyst composition with the cocatalyst, the hydrocarbon solvent may be removed by drying and the catalyst composition subsequently fed to the polymerization reactor where the activation is completed with additional amounts of the same or a different cocatalyst, if necessary.

The partially activated catalyst or the unactivated procatalyst composition and cocatalyst or additional quantities of cocatalyst are fed into the reactor or component structures thereof by the

same or by separate feed lines. Desirably, the quantity of cocatalyst employed is sufficient to produce a molar ratio based on transition metal in the procatalyst from 1000:1 to 10:1. In multiple reactors operating in series, additional quantities of procatalyst, cocatalyst or both may be added to the second or subsequent reactor(s), as desired to control polymerization conditions.

5 Suitable activators for use herein are Lewis acids, especially alkylaluminum compounds, including triethylaluminum, tri-n-butylaluminum, tri-n-hexylaluminum, and mixtures thereof, and alkylaluminum halides, such as ethylaluminum sesquichloride. Tri-n-hexylaluminum activator has been found to result in generation of broader molecular weight polymer products, particularly if the procatalyst contains more than one transition metal compound, especially titanium and hafnium
10 halides, for example a mixture of titanium tetrachloride and hafnium tetrachloride.

 In some embodiments, catalysts prepared according to the present invention have improved productivity, especially when employed in a gas phase olefin polymerization process. It is to be understood that the catalysts described herein may be used in solution, slurry or gas-phase polymerizations. Suitable monomers for polymerization include C₂-C₂₀ olefins, diolefins, cyclo-
15 olefins, and mixtures thereof. Especially suited are ethylene homopolymerization processes and copolymerizations of ethylene with C₃ to C₈ α -olefins, such as for example, 1-butene, 1-hexene, 4-methyl-1-pentene, and 1-octene.

Polymerization

20 Various reactor configurations and operating conditions may be employed as desired by the skilled artisan. In a single reactor configuration, the procatalyst may be combined with some (partially activated) or all of the cocatalyst (fully activated) and added to the reactor. Alternatively, some or all of the co-catalyst may be added to the reactor itself or to the recycle stream of the reactor system. In a dual reactor configuration, the reaction mixture including the activated procatalyst
25 along with unreacted monomers and/or the copolymer or homopolymer produced in the first reactor, is transferred to the second reactor. Additional quantities of partially or fully activated procatalyst and/or the same or a different cocatalyst may be added to the reaction mixture in the second reactor or to the reaction mixture charged thereto, if desired.

 The polymerization in each reactor is desirably conducted in the gas phase using a
30 continuous fluidized bed process. A typical fluidized bed reactor can be described as follows. The bed is usually made up of the same granular resin that is to be produced in the reactor. Thus, during the course of the polymerization, the bed comprises formed polymer particles, growing polymer particles, and catalyst particles fluidized by polymerization and modifying gaseous components introduced at a flow rate or velocity sufficient to cause the particles to separate and act as a fluid.
35 The fluidizing gas is made up of the initial feed, make-up feed, and cycle (recycle) gas, that is, comonomers and, if desired, modifiers and/or an inert carrier gas.

The essential parts of the reaction system are vertically disposed reactor vessel, the bed, the gas distribution plate, inlet and outlet piping, a compressor, cycle gas cooler, and a product discharge system. In the reactor vessel, above the bed, there is a velocity reduction zone, and, in the bed, a reaction zone. Both regions of the reactor are above the gas distribution plate and a gaseous reaction mixture is caused to flow in an upward direction through the gas distribution plate to maintain the reactor bed in a fluidized state. A typical fluidized bed reactor is further described in US-A-4,482,687, and elsewhere.

The gaseous feed stream comprising ethylene, other gaseous alpha-olefins, optionally hydrogen, condensing agent, and/or diluents, when used, are preferably fed to the reactor recycle line as well as liquid alpha-olefins and the cocatalyst solution. Optionally, the liquid cocatalyst can be fed directly to the fluidized bed. The procatalyst, which is preferably at least partially preactivated by contact with cocatalyst is preferably injected into the fluidized bed as a mineral oil slurry. Activation is generally completed in the reactor by the addition of cocatalyst. Changing the molar ratios of the comonomers introduced into the fluidized bed can vary the product composition. The product is continuously discharged in granular or particulate form from the reactor as the bed level increases due to polymerization. Adjusting the catalyst feed rate and/or the ethylene partial pressures in one or both reactors controls the production rate.

The hydrogen/ethylene mole ratio can be adjusted to control the average molecular weight of the polymer product. The alpha-olefins other than ethylene, if used, can be present in a total amount of up to 15 percent by weight of the copolymer and, if used, are preferably included in the copolymer in a total amount from 0.1 to 10 percent based on total polymer weight. The quantity of such α -olefin can be adjusted to control the density of the final product.

The residence time of the mixture of reactants including gaseous and liquid reactants, catalyst, and resin in each fluidized bed can be in the range of 1 to 12 hours and is preferably in the range of 1.5 to 5 hours. Either or both of the reactors of a dual reactor system can be operated in condensing mode, as is described in US-A's 4,543,399; 4,588,790; and 5,352,749, if desired.

In a dual reactor configuration, a relatively low melt index or low flow index (or high molecular weight) copolymer is usually prepared in the first reactor. The mixture of polymer, unreacted monomer, and activated catalyst is preferably transferred from the first reactor to the second reactor via an intercommunicating conduit using nitrogen or reactor recycle gas as a transfer medium. A preferred mode is to take batch quantities of product from the first reactor, and transfer these to the second reactor using the differential pressure generated by the recycle gas compression system. A system similar to that described in US-A-4,621,952, is particularly useful in this regard. Alternatively, the low molecular weight copolymer can be prepared in the first reactor and the high molecular weight copolymer can be prepared in the second reactor.

Regardless of the reactor employed, for production of a high molecular weight product, the mole ratio of alpha-olefin to ethylene is desirably in the range from 0.01:1 to 0.8:1, preferably from

0.02:1 to 0.35:1. The mole ratio of hydrogen to ethylene is desirably in the range of 0.001 to 0.3:1, and preferably from 0.01 to 0.2:1. Preferred operating temperatures vary depending on the density desired, with lower temperatures being employed for lower densities and higher temperatures for higher densities. Suitable operating temperature is from 70 to 110 °C.

5 For production of a low molecular weight product, the mole ratio of α -olefin to ethylene generally is in the range from 0:1 to 0.6:1, preferably from 0.001:1 to 0.42:1. The mole ratio of hydrogen to ethylene can be in the range of 0:1 to 3:1, and is preferably in the range of 0.5:1 to 2.2:1. The operating temperature is generally in the range of 70 to 110 °C. The operating temperature is preferably varied with the desired density to avoid product stickiness in the reactor.

10 The weight ratio of polymer prepared in the high molecular weight reactor to polymer prepared in the low molecular weight reactor (referred to as "split") desirably ranges from 30:70 to 80:20, and is preferably in the range of 40:60 to 65:35.

The transition metal based catalyst system including the cocatalyst, ethylene, α -olefin, and, optionally, hydrogen are continuously fed into the first reactor; the polymer/activated procatalyst mixture is continuously transferred from the first reactor to the second reactor; ethylene and, optionally, α -olefin and hydrogen, and cocatalyst are continuously fed to the second reactor. The final product is continuously removed from the second reactor.

The pressure may be the same or different in the first and second reactors. Depending on the specific method used to transfer the reaction mixture or polymer from the first reactor to the second reactor, the second reactor pressure may be either higher than or somewhat lower than that of the first. If the second reactor pressure is lower, this pressure differential can be used to facilitate transfer of the polymer/catalyst mixture from Reactor 1 to Reactor 2. If the second reactor pressure is higher, the differential pressure across the cycle gas compressor may be used as the motive force to move the reaction mixture. Suitable reactor pressures range from 200 to 500 psig (1.5–3.6 MPa) and preferably range from 250 to 450 psig (1.8–3.2 MPa). The ethylene partial pressure in the first reactor can be in the range of 10 to 150 psig (170–1,100 kPa), and is preferably in the range of 20 to 80 psig (240–650 kPa). The ethylene partial pressure in the second reactor is set according to the amount of (co)polymer desired to be produced in this reactor to achieve the split mentioned above. Increasing the ethylene partial pressure in the first reactor leads to an increase in ethylene partial pressure in the second reactor. The balance of the total pressure is provided by α -olefin other than ethylene and optionally an inert gas such as nitrogen. Other inert hydrocarbons, such as an induced condensing agent, for example, isopentane or hexane, also contribute to the overall pressure in the reactor according to their vapor pressures under the temperature and pressure experienced in the reactor.

35 Proatalyst is fed to the reactor(s) using techniques described in US-A-6,617,405 and 6,187,866 and elsewhere. In one preferred embodiment, the procatalyst is fed to the reactor partially activated with an aluminum trialkyl cocatalyst with full activation occurring in the main reactor. In

another preferred embodiment, the procatalyst is fed in an unactivated form with complete activation occurring in the reactor by contact with the cocatalyst.

In a continuous gas phase process, the partially or completely activated procatalyst composition is continuously fed to the reactor with discrete portions of any additional activator compound needed to complete the activation. The polymerization is generally conducted in a fluidized bed, in the absence of catalyst poisons such as moisture, oxygen, CO, CO₂, or acetylene in the presence of a catalytically effective amount of the catalyst composition at a temperature and at a pressure sufficient to initiate the polymerization reaction. Such processes are used commercially for the production of high density polyethylene (HDPE), medium density polyethylene (MDPE), and linear low density polyethylene (LLDPE) and are well known to the skilled artisan.

Under a given set of operating conditions, the fluidized bed is maintained at essentially a constant height by withdrawing a portion of the bed as product at a rate equal to the rate of formation of the particulate polymer product. Since the rate of heat generation is directly related to product formation, a measurement of the temperature rise of the gas across the reactor (the difference between inlet gas temperature and exit gas temperature) is determinative of the rate of particulate polymer formation at a constant gas velocity. The formation of excess fines however, can upset control of bed height and cause operability problems in the reactor.

The molecular weight of polymers made by any suitable process is conveniently indicated using melt flow measurements. One such measurement is the melt index (MI or I₂), obtained according to ASTM D-1238, Condition E, measured at 190°C and an applied load of 2.16 kilogram (kg), reported as grams per 10 minutes or dg/min. Some polymers prepared using some catalysts described herein have MI values ranging from 0.1 to 1000 grams/10 minutes. Melt flow rate (MFR or I₂1) is another method for characterizing polymers and is measured according to ASTM D-1238, Condition F, using 10 times the weight used in the melt index test above. The melt flow rate is inversely proportional to the molecular weight of the polymer. Thus, the higher the molecular weight, the lower the melt flow rate, although the relationship is not linear. The melt flow ratio (MFR) is the ratio of melt flow rate to the melt index. This correlates with the molecular weight distribution of the product polymer. Lower MFR values indicate polymers having narrower molecular weight distributions. Polymers prepared using some catalysts described herein have MFR values ranging from 20 to 40.

Average polymer particle sizes are calculated from sieve analysis data according to ASTM D-1921, Method A, using a 500 g sample. Calculations are based on weight fractions retained on the screens. Bulk Density is determined according to ASTM D-1895, Method B by pouring the resin into a 100 ml graduated cylinder to the 100 ml line without shaking the cylinder, and weighed by difference.

Polymers may also be characterized by their density. Polymers herein may have a density of from 0.85 to 0.98 g/cm³ as measured in a density gradient column in accordance with ASTM D-

792 in which a plaque is made and conditioned for one hour at 100°C to approach equilibrium crystallinity and then measured.

The following specific embodiments of the invention are especially desirable and hereby delineated in order to provide specific disclosure for the appended claims.

5 1. A Ziegler-Natta procatalyst composition in the form of solid particles comprising magnesium, halide and transition metal moieties, said particles having an average size (D50) of from 10 to 70 μm , preferably 15 to 50 μm , and most preferably from 20 to 35 μm , and characterized by a D95/D5 particle size ratio of less than or equal to 10, preferably less than or equal to 9.75.

10 2. The composition according to embodiment 1 wherein the average shell thickness/particle size ratio (Thickness Ratio) determined by SEM techniques for particles having particle size greater than 30 μm is greater than 0.2, preferably greater than 0.25, more preferably greater than 0.4 and most preferably greater than 0.45.

 3. The composition according to embodiment 1 wherein the procatalyst composition is prepared from a precursor composition corresponding to the formula:
15 $[\text{Mg}(\text{R}^1\text{OH})_d]_r\text{Ti}(\text{OR}^e)_e\text{X}_f[\text{ED}]_q$, wherein R^1OH comprises a monofunctional, linear or branched alcohol having between one and 25 carbon atoms; R^e is an aliphatic or aromatic hydrocarbon radical having 1 to 14 carbon atoms or COR' wherein R' is an aliphatic or aromatic hydrocarbon radical having 1 to 14 carbon atoms; each OR^e group is the same or different; X is independently R' , chlorine, bromine or iodine; d is 0.5 to 5; e is 0-12; and f is 1-10, ED is an electron donor; q ranges
20 from 0 to 50; and r is 0, 1, or 2.

 4. The composition of embodiment 3 wherein the precursor composition is prepared by the reaction of magnesium dichloride with a titanium compound in the presence of an alcohol.

 5. The composition of embodiment 4 wherein the transition metal compound is a titanium halide or a titanium haloalkoxide having 1 to 8 carbon atoms per alkoxide group.

25 6. The composition of embodiment 3 wherein the precursor composition is prepared by the reaction of magnesium with titanium tetrachloride in the presence of an electron donor.

 7. The composition of embodiment 1 wherein a filler is present in the solid particles in an amount of at least 15 percent based on total composition weight.

 8. A method for making the procatalyst composition of embodiment 1, the steps of the
30 method comprising: a) providing a liquid composition (slurry) comprising i) a magnesium halide compound, ii) a solvent or diluent, iii) a transition metal compound wherein the transition metal is selected from the metals of Groups 3-10 and Lanthanides of the Periodic Table of the Elements, iv) optionally an internal electron donor, and v) a filler; b) spray-drying the liquid composition to form a spray-dried particle; and c) collecting the resulting solid particles.

35 9. The method of embodiment 8 wherein the filler and/or precursor composition is present in an amount that is from 50 to 98 percent of the liquid composition.

 10. The method of embodiment 8 wherein the filler is fumed silica.

11. A process for making a polymer comprising contacting at least one olefin monomer with a procatalyst according to any one of embodiments 1-7 or with a procatalyst made by the method of any one of embodiments 8-10, and a cocatalyst under olefin polymerization conditions to form a polymer product.

5 12. A process according to embodiment 11 wherein ethylene is homopolymerized or copolymerized with one or more C₃₋₈ α -olefins.

13. A process according to embodiment 11 wherein the cocatalyst is triethylaluminum or tri(n-hexyl)aluminum.

EXAMPLES

10 It is understood that the present invention is operable in the absence of any component which has not been specifically disclosed. The following examples are provided in order to further illustrate the invention and are not to be construed as limiting. Unless stated to the contrary, all parts and percentages are expressed on a weight basis. The term "overnight", if used, refers to a time of approximately 16-18 hours, "room temperature", if used, refers to a temperature of 20-25 °C, and
15 "mixed alkanes" refers to a mixture of hydrogenated propylene oligomers, mostly C₆-C₁₂ isoalkanes, available commercially under the trademark Isopar E™ from ExxonMobil Chemicals, Inc.

Preparation of the Spray-Dried Procatalyst

A tetrahydrofuran slurry containing dissolved MgCl₂, a silane treated fumed silica filler
20 (Cabosil™ TS-610 available from Cabot Corp.) and TiCl₃, (prepared substantially according to the teachings of US-A-6,187,866) is spray-dried using an 8-foot diameter closed cycle spray dryer equipped with a rotary atomizer. The rotary atomizer speed is adjusted to produce particles with a substantially uniform particle size having a D50 of about 24 μ m. Nitrogen gas is introduced into the spray dryer at inlet temperatures from 130-160 °C and circulated within the dryer at a rate of
25 approximately 200-300 kg/hour. The slurry is fed to the spray dryer at a temperature of 35°C and at a rate sufficient to yield an outlet gas temperature of approximately 115-120 °C. The spray drying chamber pressure is maintained at a pressure slightly above atmospheric (5-7.5 Pa above atmospheric). A comparative procatalyst, is prepared using a procatalyst slurry having a lower concentration of MgCl₂, lower fumed silica content, and/or using a lower orifice velocity, as
30 indicated in Table 1. All particle dimensions are expressed in μ m. Both particles contain approximately 30 percent filler and are substantially spheroidally shaped.

Table 1

	D5	D10	D50	D90	D95	D95/D5
A*	5.3	8.2	23.5	52	55	10.4
Ex. 1	6.7	9.5	27	58	62	9.3

* comparative, not an example of the invention

Gas-Phase Ethylene Copolymerization

Linked fluidized bed, pilot scale, series polymerization reactors are used to prepare ethylene/ 1-hexene copolymers under reaction conditions substantially as disclosed in US-A-6,454,976. Under the conditions of operation, procatalyst and cocatalyst (triethylaluminum or -n-
5 hexylaluminum) are added separately to the first reactor of a dual reactor system and product is discharged into the second reactor and polymerization continued without additional quantities of procatalyst or cocatalyst being added. The first reactor is operated under conditions of low ethylene concentration to produce a high molecular weight copolymer product. The second reactor is
10 operated under high hydrogen concentration to produce a low molecular weight polymer containing minimal comonomer incorporation. These polymerization conditions favor excessive generation of resin fines.

For example, using triethylaluminum cocatalyst and catalyst composition Ex. 1, polymerization conditions are adjusted in the first reactor to produce a high molecular weight ethylene/1-hexene copolymer having 0.4 Flow Index (I21) and 0.928 g/cc density. Conditions in the
15 second reactor are adjusted to produce a final polymer product having a combined Flow Index of 7-9 and a density of 0.948 to 0.951. Excellent stable operation is achieved using catalyst composition Ex. 1 with low fines generation and no static buildup. In contrast, polymerization employing catalyst composition A generates sufficient fine particles that the polymerization must be
20 prematurely terminated due to loss of fluidized bed level control and poor polymer particle formation (chunk formation).

CLAIMS:

1. A Ziegler-Natta procatalyst composition in the form of solid particles comprising magnesium, halide and transition metal moieties, said particles having an average size (D50) of from 10 to 70 μm and characterized by a D95/D5 particle size ratio of less than or equal to 10.
- 5 2. The composition according to claim 1 wherein the average shell thickness/ particle size ratio (Thickness Ratio) determined by SEM techniques for particles having particle size greater than 30 μm is greater than 0.2.
3. The composition according to claim 1 wherein the procatalyst composition is prepared from a precursor composition corresponding to the formula:
 10 $[\text{Mg}(\text{R}'\text{OH})_r]_d\text{Ti}(\text{OR}^e)_e\text{X}_f[\text{ED}]_q$, wherein $\text{R}'\text{OH}$ comprises a monofunctional, linear or branched alcohol having between one and 25 carbon atoms; R^e is an aliphatic or aromatic hydrocarbon radical having 1 to 14 carbon atoms or COR' wherein R' is an aliphatic or aromatic hydrocarbon radical having 1 to 14 carbon atoms; each OR^e group is the same or different; X is independently R' , chlorine, bromine or iodine; d is 0.5 to 5; e is 0-12; and f is 1-10, ED is an electron donor; q ranges
 15 from 0 to 50; and r is 0, 1, or 2.
4. The composition of claim 3 wherein the precursor composition is prepared by the reaction of magnesium dichloride with a titanium compound in the presence of an alcohol.
5. The composition of claim 4 wherein the transition metal compound is a titanium halide or a titanium haloalkoxide having 1 to 8 carbon atoms per alkoxide group.
- 20 6. The composition of claim 3 wherein the precursor composition is prepared by the reaction of magnesium with titanium tetrachloride in the presence of an electron donor.
7. The composition of claim 1 wherein a filler is present in the solid particles in an amount of at least 15 percent based on total composition weight.
8. A method for making the procatalyst composition of claim 1, the steps of the
 25 method comprising: a) providing a liquid composition (slurry) comprising i) a magnesium halide compound, ii) a solvent or diluent, iii) a transition metal compound wherein the transition metal is selected from the metals of Groups 3-10 and Lanthanides of the Periodic Table of the Elements, iv) optionally an internal electron donor, and v) a filler; b) spray-drying the liquid composition to form a spray-dried particle; and c) collecting the resulting solid particles.
- 30 9. The method of claim 8 wherein the filler and/or precursor composition is present in an amount that is from 50 to 98 percent of the liquid composition.
10. The method of claim 8 wherein the filler is fumed silica.
11. A process for making a polymer comprising contacting at least one olefin monomer with a procatalyst according to any one of claims 1-7 or with a procatalyst made by the method of
 35 any one of claims 8-10, and a cocatalyst under olefin polymerization conditions to form a polymer product..

12. A process according to claim 11 wherein ethylene is homopolymerized or copolymerized with one or more C₃₋₈ α -olefins.

13. A process according to claim 11 wherein the cocatalyst is triethylaluminum or tri(n-hexyl)aluminum.

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