

APPLICATION FOR PATENT

Title: Stable Metallocene Catalyst Systems

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10 Field of the Invention

This invention relates to stabilized metallocene catalyst systems and to methods for their production and use. Specifically, these catalyst systems comprise metallocene and alkylaluminum oxane wherein the ratio of the aluminum of the
15 alkylaluminum oxane to the transition metal of the metallocene used to prepare the catalyst system is in the range of from about 80:1 to about 200:1. These catalyst systems retain their activity and may be used directly in polymerization after storage for periods of up to two months or more.

20 Background

A well-known problem associated with activated metallocene catalyst systems is their inability to remain stable and active for more than a few days or hours particularly at high temperatures. Consequently, metallocene catalyst
25 systems must be used soon after preparation in order to take advantage of their maximum productivity. Using a catalyst immediately after its production can be quite difficult particularly on a commercial scale. To date, attempts to alleviate this problem have met with limited success.

U. S. Patent No. 5,308,817 describes a particular syndiospecific metallocene which, when activated with methylalumoxane, is stable for up to 3 days with good activity. These aged catalyst systems, however, tend to cause polymerization reactor fouling and this tendency increases with increased aging
5 time.

U. S. Patent No. 5,393,851 describes a concentrated stock metallocene/alumoxane solution which may be stored for up to 14 days. Before use in polymerization, this solution must be diluted with additional alumoxane.
10 Additionally, these concentrated solutions must be stored in a relatively cool environment in order to retain activity and there can be an activity loss of from 20 to 30 percent before the solution becomes stable.

The two patents discussed above illustrate the need in the art for catalyst
15 systems and components that can be stored for long periods of time. In particular there is a need for catalyst systems that can not only be stored for long periods of time but can be stored at ambient temperatures (including high temperatures) and can be used directly in polymerization after storage. This application describes an unexpectedly improved active metallocene catalyst system that can be stored at
20 high temperature for as much as two months or more. After storage, this catalyst system can be used directly as an efficient polymerization catalyst without additional activation.

Summary

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This invention relates to a method for polymerizing olefins comprising polymerizing one or more olefins under suitable polymerization conditions in the presence of an active metallocene catalyst system comprising metallocene and an alkylalumoxane which active catalyst system has been stored for at least two days.

This invention also relates to stabilized metallocene catalyst systems comprising metallocene, alkylaluminum and optionally support material wherein the ratio of the aluminum of the alkylaluminum to the transition metal of the metallocene used to prepare the catalyst system is in the range of from about 80:1 to about 200:1.

- 5 Additionally, this invention relates to a method for preparing a metallocene catalyst system, said method comprising the steps of: (a) combining a metallocene catalyst component with an alkylaluminum wherein the ratio of the aluminum of the alkylaluminum to the transition metal of the metallocene used to prepare the catalyst system is in the range of from about 80:1 to about 200:1; and (b) storing
10 the combination for a time period of at least about two days.

Detailed Description of Preferred Embodiments

- Generally, the metallocene catalyst systems of this invention comprises
15 metallocene and alkylaluminum wherein the ratio of the aluminum of the alkylaluminum to the transition metal of the metallocene used to prepare the catalyst system is in the range of from about 80:1 to about 200:1. This catalyst system can be stored for at least about two days at relatively high temperatures without substantial loss in activity. As used herein, "storing" or "stored" means
20 allowed to sit without being used as a catalyst system or component.

- Preferably the ratio of the aluminum of the alkylaluminum to the transition metal of the metallocene used to prepare the catalyst system is in the range of from about 85:1 to about 150:1, more preferably from about 90:1 to about 125:1. The
25 composition may be stored for at least about two days, or up to about 5 days, about 7 days, about 14 days, about 21 days, about 28 days, about 35 days, about 42 days, about 49 days, about 56 days, about 63 days, about 70 days, about 77 days, about 84 days or even about 91 days or more.

Preferably the weight percent of metal on the finished catalyst system is in the range of from about 0.20 to about 1.0, more preferably from about 0.25 to about 0.85, and most preferably from about 0.30 to about 0.70.

5 The temperature during storage may be up to 60°C, preferably up to 45°C, more preferably ambient temperature or from about 20°C to about 45°C. Although the catalyst system may be stored at high ambient temperatures, higher productivity is likely to be retained if the catalyst system is stored under the coolest conditions practicable. Thus, the catalyst system may be warehoused outside or
10 only partially sheltered in most climates. Any suitable container may be used for storage. To preserve activity, the container should be air-tight and the storage atmosphere should be free of oxygen and/or water.

After storage, the catalyst system retains at least about 50% of its original
15 productivity, preferably at least about 60%, more preferably at least about 70%, even more preferably at least about 75%, even more preferably at least about 80%, even more preferably at least about 90% and most preferably at least about 95 percent of its original productivity, i.e., its productivity when less than 1 day old.

20 The metallocene and alkylaluminum are preferably combined with a support either before or after storage, preferably before storage. For purposes of this patent specification the term "support" is defined as any material upon which metallocenes and/or activators may be fixed. Preferably, the support material is a
25 porous particulate material, such as talc, inorganic oxides, inorganic chlorides and resinous materials such as polyolefin or polymeric compounds. Such materials are generally commercially available.

The preferred support materials are porous inorganic oxide materials,
30 which include those from the Periodic Table of Elements of Groups 2, 3, 4, 5, 13

or 14 metal oxides. Silica, alumina, silica-alumina, and mixtures thereof are most preferred. Other inorganic oxides that may be employed either alone or in combination with the silica, alumina or silica-alumina, are magnesia, titania, zirconia, and the like.

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Any metallocene may be used in the practice of the invention. As used herein unless otherwise indicated, "metallocene" includes a single metallocene composition or two or more metallocene compositions. Metallocenes are typically bulky ligand transition metal compounds generally represented by the formula:

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where L is a bulky ligand; A is leaving group, M is a transition metal and m and n are such that the total ligand valency corresponds to the transition metal valency.

The ligands L and A may be bridged to each other, and if two ligands L and/or A are present, they may be bridged. The metallocene compound may be full-sandwich compounds having two or more ligands L which may be cyclopentadienyl ligands or cyclopentadiene derived ligands or half-sandwich compounds having one ligand L, which is a cyclopentadienyl ligand or cyclopentadienyl derived ligand. The transition metal atom may be a Group 4, 5 or 6 transition metal and/or a metal from the lanthanide and actinide series. Zirconium, titanium, and hafnium are often preferred. Other ligands may be bonded to the transition metal, such as a leaving group, such as but not limited to hydrocarbyl, hydrogen or any other univalent anionic ligand.

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Methods for making and using metallocenes are very well known in the art. For example, metallocenes are discussed in United States Patent Nos. 4,530,914; 4,542,199; 4,769,910; 4,808,561; 4,871,705; 4,933,403; 4,937,299; 5,017,714; 5,026,798; 5,057,475; 5,120,867; 5,278,119; 5,304,614; 5,324,800; 5,350,723; and 5,391,790 each fully incorporated herein by reference.

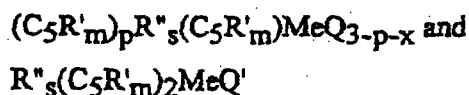
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Further, the metallocene catalyst component of the invention can be a monocyclopentadienyl heteroatom containing compound. This heteroatom is activated by either an alumoxane, an ionizing activator, a Lewis acid or a combination thereof to form an active polymerization catalyst system. These types of catalyst systems are described in, for example, PCT International Publication WO 92/00333, WO 94/07928, and WO 91/ 04257, WO 94/03506, U.S. Patent Nos. 5,057,475, 5,096,867, 5,055,438, 5,227,440 and 5,264,405 and EP-A-0 420 436, all of which are fully incorporated herein by reference. In addition, the metallocene catalysts useful in this invention can include non-cyclopentadienyl catalyst components, or ancillary ligands such as boroles or carbollides in combination with a transition metal.

In one embodiment the metallocene catalyst component is represented by the general formula $(C_p)_m MeR_n R'_p$ wherein at least one C_p is an unsubstituted or, preferably, a substituted cyclopentadienyl ring; Me is a Group 4, 5 or 6 transition metal; R and R' are independently selected halogen, hydrocarbonyl group, or hydrocarboxyl groups having 1-20 carbon atoms or combinations thereof; $m=1-3$, $n=0-3$, $p=0-3$, and the sum of $m+n+p$ equals the oxidation state of Me.

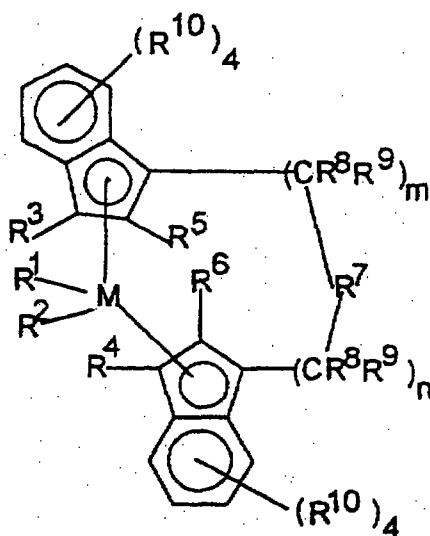
In another embodiment the metallocene catalyst component is represented by the formulas:



wherein Me is a Group 4, 5, 6 transition metal, at least one $C_5R'_m$ is a substituted cyclopentadienyl, each R', which can be the same or different is hydrogen, alkyl, alkenyl, aryl, alkylaryl or arylalkyl radical having from 1 to 20 carbon atoms or two carbon atoms joined together to form a part of a substituted or unsubstituted ring or rings having 4 to 20 carbon atoms, R'' is one or more of or a combination of a carbon, a germanium, a silicon, a phosphorous or a nitrogen atom containing radical bridging two $(C_5R'_m)$ rings, or bridging one $(C_5R'_m)$ ring back to Me,

when $p = 0$ and $x = 1$ otherwise "x" is always equal to 0, each Q which can be the same or different is an aryl, alkyl, alkenyl, alkylaryl, or arylalkyl radical having from 1 to 20 carbon atoms, halogen, or alkoxides, Q' is an alkylidene radical having from 1-20 carbon atoms, s is 0 or 1 and when s is 0, m is 5 and p is 0, 1 or 2 and when s is 1, m is 4 and p is 1.

Preferably, the metallocene is represented by the formula:



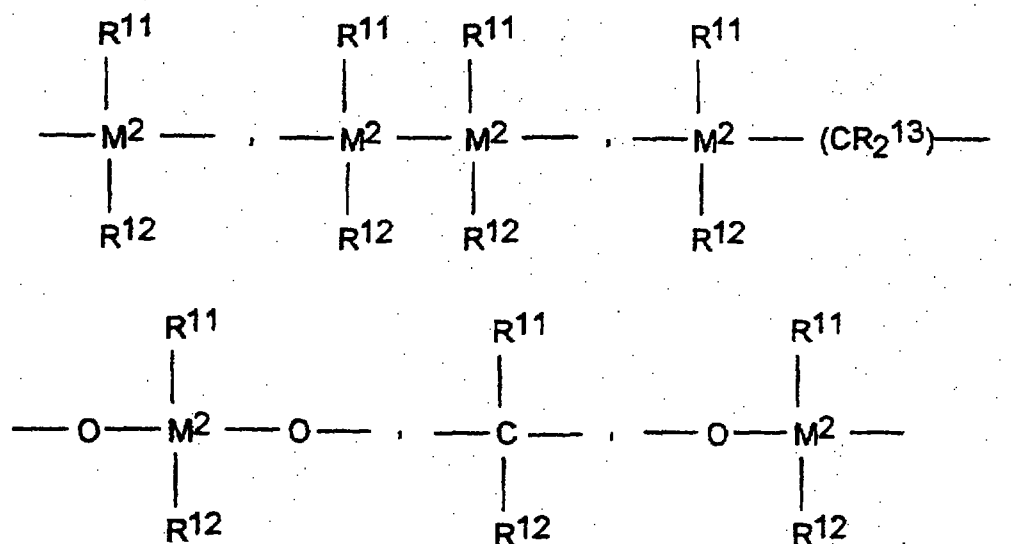
wherein M is a metal of Group 4, 5, or 6 of the Periodic Table preferably, zirconium, hafnium and titanium, most preferably zirconium;

R¹ and R² are identical or different, are one of a hydrogen atom, a C₁-C₁₀ alkyl group, preferably a C₁-C₃ alkyl group, a C₁-C₁₀ alkoxy group, preferably a C₁-C₃ alkoxy group, a C₆-C₁₀ aryl group, preferably a C₆-C₈ aryl group, a C₆-C₁₀ aryloxy group, preferably a C₆-C₈ aryloxy group, a C₂-C₁₀ alkenyl group, preferably a C₂-C₄ alkenyl group, a C₇-C₄₀ arylalkyl group, preferably a C₇-C₁₀ arylalkyl group, a C₇-C₄₀ alkylaryl group, preferably a C₇-C₁₂ alkylaryl group, a C₈-C₄₀ arylalkenyl group, preferably a C₈-C₁₂ arylalkenyl group, or a halogen atom, preferably chlorine;

R^3 and R^4 are hydrogen atoms;

- R^5 and R^6 are identical or different, preferably identical, are one of a
- 5 halogen atom, preferably a fluorine, chlorine or bromine atom, a C_1 - C_{10} alkyl group, preferably a C_1 - C_4 alkyl group, which may be halogenated, a C_6 - C_{10} aryl group, which may be halogenated, preferably a C_6 - C_8 aryl group, a C_2 - C_{10} alkenyl group, preferably a C_2 - C_4 alkenyl group, a C_7 - C_{40} -arylalkyl group, preferably a C_7 - C_{10} arylalkyl group, a C_7 - C_{40} alkylaryl group, preferably a C_7 -
- 10 C_{12} alkylaryl group, a C_8 - C_{40} arylalkenyl group, preferably a C_8 - C_{12} arylalkenyl group, a $-NR_2^{15}$, $-SR^{15}$, $-OR^{15}$, $-OSiR_3^{15}$ or $-PR_2^{15}$ radical, wherein R^{15} is one of a halogen atom, preferably a chlorine atom, a C_1 - C_{10} alkyl group, preferably a C_1 - C_3 alkyl group, or a C_6 - C_{10} aryl group, preferably a C_6 - C_9 aryl group;

- 15 R^7 is



$-B(R^{11})-$, $-Al(R^{11})-$, $-Ge-$, $-Sn-$, $-O-$, $-S-$, $-SO-$, $-SO_2-$, $-N(R^{11})-$, $-CO-$, $-P(R^{11})-$, or $-P(O)(R^{11})-$;

wherein:

- 20 R^{11} , R^{12} and R^{13} are identical or different and are a hydrogen atom, a halogen atom, a C_1 - C_{20} alkyl group, preferably a C_1 - C_{10} alkyl group, a C_1 - C_{20}

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fluoroalkyl group, preferably a C₁-C₁₀ fluoroalkyl group, a C₆-C₃₀ aryl group, preferably a C₆-C₂₀ aryl group, a C₆-C₃₀ fluoroaryl group, preferably a C₆-C₂₀ fluoroaryl group, a C₁-C₂₀ alkoxy group, preferably a C₁-C₁₀ alkoxy group, a C₂-C₂₀ alkenyl group, preferably a C₂-C₁₀ alkenyl group, a C₇-C₄₀ arylalkyl group, preferably a C₇-C₂₀ arylalkyl group, a C₈-C₄₀ arylalkenyl group, preferably a C₈-C₂₂ arylalkenyl group, a C₇-C₄₀ alkylaryl group, preferably a C₇-C₂₀ alkylaryl group or R¹¹ and R¹², or R¹¹ and R¹³, together with the atoms binding them, can form ring systems;

10 M² is silicon, germanium or tin, preferably silicon or germanium, most preferably silicon;

R⁸ and R⁹ are identical or different and have the meanings stated for R¹¹;

15 m and n are identical or different and are zero, 1 or 2, preferably zero or 1, m plus n being zero, 1 or 2, preferably zero or 1; and

the radicals R¹⁰ are identical or different and have the meanings stated for R¹¹, R¹² and R¹³. Two adjacent R¹⁰ radicals can be joined together to form a
20 ring system, preferably a ring system containing from about 4-6 carbon atoms.

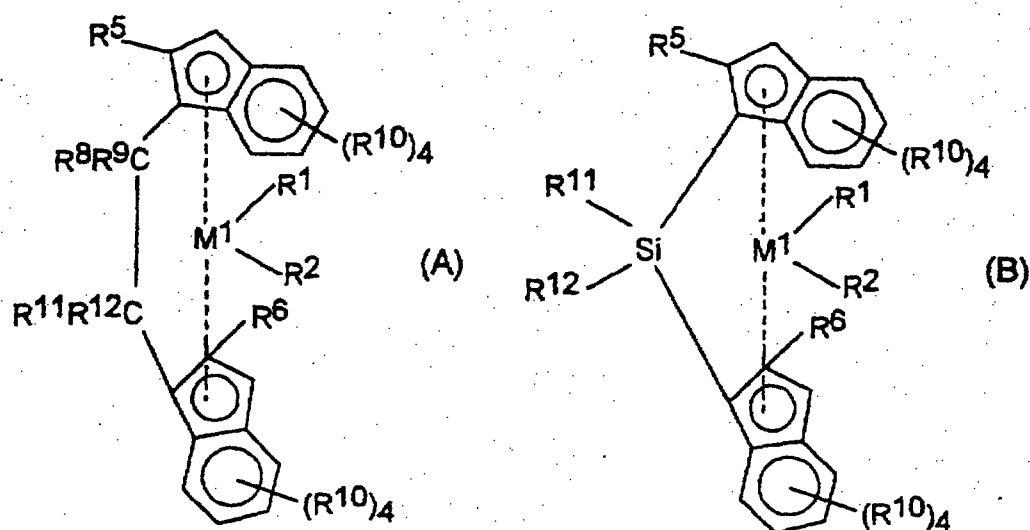
Alkyl refers to straight or branched chain substituents. Halogen (halogenated) is fluorine, chlorine, bromine or iodine atoms, preferably fluorine or chlorine.

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Particularly preferred metallocenes are compounds of the structures:

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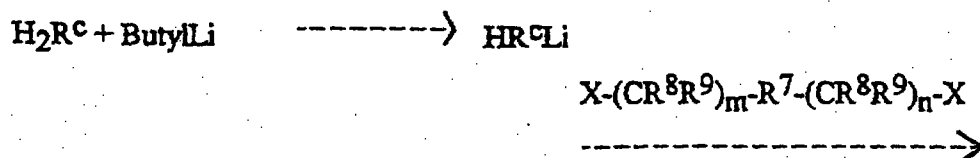
wherein:

M^1 is Zr or Hf, R^1 and R^2 are methyl or chlorine, and $R^5, R^6, R^8, R^9, R^{10}, R^{11}$ and R^{12} have the above-mentioned meanings.

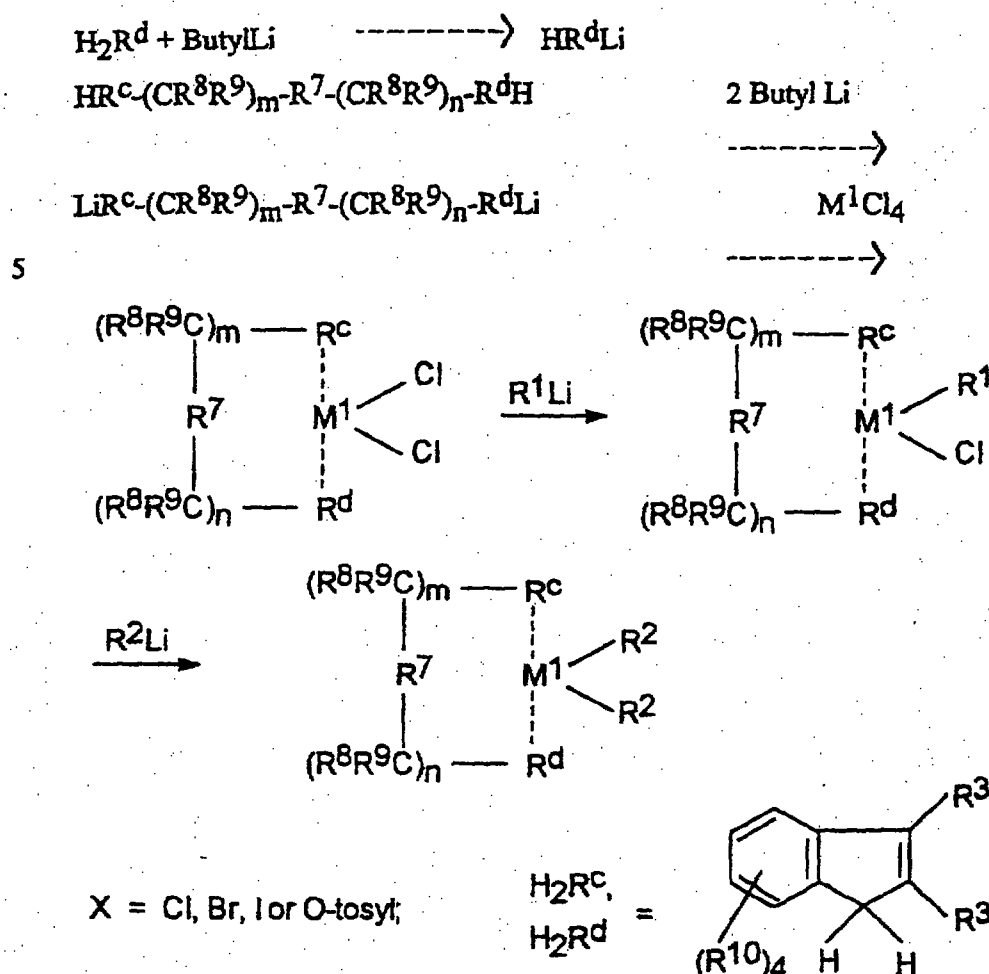
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These chiral metallocenes may be used as a racemate for the preparation of highly isotactic polypropylene copolymers. It is also possible to use the pure R or S form. An optically active polymer can be prepared with these pure stereoisomeric forms. Preferably the meso form of the metallocene is removed to ensure the center (i.e., the metal atom) provides stereoregular polymerization. Separation of the stereoisomers can be accomplished by known literature techniques. For special products it is also possible to use rac/meso mixtures.

Generally, the metallocenes are prepared by a multi-step process involving repeated deprotonations/metallations of the aromatic ligands and introduction of the bridge and the central atom by their halogen derivatives. The following reaction scheme illustrates this generic approach:



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- Additional methods for preparing metallocenes are fully described in the
- 10 Journal of Organometallic Chem., volume 288, (1985), pages 63-67, and in EP-A-320762, for preparation of the metallocenes described, both of which are herein fully incorporated by reference.

Illustrative but non-limiting examples of these metallocenes include:

- 15 Dimethylsilandiylbis (2-methyl-4-phenyl-1-indenyl)ZrCl₂
 Dimethylsilandiylbis(2-methyl-4,5-benzoindenyl)ZrCl₂;
 Dimethylsilandiylbis(2-methyl-4,6-diisopropylindenyl)ZrCl₂;

- Dimethylsilandiylbis(2-ethyl-4-phenyl-1-indenyl)ZrCl₂;
Dimethylsilandiylbis(2-ethyl-4-naphthyl-1-indenyl)ZrCl₂,
Phenyl(Methyl)silandiylbis(2-methyl-4-phenyl-1-indenyl)ZrCl₂,
Dimethylsilandiylbis(2-methyl-4-(1-naphthyl)-1-indenyl)ZrCl₂,
5 Dimethylsilandiylbis(2-methyl-4-(2-naphthyl)-1-indenyl)ZrCl₂,
Dimethylsilandiylbis(2-methyl-indenyl)ZrCl₂,
Dimethylsilandiylbis(2-methyl-4,5-diisopropyl-1-indenyl)ZrCl₂,
Dimethylsilandiylbis(2,4,6-trimethyl-1-indenyl)ZrCl₂,
Phenyl(Methyl)silandiylbis(2-methyl-4,6-diisopropyl-1-indenyl)ZrCl₂,
10 1,2-Ethandiylbis(2-methyl-4,6-diisopropyl-1-indenyl)ZrCl₂,
1,2-Butandiylbis(2-methyl-4,6-diisopropyl-1-indenyl)ZrCl₂,
Dimethylsilandiylbis(2-methyl-4-ethyl-1-indenyl)ZrCl₂,
Dimethylsilandiylbis(2-methyl-4-isopropyl-1-indenyl)ZrCl₂,
Dimethylsilandiylbis(2-methyl-4-t-butyl-1-indenyl)ZrCl₂,
15 Phenyl(Methyl)silandiylbis(2-methyl-4-isopropyl-1-indenyl)ZrCl₂,
Dimethylsilandiylbis(2-ethyl-4-methyl-1-indenyl)ZrCl₂,
Dimethylsilandiylbis(2,4-dimethyl-1-indenyl)ZrCl₂,
Dimethylsilandiylbis(2-methyl-4-ethyl-1-indenyl)ZrCl₂,
Dimethylsilandiylbis(2-methyl- α -acenaphth-1-indenyl)ZrCl₂,
20 Phenyl(Methyl)silandiylbis(2-methyl-4,5-benzo-1-indenyl)ZrCl₂,
Phenyl(Methyl)silandiylbis(2-methyl-4,5-(methylbenzo)-1-indenyl)ZrCl₂,
Phenyl(Methyl)silandiylbis(2-methyl-4,5-(tetramethylbenzo)-1-indenyl)ZrCl₂,
Phenyl(Methyl)silandiylbis(2-methyl- α -acenaphth-1-indenyl)ZrCl₂,
1,2-Ethandiylbis(2-methyl-4,5-benzo-1-indenyl)ZrCl₂,
25 1,2-Butandiylbis(2-methyl-4,5-benzo-1-indenyl)ZrCl₂,
Dimethylsilandiylbis(2-methyl-4,5-benzo-1-indenyl)ZrCl₂,
1,2-Ethandiylbis(2,4,7-trimethyl-1-indenyl)ZrCl₂,
Dimethylsilandiylbis(2-methyl-1-indenyl)ZrCl₂,
1,2-Ethandiylbis(2-methyl-1-indenyl)ZrCl₂,
30 Phenyl(Methyl)silandiylbis(2-methyl-1-indenyl)ZrCl₂,

Diphenylsilandiylbis(2-methyl-1-indenyl)ZrCl₂,

1,2-Butandiylbis(2-methyl-1-indenyl)ZrCl₂,

Dimethylsilandiylbis(2-ethyl-1-indenyl)ZrCl₂,

Dimethylsilandiylbis(2-methyl-5-isobutyl-1-indenyl)ZrCl₂,

5 Phenyl(Methyl)silandiylbis(2-methyl-5-isobutyl-1-indenyl)ZrCl₂,

Dimethylsilandiylbis(2-methyl-5-t-butyl-1-indenyl)ZrCl₂,

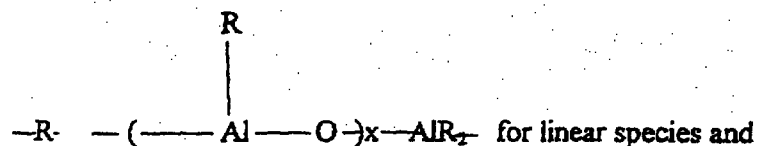
Dimethylsilandiylbis(2,5,6-trimethyl-1-indenyl)ZrCl₂, and the like.

These preferred metallocene catalyst components are described in detail in

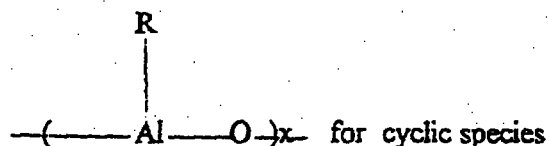
10 U.S. Patent Nos. 5,145,819; 5,243,001; 5,239,022; 5,329,033; 5,296,434;
5,276,208; and 5,374,752; and EP 549 900 and 576 970 all of which are herein
fully incorporated by reference.

Any alkylalumoxane may be used as an activator for the metallocene.

15 Generally alkylalumoxanes contain about 5 to 40 of the repeating units:



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where R is a C₁-C₈ alkyl including mixed alkyls. Particularly preferred are the
compounds in which R is methyl. Alumoxane solutions, particularly

30 methylalumoxane solutions which are preferred, may be obtained from commercial

vendors as solutions having various concentrations. There are a variety of methods for preparing alumoxane, non-limiting examples of which are described in U.S. Patent No. 4,665,208, 4,952,540, 5,091,352, 5,206,199, 5,204,419, 4,874,734, 4,924,018, 4,908,463, 4,968,827, 5,308,815, 5,329,032, 5,248,801, 5,235,081, 5,157,137, 5,103,031 and EP-A-0 561 476, EP-B1-0 279 586, EP-A-0 594-218 and WO 94/10180, each fully incorporated herein by reference.

Some MAO solutions tend to become cloudy and gelatinous over time. It may be advantageous to clarify such solutions prior to use. A number of methods are used to create gel-free MAO solutions or to remove gels from the solutions. Gelled solutions are often simply filtered or decanted to separate the gels from the clear MAO. U.S. Patent No. 5,157,137 discloses a process for forming clear, gel-free solutions of alkylalumoxane by treating a solution of alkylalumoxane with an anhydrous salt and/or hydride of an alkali or alkaline earth metal.

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The metallocene, alkylalumoxane and support material may be combined in any manner or order. Examples of suitable support techniques are described in U. S. Patent Nos. 4,808,561 and 4,701,432 (each fully incorporated herein by reference). Preferably, however, the metallocene and alkylalumoxane are combined first and their reaction product combined with the support material. Suitable examples of this technique are described in U. S. Patent No. 5,240,894 and WO 94/28034, WO 96/00243, and WO 96/00245 (each fully incorporated herein by reference).

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Preferably, a porous support such as silica is used and the volume of metallocene and activator combined with the support is less than about 4.0 times the total pore volume of the support, more preferably less than about 3.0 times the total pore volume of the support, even more preferably less than about 2.5 times the total pore volume of the support.

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The procedure for measuring the total pore volume of a porous support is well known in the art. Details of one of these procedures are discussed in Volume 1, *Experimental Methods in Catalytic Research* (Academic Press, 1968) (specifically see pages 67-96). This preferred procedure involves the use of a
5 classical BET apparatus for nitrogen absorption. Another method well known in the art is described in Innes, *Total porosity and Particle Density of Fluid Catalysts By Liquid Titration*, Vol. 28, No. 3, *Analytical Chemistry* 332-334 (March, 1956).

When the volume of solution combined with porous support material is less
10 than one times the total pore volume of the support, the support appears completely dry and free-flowing and is consequently easy to mix and transfer. When volumes above one times the total pore volume of the porous support are used, the support becomes progressively more difficult to mix and transfer as volume increases because it has the consistency of damp or wet mud. At greater
15 volumes of solution, a slurry is eventually formed such that one can observe separation of the solution and support as the silica settles. At the slurry stage, the support is easier to mix and handle. These factors should be considered when choosing solution volumes.

20 Regardless of the amount of solution used, it is preferable to combine the support and solution such that the solution is evenly distributed among the support particles. Thus it is preferable to add the solution to the support slowly either as a spray or drop-wise while the support is mixed.

25 If the catalyst system is supported, it is preferably dried at least to a free flowing powder prior to storage. Heat and/or vacuum may be used to dry the catalyst. Typically, temperature in the range of from about 25°C to about 100°C is used for a time period ranging from about 4 to about 36 hours. It may be advantageous to dry the catalyst without vacuum or with a flow of warm inert gas
30 such as nitrogen.

After drying, the final weight ratio of the aluminum of the alkylalumoxane to the metal of the metallocene as determined by elemental analysis is preferably in the range of from about 15 to about 170, more preferably from about 50 to about 150, even more preferably from about 80 to about 125.

The catalyst systems of this invention may be used directly in polymerization after storage or the catalyst system may be prepolymerized before or after storage using methods well known in the art. For details regarding prepolymerization, see United States Patent Nos. 4,923,833 and 4,921,825, EP 0 279 863 and EP 0 354 893 each of which is fully incorporated herein by reference. The catalyst systems of this invention may also be combined before or after storage with one or more additives such as scavengers. Examples of suitable scavenging compounds include triethylaluminum (TEAL), trimethylaluminum (TMAL), triisobutylaluminum (TIBAL), tri-n-hexylaluminum (TNHAL) and the like.

After storage, the catalyst system of this invention may be used in the polymerization of any monomer and optionally comonomers in any process including gas, slurry or solution phase or high pressure autoclave processes. (As used herein, unless differentiated, "polymerization" includes copolymerization and "monomer" includes comonomer.) Preferably, a gas or slurry phase process is used, most preferably a bulk liquid propylene polymerization process is used.

In the preferred embodiment, this invention is directed toward the bulk liquid polymerization and copolymerization of propylene or ethylene, particularly propylene, in a slurry or gas phase polymerization process, particularly a slurry polymerization process. Another embodiment involves copolymerization reactions of propylene or ethylene, particularly propylene, with one or more of the alpha-olefin monomers having from 4 to 20 carbon atoms, preferably 4-12 carbon atoms, for example alpha-olefin comonomers of ethylene, butene-1, pentene-1, 4-

methylpentene-1, hexene-1, octene-1, decene-1, and olefins such as styrene, cyclopentene or norbornene. Other suitable monomers include vinyl, diolefins such as dienes, for example, 1,3-butadiene, 1,4-hexadiene, norbornadiene or vinylnorbornene, acetylene, ethylidene norbornene and aldehyde monomers.

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Typically in a gas phase polymerization process a continuous cycle is employed where in one part of the cycle of a reactor, a cycling gas stream, otherwise known as a recycle stream or fluidizing medium, is heated in the reactor by the heat of polymerization. The recycle stream usually contains one or more monomers continuously cycled through a fluidized bed in the presence of a catalyst under reactive conditions. This heat is removed in another part of the cycle by a cooling system external to the reactor. The recycle stream is withdrawn from the fluidized bed and recycled back into the reactor. Simultaneously, polymer product is withdrawn from the reactor and new or fresh monomer is added to replace the polymerized monomer. (See for example U.S. Patent Nos. 4,543,399; 4,588,790; 15 5,028,670; 5,352,749; 5,405,922, and 5,436,304 all of which are fully incorporated herein by reference.)

A slurry polymerization process generally uses pressures in the range of about 1 to about 500 atmospheres or even greater and temperatures in the range of -60°C to about 280°C. In a slurry polymerization, a suspension of solid, particulate polymer is formed in a liquid polymerization medium to which ethylene and comonomers and often hydrogen along with catalyst are added. The liquid employed in the polymerization medium can be, for example, an alkane or a cycloalkane. The medium employed should be liquid under the conditions of 25 polymerization and relatively inert. Non-limiting examples of liquid mediums include hexane and isobutane.

Preferably the catalyst system after storage has a productivity of at least about 2000 g polymer/g catalyst, preferably at least about 2500 g polymer/g catalyst, most preferably at least about 3000 g polymer/g catalyst.

5 Examples

In order to provide a better understanding of the present invention including representative advantages thereof, the following examples are offered.

10 Catalyst Preparations

Example 1

In an inert N₂ glove box 0.50 g of dimethylsilanediyl-bis(2-methyl-4-phenyl-indenyl) zirconium dichloride and 18.50 g of 30 wt% DMAO-25010 solution in toluene (Albemarle Corporation, Baton Rouge, LA) were combined under stirring. Al/Zr molar ratio in the solution was 110. The resulting deep red precursor was added slowly while stirring to 10.0 g of MS948 silica (Davison Chemical Division of W. R. Grace, Baltimore, MD) previously dehydrated to 600° C in a stream of flowing N₂. The mud was dried at 28-29 inches of mercury vacuum until 15.56 g of free flowing, finely divided solid was obtained. Testing showed that the amount of volatiles in the solid was reduced to 1.1% by weight. Elemental analysis showed 15.41% Al and 0.55% Zr.

25 Example 2

In an inert N₂ glove box 0.379 g of dimethylsilanediyl-bis(2-methyl-4-phenyl-indenyl) zirconium dichloride and 14.10 g of 30 wt% DMAO-25010 solution in toluene (Albemarle Corporation, Baton Rouge, LA) were combined under stirring. Al/Zr molar ratio in the solution was 110. The resulting deep red

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precursor was added slowly while stirring to 10.0 g of MS948 silica (Davison Chemical Division of W. R. Grace, Baltimore, MD) previously dehydrated to 600° C in a stream of flowing N₂. The mud was dried at 28-29 inches of mercury vacuum until 15.56 g of free flowing, finely divided solid was obtained. Elemental analysis showed 16.55% Al and 0.29% Zr.

Comparative Example 3

In an inert N₂ glove box 0.25 g of dimethylsilanediyl-bis(2-methyl-4-phenyl-indenyl) zirconium dichloride and 18.53 g of 30 wt% DMAO-25010 solution in toluene (Albemarle Corporation, Baton Rouge, LA) were combined under stirring. Al/Zr molar ratio in the solution was 217. The resulting deep red precursor was added slowly while stirring to 10.0 g of MS948 silica (Davison Chemical Division of W. R. Grace, Baltimore, MD) previously dehydrated to 600° C in a stream of flowing N₂. The mud was dried at 28-29 inches of mercury vacuum until 15.61 g free flowing, finely divided solid was obtained. Testing showed that the amount of volatiles in the solid was reduced to 0.7% by weight. Elemental analysis showed 15.77% Al and 0.19% Zr.

Example 4

In an inert N₂ glove box 0.26 g of dimethylsilanediyl-bis(2-methyl-indenyl) zirconium dichloride and 13.25 g of 30 wt% MAO solution in toluene (Albemarle Corporation, Baton Rouge, LA) were combined under stirring and 5.60 g of toluene added. Al/Zr molar ratio in the solution was 126. The resulting deep red precursor was added slowly while stirring to 10.0 g of MS948 silica (Davison Chemical Division of W. R. Grace, Baltimore, MD) previously dehydrated to 600° C in a stream of flowing N₂. The mud was dried at 28-29 inches of mercury vacuum until 14.94 g free flowing, finely divided solid was obtained. Elemental analysis showed 16.49% Al and 0.45% Zr.

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Comparative Example 5

In an inert N₂ atmosphere 850 g of dimethylsilanediyl-bis(2-methyl-indenyl) zirconium dichloride was combined with 15 gallons toluene and 165 lbs of 30 wt% methylalumoxane solution in toluene (Albemarle Corporation, Baton Rouge, LA) was added to form the precursor having an Al to Zr ratio of 210. Separately 150 lbs of MS948 silica (Davison Chemical Division of W. R. Grace, Baltimore, MD) previously dehydrated to 600°C in a stream of flowing N₂ was added to a 200 gallon reactor. The precursor was added to the silica while stirring. Then 28-29 inches of mercury vacuum was applied to the reactor while the reactor jacket was heated to 160-165°F. After 7.5 hours the catalyst was collected as a free flowing powder. Testing showed that the amount of volatiles in the solid was reduced to 3.35% by weight. Elemental analysis showed 9.28% Al and 0.17% Zr.

Catalyst Stability Evaluation

An oven filled with N₂ and thermostatted at 100°F (34°C) was used to heat stainless steel cylinders of catalyst for the stability study. The cylinders were charged with catalyst inside a N₂ purged glove box. Before sealing the cylinder 15 psi of N₂ pressure was applied to prevent contamination of the catalyst during cylinder handling in air. At preset times a cylinder was removed from the oven, transferred to the glove box and the contents sampled. The cylinder was returned to the oven and heating continued. The aged catalyst samples were tested for polymerization activity as described below.

Catalyst Polymerization Evaluation

A 2 liter autoclave reactor previously flushed with N₂ and containing triethylaluminum (0.25 mL of a 1 M solution in hexane) and 1000 mL of propylene was heated to a temperature of 70°C. A 75 mg sample of the catalyst sample prepared and aged as above was slurried in 2 mL of hexane and charged with 250 mL of propylene to start the reaction. After one hour the reactor was cooled, vented, purged with N₂ for 20 minutes and then opened. The granular polypropylene was transferred to a ceramic dish and allowed to dry in a fume hood overnight. The next day the polymer was further dried in vacuo at 75°C for one hour. The final dried polymer was weighed.

Polymerization Results

Table I summarizes stability of catalyst activity after aging at 100°F (34°C).

Table 1

Catalyst Example	Al/Zr ^(a)	Productivity after heat aging for hours shown ^(b)					
		0	40	85	157	250	325
1	110	3144	nd ^(c)	nd	3115	3056	3105
Comp. 3	217	2680	1895	1811	1672	1736	1540

(a) Precursor molar ratio.

(b) Grams PP per g catalyst heat aged at 100°F (34°C) for time shown.

(c) not determined.

The data show that the catalyst of Example 1 having a lower Aluminum to Zirconium molar ratio was stable to heat aging at 100°F (34°C) while the catalyst

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of Comparative Example 3 at three times the ratio lost 30% catalyst activity after 40 hours and about 45% after about 2 weeks.

The 100°F (34°C) heat aging study of the catalyst of Example 1 was continued as shown in Table 2.

Table 2

Days	Productivity ^(a)
21.4	3017
28.4	2813
34.4	2704
42.3	2723
56.3	2696
65.2	2873
90.2	2109

(a) Productivity (g PP per g catalyst).

The 100°F heat aging study of the catalyst of Example 2 is shown in Table

Table 3

Days	Productivity ^(a)
0	3216
5.8	2819
18.7	2443
32.6	2480
43.5	2528
53.4	2647
68.4	2419

(a) Productivity (g PP per g catalyst).

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The data show that except for a small loss in activity, the catalyst maintains effective activity for more than two months at 100°F (34°C).

- 5 The results of another 100°F (34°C) heat aging comparison with a different metallocene are shown in Table 4.

Table 4

Days	Example 3	Comp. Example 4
3	-(a)	1788 ^(b)
5	3984	-
7.7	3903	-
10	-	1560
15.7	3863	-
21	-	1353
22.6	3589	-
28.1	-	1197
33.8	3180	-
35	-	1140
42	-	1141
43.6	3647	-
53.5	3677	-
60	-	869
68.4	3373	-

(a) not determined.

(b) Productivity (g PP per g catalyst).

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- 15 The catalyst of Example 4 having an Al/Zr molar ratio of 126 was more stable to activity loss than the catalyst of Comparative Example 5. The latter having an Al/Zr of 210 lost about 50% activity after heat aging for 2 months while the catalyst with the ratio of the instant invention maintained about 85% activity in about the same time period.

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While the present invention has been described and illustrated by reference to particular embodiments, it will be appreciated by those of ordinary skill in the art that the invention lends itself to many different variations not
5 illustrated herein. For these reasons, then, reference should be made solely to the appended claims for purposes of determining the true scope of the present invention.

Although the appendant claims have single dependencies in accordance
10 with U.S. patent practice, each of the features in any of the appendant claims can be combined with each of the features of other appendant claims or the main claim.



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THIS SHEET HAS BEEN
REPLACEDClaims

1. A method for polymerizing olefins comprising contacting one or more olefins under suitable polymerization conditions with an active metallocene catalyst system
5 comprising metallocene and an alkylaluminum which active catalyst system has been stored for at least two days.
2. The method of claim 1 wherein the time period is at least 14 days.
- 10 3. The method of claim 1 wherein the time period is at least 35 days.
4. The method of claim 1 wherein the time period is at least 56 days.
5. The method of any of the preceding claims wherein the ratio of the aluminum of
15 the alkylaluminum to the transition metal of the metallocene used to prepare the catalyst system is in the range of from 85:1 to 150:1.
6. The method of any of the preceding claims wherein the catalyst system further comprises a support material.
- 20 7. The method of any of the preceding claims wherein the catalyst system has been stored at a temperature in the range of from 20°C to 45°C.
8. The method of claim 4 wherein the catalyst system productivity is at least 75%
25 of its original productivity before storage.
9. A method for preparing a metallocene catalyst system, comprising the steps of:



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- (a) combining a metallocene catalyst component with an alkylalumoxane wherein the ratio of the aluminum of the alkyl alumoxane to the transition metal of the metallocene is in the range of from 80:1 to 200:1; and
- 5 (b) storing the combination for a time period of at least two days.
10. The method of claim 9 wherein the time period is at least 7 days.
11. The method of claim 9 wherein the time period is at least 21 days.
- 10 12. The method of claim 9 wherein the time period is at least 49 days.
13. The method of claim 9 wherein the time period is at least 56 days.
- 15 14. The method of claims 9 - 13 wherein the ratio of the aluminum of the alkyl alumoxane to the transition metal of the metallocene is in the range of from 90:1 to 125:1.
15. The method of claims 9 - 14 further comprising the step of combining the
- 20 metallocene and alkylalumoxane with support material.
16. The method of claims 9 - 15 wherein the support material is a porous inorganic oxide and the metallocene and alkylalumoxane are combined first and their reaction product combined with the porous support.
- 25 17. The method of claims 9 - 16 wherein the combination is stored at a temperature in the range of from 20°C to 45°C.
18. A metallocene catalyst system prepared by the method of claim 9.

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* C L M S *

Claims

1. A method for polymerizing olefins comprising contacting one or more olefins under suitable polymerization conditions with an active metallocene catalyst system comprising metallocene and an alkylalumoxane wherein the ratio of the aluminum of the alkylalumoxane to the transition metal of the metallocene used to prepare the catalyst system is in the range of from 85:1 to 150:1 and wherein the active catalyst system has been stored at a temperature in the range of from 20°C to 45°C for at least two days.
2. The method of claim 1 wherein the time period is at least 14 days.
3. The method of claim 1 wherein the time period is at least 35 days.
4. The method of claim 1 wherein the time period is at least 56 days.
5. The method of any of the preceding claims wherein the catalyst system further comprises a support material.
6. The method of claim 4 wherein the catalyst system productivity is at least 75% of its original productivity before storage.
7. A method for preparing a metallocene catalyst system, comprising the steps of:
 - (a) combining a metallocene catalyst component with an alkylalumoxane wherein the ratio of the aluminum of the alkyl alumoxane to the transition metal of the metallocene is in the range of from 80:1 to 200:1 said combination excluding a stabilizing olefin having the general formula $R_1R_2R_3CCH=CH$ where R_1 , R_2 , and R_3 are alkyl groups with carbon numbers ranging from 1-20; and



(b) storing the combination at a temperature in the range of from 20°C to 45°C for a time period of at least two days.

- 5 8. The method of claim 7 wherein the time period is at least 7 days.
9. The method of claim 7 wherein the time period is at least 21 days.
10. The method of claim 7 wherein the time period is at least 49 days.
- 10 11. The method of claim 7 wherein the time period is at least 56 days.
12. The method of claims 7 - 11 wherein the ratio of the aluminum of the alkyl alumoxane to the transition metal of the metallocene is in the range of from 90:1 to 15 125:1.
13. The method of claims 7 - 12 further comprising the step of combining the metallocene and alkylalumoxane with support material.
- 20 14. The method of claims 7 - 13 wherein the support material is a porous inorganic oxide and the metallocene and alkylalumoxane are combined first and their reaction product combined with the porous support.
- 25 15. A metallocene catalyst system prepared by the method of claim 7.



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(71) Applicant: EXXON CHEMICAL PATENTS INC. [US/US];
5200 Bayway Drive, Baytown, TX 77520-5200 (US).

(72) Inventor: SPECA, Anthony N.; 4306 Hill Forest Drive,
Kingwood, TX 77345 (US).

(74) Agents: SCHMIDT, C., Paige et al.; Exxon Chemical Com-
pany, P.O. Box 2149, Baytown, TX 77522-2149 (US).

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(57) Abstract

This invention relates to stabilized metallocene catalyst systems and to methods for their production and use. Specifically, these catalyst systems comprise metallocene, alkylalumoxane and optionally support material wherein the ratio of the aluminum of the alkyl alumoxane to the transition metal of the metallocene used to prepare the metallocene is in the range of from about 80:1 to about 200:1. These catalysts retain their activity and may be used directly in polymerization after storage for up to two months or more at ambient temperature.